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Rational design of two-dimensional nanofillers for polymer nanocomposites toward multifunctional applications

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Abstract

Nanocomposites consisting of two-dimensional (2D) nanostructured fillers embedded in a polymer matrix find ample opportunities to design multifunctional materials for new applications stemming from the nanofillers' exceptional properties. Despite similar geometries, different 2D materials such as graphene, hexagonal boron nitrides, MXene, and transition metal dichalcogenides exhibit vastly different electrical, thermal, optical and electromagnetic characteristics, providing an exciting pathway to creating composites with tailored multifunctional properties. The key is to rationally assemble 2D nanostructured fillers in the matrix with controlled multiscale structures so that their unique properties can be translated into the composites. This paper is dedicated to offering an overview of recent advances empowering the development of 2D nanofiller/polymer composites in the context of novel synthesis and assembly techniques, multiscale structural characteristics, multifunctional properties and emergent applications. Special emphasis is placed on identifying the critical relationships between the material parameters, processing conditions, structures created and properties of final products across nano-, micro-, and macroscales. The real-world understanding enables rational design of composites toward multifunctional applications in the emerging fields of flexible electronics, wearable sensors, energy storage, conversion and harvesting.

Keywords: 2D nanofillers; 3D nanocomposites; rational assembly; multiscale structure; multifunctional properties

Acronyms and Symbols

Acronyms	
0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
ABS	Acrylonitrile butadiene styrene
AC	Alternating current
AFM	Atomic force microscopy
BFC	Bidirectional freeze-casting
BNF	Boron nitride foam
BNNS	Boron nitride nanosheet
BOPP	Biaxially oriented polypropylene
CNT	Carbon nanotube
CS	Chitosan
CVD	Chemical vapor deposition
<i>c</i> -BCB	Cross-linked benzocyclobutene
DC	Direct current
DIW	Direct ink writing
DMF	N, N-dimethylformamide
EFA	Electric field assisted alignment
EG	Expanded graphite

EM	Electromagnetic
EMI	Electromagnetic interference
EPD	Electrophoretic deposition
EV	Electric vehicle
GA	Graphene aerogel
GF	Graphene foam
GIC	Graphite intercalated compound
GNP	Graphite nanoplatelet
GO	Graphene oxide
GWF	Graphene woven fabric
<i>h</i> -BN	Hexagonal boron nitride
HI	Hydroiodic acid
IC	Intercalation compound
IPD	Interparticle distance
ITO	Indium tin oxide
LB	Langmuir–Blodgett
LbL	Layer-by-layer
LC	Liquid crystal
LED	Light-emitting diodes
m-rGO	Magnetized rGO
MGW	Multilayer graphene web
MOF	Metal organic framework
NMP	N-methyl-2-pyrrolidone
ns-CuBDC	Copper 1,4-benzenedicarboxylate nanosheets

OTR	Oxygen transmission rate
P(VDF-TrFE)	Poly(vinylidene fluoride-trifluoroethylene)
P(VDF-TrFE-CFE)	Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene)
PANF	Polyaramid nanofiber
PANI	Polyaniline
PC	Polycarbonate
PCM	Phase change material
PDMS	Polydimethylsiloxane
PEDOT: PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PEG	Polyethylene glycol
PEI	Polyetherimide
PET	Polyethylene terephthalate
PI	Polyimide
PMMA	Poly(methyl methacrylate)
POM	Polarized optical microscopy
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVA	Polyvinyl alcohol
PVDF	Poly(vinylidene fluoride)
PW	Paraffin wax
rGO	Reduced Graphene Oxide
ROM	Rule of mixtures

SA	Sodium alginate
SE	Shielding effectiveness
SEM	Scanning Electron Microscope
SGO	Small graphene oxide
TCF	Transparent conductive films
TEM	Transmission Electron Microscopy
TIM	Thermal Interface Material
TMD	Transition metal dichalcogenide
UFC	Unidirectional freeze-casting
UGA	Unidirectional graphene aerogel
ULGO	Ultra-large graphene oxide
VAF	Vacuum assisted filtration
vdW	van der Waals
Symbols	
α	Aspect ratio
k	Dielectric constant
ρ	Density
D	Diameter
n	Number of atomic layers
V_c	Percolation threshold
T_g	Glass transition temperature
T_m	Melting temperature
σ	Electrical conductivity
κ	Thermal conductivity
E	Young's modulus

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1. Introduction

Multifunctional materials with specifically tailored properties are pivotal underpinnings of many emerging technological fields, such as wearable electronics, energy storage and conversion, and environmental remediation. Polymer nanocomposites consisting of nanostructured fillers embedded in a polymer matrix constitute an intriguing class of advanced materials with multifunctional properties originating from the nano-fillers. Two-dimensional (2D) materials, represented by graphene, with only one atomic layer in thickness are becoming increasingly important fillers for composite applications due to their immense surface areas arising from the 2D geometry.[1,2] Over the past decade, many novel 2D materials beyond graphene have been synthesized, such as hexagonal boron nitride (*h*-BN),[3] transition metal carbides and nitrides (MXene)[4] and numerous transition metal dichalcogenides (TMDs),[5] with their distinct optical, electromagnetic and transport properties combined with mechanical flexibility and robustness. In principle, harnessing such excellent properties of 2D materials could yield nanocomposites with staggering multifunctional characteristics. However, it is challenging to fully translate their excellent properties to bulk nanocomposites using conventional design and synthesis strategies, which involve direct mixing of individual nanofillers with molten or liquid polymers to achieve homogeneous dispersions.[6] The limitations are mainly threefold: (i) the difficulties in producing high-quality 2D materials with consistent number of layers, lateral dimensions and surface chemistries; (ii) the difficulties in achieving uniform dispersion of nanofillers without agglomeration in a polymer matrix, especially when the filler content is high; and (iii) the lack of effective strategy to rationally assemble 2D materials into three-dimensional (3D) structures with controllable orientations, spatial distributions and relative contents within a polymer matrix.

Novel synthesis techniques beyond simple mixing have recently been developed to maximize the ameliorating benefits of 2D materials in polymer nanocomposites. Among the key approaches is the multiscale design of the composite structures enabled by rational assembly across different length scales, from 2D nanofillers with controlled dimensions, crystallinities and surface chemistries to a macroscopic architecture with long-range ordered microstructures having controlled dispersion, orientation, interconnection and filler content. The rationally assembled 2D nanofillers in the form of 2D aligned or 3D interconnected structures in a polymer matrix represents a promising route to yield transformative nanocomposites with tailored mechanical, optical, electromagnetic and transport properties arising from the composite constituents' inherent characteristics. Despite substantial efforts in the development of novel synthesis techniques to achieve various structures using 2D nanofillers, there is still lack of understanding of optimizing end structures for specific applications involving multiple desired properties. This is partly ascribed to large variation in the quality of 2D nanofillers in terms of their geometries, crystallinities and surface chemistries induced by different synthesis methods. In addition, the optimum multiscale structures highly depend on specific applications. For example, a high content of aligned 2D fillers along the loading direction maximize mechanical reinforcement, whereas a 3D interconnected network with a low percolation threshold is preferred to deliver isotropic conductivities as a conductive composite. The multifunctional applications will therefore even require contradictory multiscale structures because the desired functional properties may be of mutually exclusive natures. For example, high dielectric constant and low dielectric loss are usually mutually exclusive in a composite but highly desired for applications such as electroactive actuators and electrical energy storage applications.[7] To meet the stringent requirements imposed by desired multifunctional applications, it is of paramount importance to establish a thorough understanding on the process-structure-property relationship so that

multiple properties can be tailored simultaneously according to specific applications. While several excellent reviews have been published in relevant topics, including the synthesis of 2D materials,[8–13] macroscopic assembly of 2D materials,[14–18] composites made from 2D materials,[1,2,19] and their properties and applications,[20–24] the fundamental relationships between important processing parameters, multiscale structures and the resulting multifunctional properties of 2D nanofiller/polymer composites are yet to be explored.

This review is dedicated to offering a critical discussion on state-of-the-art development of 2D nanofillers as functional additives for polymer nanocomposites in the context of their synthesis and rational assemblies, multiscale structural characteristics, multifunctional properties and emerging applications (Figure 1). Among the large varieties of 2D nanomaterials, we focus mainly on those employed in fabricating nanocomposites, from graphene and its derivatives to other emerging counterparts, such as *h*-BN, MoS₂ and Ti₃C₂T_x, the last two being the representatives of the so-called ‘materials beyond graphene’, TMDs and MXene. The synthesis and properties of other types of TMDs and MXene are only briefly discussed as they are less frequently used for composite applications. We aim to highlight the process-structure-property relationships across different length scales, which can guide the rational design towards tailored multifunctionalities in composites. First, different synthesis techniques developed of 2D nanofillers are discussed, focusing on their impacts on nanoscopic structural characteristics such as dimensions, crystallinities and surface chemistries, and the resulting intrinsic properties of 2D fillers. Then, the design strategies and rational assembly techniques of 2D fillers in polymer matrices are reviewed, scrutinizing critical processing parameters which affect the microscopic structural features, such as their dispersion, orientation, interconnection and filler content. These microscopic structures constitute bulk assemblies of different macroscopic shapes including one-

dimensional (1D) fibers, 2D films and three-dimensional (3D) architectures, whose multifunctional properties are correlated with their nano-to-microscopic structures in an effort to identify the process-structure-property relationships. Based on these relationships, strategies to achieve multiple, desired properties are demonstrated with specific applications enabled by the assembled composites with tailored multifunctionalities in emerging areas of flexible electronics, energy storage, conversion and harvesting.

2. Synthesis of high-quality 2D nanofillers

The qualities of 2D fillers are important factors determining the properties of nanocomposites not only by their inherent properties but also by affecting the interfacial properties between the fillers and polymer matrices. Three main criteria in assessing the qualities of 2D fillers for composite applications are: (i) the aspect ratio, i.e., the ratio of lateral dimension to thickness; (ii) the lattice crystallinity; and (iii) the type and amount of functional groups. The synthesis of 2D nanofillers with high aspect ratios, few lattice defects and proper functional groups for interfacial interactions with polymer matrices is essential to achieving desired functional properties of composites. While the synthesis techniques of 2D materials were summarized in previous review articles,[8–13] the important attributes required for achieving their high qualities particularly for composite applications have not been specifically identified. Therefore, we critically discuss the synthesis parameters of different techniques to identify their correlations with the qualities of resulting 2D nanofillers and to highlight their respective advantages and disadvantages for composite applications.

Techniques employed to synthesize 2D nanofillers and their resulting qualities in terms of aspect ratios, lattice crystallinities and functionalization are summarized in Table 1. [These techniques can be divided into two categories, namely: \(i\) solvent-based exfoliation from bulk crystals and \(ii\) template-based chemical vapor deposition \(CVD\) from precursor gases.](#)

2.1. Solvent-based exfoliation

2.1.1. Exfoliation assisted by mechanical force

Solvent-based exfoliation is a versatile method for composite fabrication because the exfoliated 2D nanofillers can be directly mixed with molten polymers or monomers in solvents and processed using conventional solution mixing techniques. The exfoliation process is essentially the separation of individual 2D layers from the bulk by an external force to overcome the interlayer cohesive energies (Figure 2a). The most straightforward approach is the direct exfoliation of bulk crystals in solvents using ultrasonication or high-shear mixing, which provides mechanical energies beyond those of interlayer van der Waals (vdW) forces to facilitate exfoliation. A range of 2D materials, including graphene,[37,38] boron nitride nanosheets (BNNSs),[39] metal organic frameworks (MOFs),[41] WS₂ [39] and MoS₂ [39,40], were successfully exfoliated from their bulk crystals using this technique. The main advantage of direct exfoliation is that highly crystalline lattice structures with few defects could be preserved in 2D nanosheets. As a result, the Raman D- to G-band intensity ratio, I_D/I_G , remained very low, varying from 0.1 to 0.4, for graphene obtained by ultrasonication or shear mixing of graphite in *N*-Methyl-2-pyrrolidone (NMP) (Figure 2b),[37,38] a reflection of a high-quality graphitic structure with few defects. However, the lack of functional groups makes the dispersion of 2D sheets only possible in organic solvents. Moreover, the monolayer yield in the final dispersion is relatively low, e.g., less than 10 % for graphene, with predominantly few- and multi-layer nanosheets even after prolonged sonication and shear mixing. Sonication in a bath sonicator using a low power for short time (~ 30 min) produced graphene sheets with typical lateral dimensions of a few micrometers [38] while shear mixing yielded nanosheets of 300 – 800 nm in sizes.[37] However, excessive sonication has to be avoided as it reduces the lateral dimensions of graphene sheets to smaller than 1 μ m. The length (L) of graphene decreased from ~3 to 1 μ m while the width (W) reduced from ~1 μ m to 300 nm when the sonication time (t) increased, as shown in

Figure 2c.[65] Both L and W followed a power law dependence on sonication time, t , as $L \propto t^{-0.5}$ and $W \propto t^{-0.5}$, which is similar to the case of 1D CNT and in agreement with theoretical predictions.[66]

2.1.2. Functionalization-assisted exfoliation

Strong interlayer interactions between 2D sheets make direct exfoliation rather inefficient with low yields of monolayers. To overcome the interlayer interactions, strong oxidizing agents, such as potassium permanganate (KMnO_4) and sulfuric acid (H_2SO_4), were used to form graphite intercalation compounds (GICs) consisting of intercalated and functionalized multilayer graphite. The ensuing expansion of interlayer spacing by thermal shock at an elevated temperature significantly weakens the interlayer vdW energies and therefore monolayer GO sheets are readily exfoliated from GICs at high yields of over 90 % under mild sonication. Such functionalization-assisted exfoliation of monolayer GO from graphite involving two-step oxidation was first developed by Hummers [42] and later modified to ensure complete oxidation of graphite [67]. The abundant oxygenated functional groups facilitated the exfoliation of monolayer GO and their stable dispersion in water while the absence of prolonged sonication also led to relatively large lateral dimensions of GO sheets over 1 μm with aspect ratios of more than 10^3 . Such large aspect ratios gave rise to the formation of liquid crystals (LCs) in aqueous solutions, which are essential to self-assembly of GO sheets to form various 3D assemblies (see Section 4.1).[68,69] However, the sp^2 bonded lattice structures were severely altered in the presence of functional groups (with Raman $I_D/I_G = 0.8$ to 1, Figure 2b), leading to much inferior electrical and thermal conductivities of GO compared to pristine graphene, see Section 3.2.2. Hence, chemical or thermal reduction was needed prior to composite fabrication if high conductivities were required.[43,70]

Other 2D nanofillers, such as BNNSs, WS₂ and MoS₂, were also exfoliated to some extent using the modified Hummers method [44] or other chemicals such as sodium hydroxide [47,50]. The partial ionic bonds between the layers, *i.e.* lip-lip interactions, and the slightly shorter interlayer distance than in graphite, *i.e.* 3.33 vs 3.35 Å, make *h*-BN much more difficult to exfoliate than graphene.[56] The oxidants or hydroxides were difficult to intercalate into the *h*-BN layers and hydroxyl functionalization took place at the edges.[44] Consequently, the resulting BNNSs consisted of stacked layers with thicknesses ranging 3 to 4 nm and lateral sizes of 2 to 3 μm.[47,50] Their thicknesses were further reduced by applying excessive shear forces through ball milling in the presence of sodium hydroxide, urea or furoic acid.[45,46,48] Nonetheless, the lateral dimensions were also simultaneously reduced because of the high energy applied in ball milling. In addition, unlike GO sheets, the yields of monolayer BNNS were extremely low because of the ineffective intercalation by the functionalizing agents. The aspect ratios of BNNSs obtained from functionalization-assisted exfoliation remained low, ranging from 10² to 10³, within a similar range to ultrasonication-assisted exfoliation (Figure 2d). The hydroxyl and amine functional groups present at the edges of BNNSs are nevertheless beneficial to dispersion and interfacial interactions with polymer matrices.

2.1.3. Intercalation-assisted exfoliation

The modified Hummers method involves the exfoliation of graphite oxide into monolayer GO using sonication, which inevitably breaks large GO sheets into smaller pieces. Maintaining large lateral dimensions and aspect ratios of GO sheets require completely circumventing the use of damaging ultrasonication process.[73] In this regard, a pre-exfoliation step involving intercalation of H₂SO₄ and HNO₃ followed by thermal expansion to expanded graphite (EG) was introduced before oxidation with KMnO₄. [53] The use of EG as starting material with much larger interlayer spacings than GICs made the exfoliation

possible under mechanical stirring, so that the detrimental sonication step was completely eliminated. Such intercalation-assisted exfoliation yielded ultra-large GO (ULGO) monolayers with an average lateral size of $\sim 30 \mu\text{m}$,^[55] significantly larger than those produced using the modified Hummers method. Thus, the aspect ratio reached an ultrahigh value of 3×10^4 , enabling the formation of LCs at a very low GO concentration of 0.1 wt %.^[55] The significance of LC formation at low concentration will be discussed in Section 4.1.

Apart from GO, other 2D nanofillers have also been exfoliated using proper intercalants. Graphite was intercalated with acids, such as H_2SO_4 , HNO_3 and HCOOH , and exfoliated into graphite nanoplatelets (GNPs) having a few nanometers in thickness and up to $\sim 50 \mu\text{m}$ in lateral dimension.^[53,74] Albeit in the form of multilayer sheets, GNPs are not as heavily oxidized as GO thanks to the absence of strong oxidants, making them inherently conductive without further reduction. Reducing the thickness to monolayers is contingent on the achievement of stage-1 GICs with appropriate intercalants. It is reported that heating GICs in non-oxidizing acids, including H_2SO_4 and H_3PO_4 , for complete drying led to the formation of stage-1 GICs,^[75] and further exfoliation to monolayer graphene was achieved in organic solvents with medium polarities.^[51] Surprisingly, the same strategy has also been proven to be applicable to *h*-BN for which intercalation was considered more difficult. Acids like H_2SO_4 and H_3PO_4 were able to slowly intercalate into *h*-BN to form stage-1 intercalation compounds (ICs) in the absence of solvents.^[76] Monolayer BNNSs were achieved at high yields of over 80 % in *n*-pentanol from the stage-1 *h*-BN ICs.^[51] The lateral dimensions of these monolayer BNNSs were as large as tens of microns, yielding aspect ratios of over 10^4 . It should be noted that no chemical reactions between the solvent-free acids and graphite or *h*-BN occurred during intercalation, which is completely different from the modified Hummers method where oxidizing agents were used together with intercalant acids. This also

means that pristine graphene and BNNSs without functional groups can be achieved using this method.[51,52] The Raman I_D/I_G of graphene and GNPs obtained was ~ 0.1 (Figure 2b),[51–53] corroborating their high-quality structures with few defects. Other suitable intercalants for h-BN include alkali metal ions (Li^+),[56] gas molecules (N_2),[57] and ionic liquids.[52] These intercalants are not as efficient as solvent-free acids in forming stage-1 h-BN ICs because the obtained BNNSs were mostly in the form of few- or multi-layers. Intercalants, like ionic liquids and Li^+ , were found effective in intercalating MoS_2 . [52,58] Layered MOF crystals were also intercalated with organic compounds such as 4,4'-dipyridyl disulfide for exfoliation into 2D MOF sheets with controlled thicknesses and high yields.[59] While graphene, BNNSs and MoS_2 can be intercalated and exfoliated directly from their layered bulk forms, MXene requires etching of metal layers in the bulk MAX phase before intercalation and exfoliation. MXene is a group of 2D early transition metal carbides or nitrides with a composition of $\text{M}_{n+1}\text{X}_n\text{T}_x$, where M is a transition metal (Ti, V, Nb, etc.), X is nitrogen or carbon, and T is surface functional groups (-OH, -F, -O-, etc.). One of the most widely studied 2D MXene is $\text{Ti}_3\text{C}_2\text{T}_x$, which is obtained by etching Al layers in Ti_3AlC_2 followed by exfoliation.[12] The lattice crystallinities, lateral dimensions and types of surface functional groups of the 2D $\text{Ti}_3\text{C}_2\text{T}_x$ sheets depend on the etchants and exfoliation techniques employed. Two types of etchants are commonly used, namely, HF or their salts and LiF-HCl solutions. Strong etchants, such as HF and their salts, tend to introduce fluorine functional groups while producing small flakes with a large number of defects. Mild etchants containing LiF and HCl create fewer fluorine groups, yet smaller number of defects. Moreover, the *in-situ* intercalation of Li^+ into the etched galleries facilitates exfoliation under mild mechanical stirring, producing 2D $\text{Ti}_3\text{C}_2\text{T}_x$ sheets with large lateral sizes and high aspect ratios. Other types of MXene, such as Ti_2CT_x and $\text{Mo}_2\text{TiC}_2\text{T}_x$, were also exfoliated from their bulk MAX phases using similar techniques.[4]

Amongst the above three solvent-based exfoliation methods, intercalation-assisted exfoliation is considered the most effective in producing 2D nanofillers with few defects and high aspect ratios (Figure 2b and d). Taking BNNSs as an example, the intercalants can expand the interlayer spacing from 0.33 nm in h-BN to 0.74 nm in ICs, significantly reducing the interlayer vdW energies that need to be overcome for the separation of individual BNNSs.[76] Consequently, mild mechanical stirring or high-shear mixing are sufficient without the need of excessive sonication steps for successful exfoliation.[51] The mild processing conditions can minimize the damage to the BNNS layers, allowing high aspect ratios of over 10^4 . This value is much higher than those obtained from direct exfoliation or functionalization-assisted exfoliation (Figure 2d), both of which rely heavily on the high energy provided by ultrasonication. The high aspect ratios of 2D nanofillers play an important role in the assembly into 3D structures, which will be discussed in Section 4.

A major drawback of 2D nanofillers obtained via intercalation-assisted exfoliation is the lack of functional groups, requiring additional functionalization steps to improve the dispersion and interfacial interactions with polymer resins for composite fabrication. The functionalization of 2D nanofillers can be broadly categorized into chemical and physical functionalization. Chemical functionalization refers to the covalent attachment of functional groups onto the basal planes or edges of 2D nanofillers through chemical reactions. GO sheets contain numerous oxygenated functional groups that serve as sites for further functionalization through various reactions, such as nucleophilic or electrophilic substitution, condensation, and addition.[77] As a consequence, abundant functional groups, such as amino groups, silane groups, diazonium salt, and long-chain polymers, are readily attached onto the surface of GO sheets. The basal planes of graphene are not as chemically reactive as those in GO sheets because of much fewer active sites in graphene.[78] Therefore, activation of carbon is needed to improve the reactivity of graphene for functionalization.[78] GICs

intercalated with alkali metal ions such as potassium cations were found to exhibit negative charges on the surface after exfoliation, making the carbon atoms reactive with electrophilic groups and radicals in solution.[79] Similar approaches have also been applied to equally inert BNNS by taking the advantage of partially ionic B-N bonds where the B atoms have partial positive charges while the N atoms have partial negative charges.[8] A few functional groups, such as hydroxyl,[80] amine,[81] ether,[80] and butyl [82] groups, have been attached to the basal plane of BNNS after exfoliation in solvents. These functional groups contribute to improved interfacial interactions between the 2D nanofillers and polymer matrices by forming strong covalent bonds at the interfaces, leading to enhanced mechanical properties of composites.[82,83] However, chemical functionalization inevitably alters the characteristics of in-plane covalent bonds, impacting the electron and phonon transport properties which in turn adversely affect the electrical and thermal conductivities of composites. Physical functionalization, also known as non-covalent functionalization, only involves physical adsorption of molecules onto the surface of 2D nanofillers and therefore does not damage their lattice structures. A number of non-covalent functionalizing agents, including surfactants, small aromatic molecules, and polymer chains, have been widely explored to adsorb onto the surface of GO, graphene and BNNS through vdW forces, electrostatic forces, and π - π interactions.[8,77,78] These non-covalently functionalized 2D nanofillers were uniformly dispersed in the solution because of reduced surface tension. Although the resulting interfacial bond with a polymer resin is not as strong as their chemically functionalized counterparts, non-covalently functionalized 2D nanofillers are commonly used for effectively improving the functional properties of composites as the damages to in-plane crystal structures of 2D nanofillers are less severe.

2.2. CVD

2D materials including graphene[60,61], BNNSs[62–64] and some TMDs,[10,11] such as MoS₂, WS₂ and MoSe₂, can be grown on a Cu, Ni or SiO₂ substrate using the CVD technique. In a typical process, the precursor gases as well as the protective gases like Ar or H₂ are fed into a tube furnace at an elevated temperature and 2D materials with polycrystallinities are deposited on the substrate upon cooling. The lateral dimensions of CVD-grown 2D materials, such as graphene and BNNSs, can be in the order of centimeters[60,64], while the number of graphene layers in a sheet can be controlled by varying the feeding rate of precursor gases.[13] The Raman I_D/I_G of CVD-grown graphene was typically less than 0.3, indicating their high-quality crystal structures (Table 1).[60,61]

The CVD method can produce mono- or few-layer 2D materials with higher qualities, larger lateral dimensions and better controlled thicknesses than the solution-based exfoliation techniques. Moreover, depending on the shape of templates, the technique can produce 2D materials with different bulk morphologies which can serve as pre-dispersed fillers eliminating the issue of nanofiller dispersion in the polymer matrices. More details of CVD-grown 2D nanofillers are discussed in the context of composite fabrication in Section 4.3.2.

It is relevant to note the costs of different synthesis techniques of 2D nanofillers and their viability for mass production because large quantities of 2D nanofillers are normally needed for composite applications. Solvent-based exfoliation techniques are promising for large-scale production of 2D nanofillers because of the low cost and availability of bulk precursors.[9] It is estimated that graphene sheets can be produced at mass production rate of 5.3 g/h using shear mixing in NMP, far exceeding that of CVD technique (~ 1 g/h).[37] Nevertheless, some 2D nanofillers can only be exfoliated effectively in high-boiling-point solvents, such as NMP and DMF, which are toxic and may give rise to additional costs required when dealing with their health and environmental issues. In addition, the qualities of 2D nanofillers produced by exfoliation, other than graphene, are rather inconsistent with

many defects and small sizes. The CVD process is expensive because of the high costs arising from large energy consumption during operation and removal of metal substrates.[84] Nonetheless, cost-effective production of 2D nanofillers through CVD may be possible if industrial-scale equipment is available to facilitate the roll-to-roll process.[85] The high quality of CVD-grown 2D nanofillers is the main incentive for the development of industrial-scale CVD processes.

3. Physical and mechanical properties of 2D nanofillers

3.1. Intrinsic properties of 2D nanofillers

The intriguing properties of 2D materials are among the most important impetuses for their potential applications in multifunctional nanocomposites. The mechanical, electrical and thermal properties of various 2D materials along the in-plane directions are summarized in Table 2. Notably, monolayer, defect-free graphene is considered the strongest material on earth with an in-plane elastic modulus of 1 TPa and a tensile strength of 125 GPa owing to the strong sp^2 -carbon bonds.[86] Although other 2D materials, including BNNS,[87] MoS₂, [88,89] WS₂, [90] Ti₂CT_x, and Ti₃C₂T_x sheets, [91] exhibit lower moduli and strengths than those of graphene, they are still appreciably stiff and strong with moduli varying in the range of 300 to 800 GPa and strengths of 30 to 70 GPa. It is noted that these excellent mechanical properties are obtained from monolayer 2D sheets with few defects, as the strength reaches the theoretical limit of about 10 % of the modulus.[89] The excellent mechanical properties not only make 2D materials promising fillers for mechanical reinforcements, but also constitute the foundation for their multifunctional applications. The electrical conductivities of 2D materials differ by many orders of magnitude, ranging from highly conductive MXene [27,92,93] and graphene to semiconducting WS₂ and MoS₂ and insulating BNNS. Such a wide range makes it possible to tailor the electrical properties of composites for specific end applications by choosing appropriate 2D fillers or their hybrids

with an appropriate combination. In terms of thermal conductivities, pristine monolayer graphene in a suspended state shows an ultrahigh value of $\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$, [94] exceeding that of diamond and is the highest among all known materials. Although suspended few-layer BNNSs have a lower thermal conductivity of $360 \text{ Wm}^{-1}\text{K}^{-1}$, [95] their insulating nature makes it useful for applications requiring both thermal conduction and electrical insulation. These excellent thermal conductivities arise from their unspoiled hexagonal crystal structures so that phonons can transport without scattering. The suspended sheets also ensure free vibrations of out-of-plane phonons without damping, contributing to high thermal conductivities.

3.2. Extrinsic factors affecting the properties of 2D nanofillers

The above excellent properties are measured along the in-plane direction of suspended monolayer 2D nanosheets with few crystal defects. However, the 2D sheets fabricated using common processing techniques inevitably contain numerous defects and functional groups, and sometimes more than a few atomic layers. In addition, because these 2D nanofillers are embedded in the polymer matrices rather than in the suspended states, they may not orient with their planes along the desired directions when made into composites. Therefore, several factors that can affect the efficacy of 2D nanofillers in improving the properties of composites should be given due attention, namely, anisotropic structures, defects and functional groups and number of layers, as schematically indicated in Figure 3a.

3.2.1. Anisotropic structures

Owing to the anisotropic structures and bonding characteristics of 2D nanofillers with strong in-plane covalent bonds but weak interlayer vdW forces, their physical and mechanical properties naturally become anisotropic along the in-plane and through-the-thickness directions. For example, the thermal conductivity of graphite in the thickness direction is only $\sim 6 \text{ Wm}^{-1}\text{K}^{-1}$, almost three orders of magnitude lower than the in-plane value, due to the

stronger phonon scattering through the interlayer vdW bonds than the in-plane C-C covalent bonds (Figure 3b).[113] Other important properties, such as electrical conductivity and mechanical properties, also exhibit significant anisotropy, giving rise to anisotropic properties of graphene-polymer composites.[29,83,114] Therefore, if the excellent in-plane properties are to be best utilized in composites, the orientations of 2D nanofillers need to be carefully designed. The strategies to fabricate highly aligned nanofiller in composites are discussed in Section 4.

3.2.2. Defects and functional groups

The properties of 2D nanofillers are sensitive to crystal defects and functionalization, which are inevitably introduced during their syntheses. Monolayer graphene prepared from CVD contained numerous grain boundaries or wrinkles, resulting in a lower modulus of ~ 500 GPa, almost half the defect-free monolayer graphene sheet (~ 1 TPa).[97,98] Chemically-derived GO and rGO sheets had even inferior moduli ranging from 200 to 250 GPa associated with the presence of functional groups (Figure 3c).[100,103] These defects and functional groups altered part of the sp^2 -hybridized carbon to a sp^3 structure,[115,116] inducing wrinkles and weakening the interatomic bonds and thus degrading the modulus. In addition to mechanical properties, electrical and thermal conductivities of graphene are also substantially reduced by defects and functional groups through the scattering of electrons and phonons at the sp^3 sites.[117,118] In view of the deleterious effects of functional groups on transport properties of GO, chemical or thermal reductions are usually carried out to remove them so as to partially recover the sp^2 C-C bonds.[117] Even after reductions, however, both conductivities of rGO still remain far below those of pristine graphene (Table 2). In summary, functionalization is detrimental to the intrinsic properties of 2D nanofillers although functional groups are necessary to improve the dispersion and interfacial interactions with

polymer matrices. A compromise must be implemented between the inherent properties of 2D nanofillers and interfacial properties in the composites.

3.2.3. Number of atomic layers (n)

The excellent inherent properties of monolayer 2D sheets originate from the strong in-plane covalent bonding. With increasing n , the emergence of weak interlayer vdW bonds lead to degraded properties of 2D nanofillers. For example, the modulus and strength of graphene decreased by 30 % when n was increased to 8 as a result of the interlayer slippage.[87] The thermal conductivity of suspended graphene also decreased with increasing n , converging to the value of bulk graphite ($\sim 1300 \text{ Wm}^{-1}\text{K}^{-1}$) beyond 4 layers, as shown by green triangles in Figure 3d.[119] The sharply reduced properties across the dimensional transition from 2D to 3D may suggest the advantage of monolayer over multilayer 2D sheets in reinforcing composites. However, there is an overlooked effect that the surrounding polymer might have when 2D nanofillers are incorporated in the matrix: the effect of n on some properties may be completely reversed. For example, the presence of substrates or residual polymers significantly reduced the in-plane thermal conductivities of mono- [120] and bilayer [121] graphene to $500\text{-}600 \text{ Wm}^{-1}\text{K}^{-1}$ (blue diamonds in Figure 3d), which is almost an order of magnitude lower than $\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$ of suspended graphene. Similarly, the polymer residue on suspended few-layer h -BN reduced its in-plane thermal conductivity from ~ 360 to $\sim 250 \text{ Wm}^{-1}\text{K}^{-1}$. [95] These findings are attributed to the scattering of out-of-plane phonons in graphene or h -BN sheets by the surrounding substrate or polymer, signifying similarly reduced thermal conductivities when they are embedded in polymer matrices.[122] With increasing n , however, the thermal conductivities of graphene supported on a SiO_2 substrate (blue diamonds in Figure 3d) or embedded between SiO_2 layers (purple circles in Figure 3d) increased to the limit of bulk graphite,[123,124] exhibiting a completely different trend from the suspended counterparts. By the same token, multilayer graphene is found more efficient

in improving the thermal conductivity of polymer composites than monolayer ones, because the inner layers in multilayer graphene are insensitive to the adverse effect of surrounding matrix.[122]

4. Design strategies and assembly techniques

The excellent properties of 2D nanofillers combined with their immense surface areas make them particularly promising as reinforcements for nanocomposites. In principle, harnessing the potential of 2D nanofillers could yield nanocomposites with staggering multifunctional properties. However, translating their excellent inherent properties to the bulk nanocomposites is not trivial. In conventional strategies, a small amount of nanofiller is directly mixed with a monomer or a polymer resin followed by dispersion using ultrasonication or shear-mixing,[6] to achieve random orientation of nanofillers. The drastically augmented viscosity of polymer with increasing filler content beyond a few wt % makes their dispersion and processing of nanocomposites very challenging. Therefore, the properties of resulting composites are often far inferior to the predictions from the known inherent properties of 2D nanofillers. For multifunctional applications where a combination of properties is desired, the required microstructures can be even contradictory for different properties, which warrants more meticulous design to rationally gather the nanofillers. One possible solution is to assemble the 2D building blocks in a controllable manner such that their orientations, distributions and interconnections are tailored to achieve preferred effects in the final composite products. This can be done either *in-situ* in the presence of polymer(s), or using predefined templates followed by subsequent infiltration of polymer(s). Depending on the driving force employed in the assembly process, the design strategies can be divided into three categories, namely, (i) the self-assembly based on the LC phase formation in aqueous solutions or liquid polymers; (ii) the forced assembly driven by external forces; and

(iii) the assembly directed by well-defined templates. The nature and characteristics of these assembly strategies are discussed in the following.

4.1. LC phase assisted self-assembly

4.1.1. LCs of graphene and GO

LCs are soft matters or anisotropic particles in an intermediate phase between amorphous liquids and crystalline solids with combined characteristics of mobility and ordering. 2D nanosheets can form lyotropic LC most commonly with nematic phases in aqueous or solvent solutions according to the excluded volume theory.[125–127] While pristine graphene is superior to GO counterparts in terms of many inherent properties arising from its highly crystalline structure with fewer defects, its processing in solvents, especially in water, is challenging. Liquid phase exfoliation of bulk graphite by ultrasonication [39] or using shear forces [37] in high-boiling-point solvents such as NMP can yield pristine graphene, but usually at a very low concentration of less than 1 mg mL^{-1} . [38] Moreover, high-energy sonication and high-speed shear often result in very small sizes yet low yields of monolayers with an aspect ratio of several hundreds, which is too low to form LCs at a typical concentration lower than 1 mg mL^{-1} . Replacing organic solvents with chlorosulfuric acid as the medium resulted in exfoliation into graphene at a high concentration of $\sim 2 \text{ mg mL}^{-1}$. [128] Nevertheless, nematic phases were only observed after condensing to a much higher concentration of over 20 mg mL^{-1} by centrifugation, which was signified by the schlieren textures under the polarized optical microscopy (POM), as shown in Figure 4a. In short, the relatively low aspect ratio of graphene achieved in the liquid phase impedes the isotropic-nematic phase transition, making the formation of LCs difficult, especially at a low concentration.

By contrast, GO LCs are more readily observed. While lamellar and chiral phases have been reported for GO gels [129] and GO dispersions with narrow size polydispersity,[130] the

most common LCs observed for GO dispersions is the nematic phase, first reported by several groups in 2011.[55,68,69,131] The formation of LCs in GO dispersions was revealed by POM and their rheological properties. As shown in Figure 4b, GO dispersed in DI water showed typical birefringence of nematic phases under the POM, featuring dark and bright schlieren textures with mostly $\pm 1/2$ disclinations.[68] The viscosity of GO aqueous solutions decreased with increasing shear rate (Figure 4c), suggesting organization of GO sheets under the shear flow and confirming the formation of LCs.[69] The critical concentration for transition from the isotropic phase to nematic LCs [55,68,69,131] are compared with other 1D rod-like and 2D layered materials, including CNTs,[132] clays,[125] phosphates,[133] transition metal oxides [134] and graphene [128], as summarized in Figure 4d. The critical concentration varied approximately inversely with aspect ratio in a log-log plot, in agreement with the theoretical predictions for rod-like and disc-shaped particles given by [55,127]

$$\frac{4}{\pi d} C \alpha = 4.12, \quad (1)$$

where C is the concentration in dispersion (in g m^{-3}), $\alpha (= D/t)$ is the aspect ratio, and d is the mass density of 2D particles. The critical concentration for GO LCs was only 0.1 wt % or equivalent 1 mg mL^{-1} , [55] much lower than that of graphene counterpart, which is credited to several ameliorating factors. The abundant hydrophilic functional groups allowed GO sheets to uniformly disperse in water. More importantly, GO sheets were mostly monolayers with lateral sizes as large as tens of microns, leading to an ultrahigh aspect ratio of more than 10^4 . Such a high degree of anisotropy made the formation of LCs much easier in GO dispersion than others. Apart from the aspect ratio, polydispersity in size [135,136] and shape [137] of 2D particles can also affect the LC formation.

Besides water, GO sheets were also dispersed in common organic solvents, such as NMP, N,N-dimethylformamide (DMF) and N-cyclohexyl-2-pyrrolidone, and exhibited nematic phases similar to those dispersed in water.[138,139] It should be noted that only polar

solvents can disperse GO effectively, meaning that GO LCs cannot form in non-polar organic solvents, such as toluene and chloroform. The capability of forming nematic LCs of GO in polar organic solvents has practical implications to apply GO sheets in non-aqueous environments. For the rational assembly of GO/polymer nanocomposites, the stability of GO LCs in the presence of polymer molecules is particularly pertinent. As the viscosity of GO dispersion increases drastically with the addition of polymers, liquid crystalline phases in GO/polymer dispersions are not as commonly observed. Figure 4e shows a POM image of a 2 wt % GO/epoxy latex mixture in water, exhibiting birefringence similar to that of GO aqueous dispersions.[83] Both the low-viscosity aqueous medium of waterborne epoxy and the large size of GO sheets contributed to the formation of LCs. Besides aqueous media, polyacrylonitrile-grafted GO sheets also showed nematic phases in DMF.[140]

4.1.2. LCs of *h*-BN, MoS₂ and Ti₃C₂T_x

Notwithstanding the rich mesophases of GO colloids, limited successes have been achieved when it comes to the formation of LCs in dispersions containing *h*-BN, MoS₂ and Ti₃C₂T_x nanosheets. The reasons are twofold, namely, (i) the relatively small lateral dimensions of these nanosheets obtained through the liquid phase exfoliation, and (ii) their poor dispersion in aqueous or organic solvents. Therefore, significant efforts have been made towards achieving large-size 2D sheets and better dispersion in solvents. MoS₂ is a typical 2D TMD which can be synthesized through liquid phase exfoliation.[50,52,58] However, exfoliation of natural MoS₂ powder produced MoS₂ nanosheets with submicron sizes,[5] which are too small to form LCs at relatively low concentrations. To address this issue, hexagonal MoS₂ crystals with large grain sizes were grown along the [0001] direction (Figure 5a).[141] Such a preferred orientation led to weak interlayer interactions, facilitating exfoliation to mostly monolayer MoS₂ sheets with large lateral sizes of up to 20 μm (Figure 5b). The resulting high aspect ratio facilitated the formation of nematic phases at a concentration of 0.5 mg mL⁻¹ in a

hexane solvent (Figure 5c). $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets obtained from liquid phase exfoliation had an average lateral dimension of 200 nm, as shown in Figure 5d.[142] With such small sizes, nematic phases could be formed in $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous dispersion only at an ultrahigh concentration of 250 mg mL^{-1} . To further increase the packing order, the $\text{Ti}_3\text{C}_2\text{T}_x$ aqueous dispersion was mixed with a surfactant C_{12}E_6 (hexaethylene glycol monododecyl ether), which induced stronger interactions between the $\text{Ti}_3\text{C}_2\text{T}_x$ sheets by forming hydrogen bonds with $-\text{O}$ or $-\text{F}$ groups on their surface (Figure 5e). This colloid system exhibited fan-like textures under POM (Figure 5f), indicating the formation of lamellar phases with the help of surfactant.

The LC phases observed in aqueous or organic solvent dispersions of 2D nanosheets signify the potential of achieving long-range orders in macroscale assemblies or nanocomposites using versatile solution-based techniques. The abundant mesophases offer rare opportunities to exploit high degree of orientation and unique morphologies of 2D sheets in nanocomposites.

4.1.3. Self-assembly of 2D LCs

The LC nature of anisotropic 2D nanosheets facilitates the spontaneous development of nematic order in aqueous or organic media. Such a process is driven by entropy due to the excluded volume effect without the need of external stimuli. Upon removal of solvent, these 2D nanosheets self-assemble into a bulk structure with microscopic orders inherited from the nematic phases. Depending on the type of solvent removal process, such as solution casting and sol-gel freeze-drying, bulk assemblies with different microscopic morphologies can be constructed. Figure 6a presents a schematic of pressure-temperature relationship with regard to two self-assembly routes as the solvent removal processes, which are discussed in the following.

Solution casting. The most straightforward way is the direct evaporation of solvents at ambient or elevated temperatures (Figure 6a, i). LCs consisting of high-aspect-ratio GO sheets self-aligned into a layered structure with an orientation vector n perpendicular to the horizontal plane.[55] Upon solvent evaporation, GO LCs self-assembled into highly-aligned GO films (Figure 6b).[55,138] Such self-alignment of GO LCs was also achieved even in the presence of polymer molecules, resulting in highly aligned graphene/polymer nanocomposites after polymerization.[83,143,144] GO sheets self-aligned in an epoxy matrix after simple casting of the GO/waterborne epoxy solution into a flat mold, as shown in Figure 6c-d.[83] Several criteria must be satisfied to achieve the self-alignment, namely, (i) a high aspect ratio of 2D nanosheets, (ii) a high concentration of 2D nanosheets in the dispersion, and (iii) a low viscosity medium, such as water or waterborne polymers. The excluded volume between the high-aspect-ratio 2D nanosheets drives the formation of LCs above the critical concentration to maximize the entropy, whereas the low viscosity medium guarantees the free movement of individual 2D sheets during the course of rearrangement. Therefore, 2D LCs other than GO can hardly form a highly aligned structure by simple solution casting because of the limited lateral dimensions and solubility of nanosheets in water. Nonetheless, the self-alignment of LCs offers a simple yet effective strategy to fabricate aligned 2D films and polymer nanocomposites.

Sol-gel freeze-drying. The second solvent removal strategy is the freeze-drying, also known as lyophilization. In this approach, the dispersion containing 2D LCs is first rapidly quenched to immobilize 2D nanosheets using ice or frozen solvent crystals, followed by sublimation of ice or frozen solvent under a low pressure (Figure 6a, ii). Due to the rapid growth of ice crystals, the ordered microstructure of 2D LCs is replicated in the freeze-dried product. Figure 6e shows the morphology of a freeze-dried aqueous dispersion of 0.5 wt % GO. The GO sheets tended to bend around two $\pm 1/2$ disclinations, as indicated by the + and – signs,

with aligned sheets in between.[68] The freeze-dried $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets from an aqueous solution showed a slightly different morphology (Figure 6f). The much smaller lateral sizes of $\text{Ti}_3\text{C}_2\text{T}_x$ sheets ranging 200 to 300 nm than GO sheets of a few to tens of micrometers led to much smaller domains of aligned 2D sheets, *i.e.*, $\sim 10\ \mu\text{m}$ for $\text{Ti}_3\text{C}_2\text{T}_x$ vs $\sim 100\ \mu\text{m}$ for GO. Moreover, the much higher concentration of $250\ \text{mg mL}^{-1}$ $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets required for LC formation resulted in smaller pore sizes than for GO. Hence, the freeze-dried $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets exhibited more random arrangement on a macroscopic scale.

The degree of order for nematic 2D LCs appears extensive only on a microscale, while the bulk assemblies made from direct freeze-drying tend to feature a porous structure with locally aligned 2D nanosheets (Figure 6e, f). To achieve long-range alignment, the morphologies of 2D LCs need to be controlled. One effective approach is the use of ultra-large nanosheets. As mentioned previously, the ULGO sheets self-assembled into a layered structure in an aqueous medium due to the excluded volume effect.[55] Such an attribute of self-alignment was exploited to fabricate aligned graphene aerogels (GAs) using a one-step reduction and sol-gel process, as shown in Figure 7a.[29] The ULGO sheets with an average area of $\sim 200\ \mu\text{m}^2$ (Figure 7b) were reduced by hydroiodic acid (HI) before the sol-gel process and freeze-drying. The GA made from a $2\ \text{mg mL}^{-1}$ GO dispersion exhibited a highly porous, anisotropic structure consisting of mostly horizontally-aligned rGO sheets and some vertically-oriented sheets connecting the horizontal skeleton (Figure 7c-d). This is in stark contrast with the GAs made from low concentration GO dispersions or small GO sheets, which showed almost random orientations. The self-alignment of ULGO sheets was an entropy-driven process to minimize the excluded volume, and the steric hindrance between the highly concentrated GO sheets prevented re-orientation of GO sheets in the low-viscosity media. Another approach to control the morphology of self-assembled GO sheets is tuning the pH value of a GO aqueous dispersion.[145] In alkaline media such as KOH solution, GO LCs with a highly ordered

microstructure were observed as a consequence of the enhanced electrostatic repulsion induced by hydroxide (OH^-) (Figure 7e). Such long-range ordered GO LCs tended to align along the inner surface of the reaction tube (Figure 7f). After hydrothermal reduction and freeze-drying, the GA exhibited a concentric microstructure with better aligned rGO sheets close to the surface than in the inner core (Figure 7g-h). The porous GAs allowed the infiltration of polymer resins to achieve composites containing an inherently interconnected GA with an ordered arrangement.

4.2. External field assisted assembly

The LC-based self-assembly is a simple yet effective strategy without resorting to external stimulation. However, long-range orders in the bulk assemblies or nanocomposites can only be achieved for GO nanosheets under certain conditions. Other 2D nanofillers, such as BNNS, MoS_2 and $\text{Ti}_3\text{C}_2\text{T}_x$, cannot be self-assembled into highly ordered structures due to either limited arrangement of LCs or lack of LC phases in the liquid environment. Therefore, external forces in the form of mechanical, electric and magnetic fields are required to assist the assembly process such that long-range orders can be established using the 2D nanosheet building blocks. The assembly processes assisted by various mechanical forces are discussed in the following.

4.2.1. Mechanical force assisted assembly

The non-Newtonian characteristic of LC (Figure 4c) suggests that the macroscopic orientation of 2D nanosheets can be tuned using external forces. Indeed, macroscopic alignment of 2D nanosheets was observed by unidirectionally drawing GO/polymer gels into 1D fibers[68] and GNP/polyethylene[146] or BNNS/polyvinyl alcohol (PVA)[147] composites into 2D films. However, such a mechanical drawing approach is inefficient for mass production. In practice, assemblies assisted by a shear force and a flow are two main strategies to obtain bulk materials.

Tape casting. A versatile technique to induce a shear field is tape casting, also known as doctor blading in industrial production. In a typical process, the doctor blade moves in the direction parallel to the substrate, inducing a non-uniform shear field in the cross-section between the blade and the substrate. Such a shear field can overcome the random orientation of LCs, leading to alignment of 2D nanosheets in the wake depending on the type of LC phases. For most 2D nanosheets including GO, the LCs observed are nematic phases in which they were aligned horizontally parallel to the shear field (Figure 8a).[148] In sharp contrast, the lamellar phases of $\text{Ti}_3\text{C}_2\text{T}_x$ LCs achieved by adding a surfactant in the aqueous dispersion were aligned perpendicular to the shear field (Figure 8b).[142] In the lamellar phase, torques were induced perpendicular to the shear field, leading to vertical alignment of the MXene sheets (Figure 8b). The degree of alignment of 2D nanosheets and the uniformity of films depend on many factors, including the viscosity of dispersion, the polydispersity in size of 2D nanosheets, the shear rate and the gap between the blade and substrate. Other 2D materials without LC phases, such as BNNSs [149,150] and MoS_2 [151], could also be aligned using tape casting, especially in the presence of polymers. The addition of a polymer resin increased the viscosity of 2D dispersion, which proportionally increased the shear stress generated during alignment. Nevertheless, the degree of alignment in BNNS/PVA [149,150] and MoS_2 /polyimide (PI) [151] nanocomposites was not as high as in GO/[polyethylene glycol \(PEG\)](#) nanocomposites [152] because of the lack of LC phases in the former composites. The tape casting technique can be easily scaled up for mass production by replacing the lab-scale doctor blade with an industrial scale rotogravure machine with roll-to-roll production capabilities.[148]

Wet spinning. Notwithstanding the versatility and scalability of the tape casting technique, the aligned morphology can only be achieved in the form of 2D thin films/coatings as the magnitude of shear field diminishes significantly with increasing thickness. An alternative

strategy is using the flow to direct the assembly of 2D nanosheets in solution. The unidirectional flow can be generated by pushing the solution through a die of a uniform cross-section (Figure 8c1). This strategy is well established in the fiber spinning process, such as wet spinning and electrospinning, where various nanomaterials are *in-situ* assembled into 1D fibers of different scales.[32,153] The wet spinning process also harnessed rich LC phases of GO dispersion by controlling the orientation of GO sheets.[17] The GO LC solution was injected into a spinneret, through which GO LCs were oriented along the fiber axis by the shear field generated during spinning through the small nozzles.[154] After continuous extrusion into the coagulation bath followed by drying and reduction, rGO/polymer composite fibers with rGO sheets oriented along the fiber length were achieved (Figure 8c2).[130,140,154] The cross-section of the fibers, however, featured densely packed, yet randomly distributed rGO sheets. By replacing the conventional drying process with freeze-drying [155] or supercritical drying [156], graphene aerogel fibers with aligned pores along the fiber axis could be fabricated (Figure 8c3). These pores were further impregnated with molten polymer resins to achieve graphene/polymer composite fibers.[156] The spinnability of GO dispersions depended strongly on their LC formation behaviors, which were determined by the size, concentration and polydispersity of GO sheets. Because of their small sizes and scarce LC phases, only a limited success was achieved for other 2D nanosheets, including MoS₂ and Ti₃C₂T_x, to form continuous fibers.[141,157] For example, although MoS₂ LCs were spinnable into neat MoS₂ fibers,[141] Ti₃C₂T_x nanosheets could be spun into fibers only after hybridizing with GO sheets due to the lack of inherent LC phases.[157,158]

Vacuum assisted filtration (VAF). Another important technique taking advantage of flow fields is VAF, which does not rely on the formation of LC phases and thus pertinent to a wide variety of 2D materials. Different from the spinning process where 2D nanosheets are aligned

along the solution flow direction, VAF enables 2D nanosheets to assemble perpendicular to the flow direction. In a typical process, a 2D nanosheet dispersion with or without a polymer is filtered through a porous membrane assisted by a vacuum pressure, as shown in Figure 8d1. The pores of submicron size in the membrane filter out tiny solvent molecules while preventing the passage of 2D nanosheets and polymer macromolecules, accumulating an aggregated mass above the membrane (Figure 8d2). The loose aggregate is further compressed as the solvent evaporates, aligning the anisotropic 2D nanosheets perpendicular to the flow direction and thus yielding a flexible thin film comprising highly-aligned 2D building blocks after drying (Figure 8d3). The alignment of 2D nanosheets is revealed to be correlated to their lateral dimensions: larger GO sheets are shown to yield a higher degree of alignment than their smaller counterparts in GO papers (Figure 8d4).[70] The VAF approach has two major advantages over other external field assisted assembly techniques. First, nematic phases are unnecessary for VAF to achieve highly-aligned structures. Therefore, a range of 2D nanosheets without LC phases, including BNNSs,[159,160] $\text{Ti}_3\text{C}_2\text{T}_x$, [27,161–165] and MoS_2 , [166] were also assembled into highly-aligned films by VAF, which were not possible using shear forces. Moreover, highly-aligned films/papers containing hybrid nanofillers, such as GO/BNNS papers [167] and GO- MoS_2 /polyurethane (PU) composites,[168] could also be fabricated using VAF. Second, the film thickness can be tuned by controlling the concentration and total volume of 2D nanosheets or their polymer dispersions, allowing the fabrication of films with a wide range of thicknesses from membranes of only a few hundred nanometers [169] (Figure 8d5) to freestanding papers with a micrometer thickness. On the other hand, the disadvantage of VAF lies in its time-consuming process, especially when polymers are involved and thick films are to be produced, making it less attractive for industrial applications than the alignment by shear fields. Moreover, the viscosity of precursor dispersion has to be low to allow efficient

filtration. Therefore, only low-molecular weight polymers such as Chitosan,[170] PVA,[161,171] poly(diallyldimethylammonium chloride),[159,161] sodium alginate (SA) [27] and PU [168] are suitable for the VAF process. Nevertheless, the highly-aligned layered structure produced by VAF resembles the unique brick-and-mortar structure seen in many biological systems such as nacre, making VAF an intriguing approach for developing novel bioinspired composites made from 2D nanosheets.[172]

Other techniques. The shear forces and flow fields used in the above techniques are mild and therefore can only be applied to low-viscosity solutions containing neat 2D nanosheets or soluble polymers. For high-viscosity polymer matrices or those insoluble in water or solvents, the melt extrusion technique can be a favorable alternative. It is an environmentally benign process without the need of solvents, and is commonly used in the industry for fabricating thermoplastic composites. For example, 2D nanosheets in the form of powder such as BNNSs can be directly mixed with HDPE pellets before feeding into a twin screw extruder, where HDPE melts at an elevated temperature and BNNSs are aligned in the viscous polymer by strong shear fields generated during high-speed rotation of twin screws.[173]

The mechanical force assisted assembly utilizes shear and flow fields to assemble 2D nanosheets in solutions or polymers into 1D fibers or 2D films by aligning them along the fiber axis or the horizontal plane. The high in-plane properties of 2D nanosheets favor the controlled orientation, giving rise to excellent mechanical and transport properties along the alignment direction, which are discussed in Sections 5 and 6.

4.2.2. Electric field assisted assembly

Electric field induced alignment. Conductive or dielectric particles in a polymer solution can be polarized by applying an external electric field to introduce a dipole moment by means of the mismatch in electron conduction or dielectric constant between the particles and the surrounding polymer matrix.[175] For anisotropic nanofillers, such as 1D nanotubes and 2D

nanosheets, the dipole moment is usually not aligned in the direction of electric field, generating a torque which rotates the anisotropic nanofillers when it is larger than the viscous torque exerted by the surrounding polymer matrix (Figure 9a). Both the direct current (DC) and alternating current (AC) electric fields have long been used for the alignment of 1D CNTs in polymer matrices,[176–178] between which the AC field is known to induce better alignment of CNTs than the DC counterpart[176]. This is because anisotropic nanofillers with surface charges tended to move towards one electrode with an opposite charge under a constant DC field, gathering of fillers on one electrode.[179] On the other hand, the AC field drives the formation of percolating networks from both electrodes, mitigating the possibility of nanofiller aggregation on one electrode.[180] The resulting CNTs/polymer composites showed better electric and mechanical properties thanks to the formation of preferentially concentrated and interconnected CNTs along the alignment direction.[178] The degree of alignment depends on a number of factors, including the shape and size of nanofillers, the field strength, the dielectric constant of nanofillers and the viscosity of polymer solution.[175] 2D nanosheets may encounter higher drags in the viscous polymer in view of their larger surface areas, requiring a higher electric field to rotate than 1D CNTs. Conductive GNPs were aligned showing a chain-like structure in the liquid epoxy after 10 min of exposure to an AC field of 25 V/mm (Figure 9b-c).[181] In comparison, insulating BNNSs required a much higher electric field for rotation to take place in the liquid polymer because of the smaller dielectric constant difference with polymer than conductive GNPs.[182]. While higher field strengths are desired to achieve alignment in a shorter period time, the upper limit is governed by the dielectric breakdown strength of polymer matrix. A lower viscosity of polymer is also beneficial to a shorter alignment time. The electrical field induced alignment is used mainly for the alignment of 2D nanofillers in liquid resin in the absence of solvents because the aligned networks may be destructed during solvent evaporation. Resins are

normally cured *in-situ* while the 2D nanofillers are aligned so that the aligned networks are preserved in the composites after removing electrodes.

The alignment of 2D nanosheets in a polymer occurs in the direction of electric field and thus perpendicular to the electrodes, allowing the controlling of alignment direction depending on the position of electrodes. This makes the application of electric fields more convenient than other alignment methods, such as shear alignment, when vertical alignment is required. Besides, bulk composites with highly-aligned 2D nanosheets can also be readily fabricated using electric fields, whereas other shear or flow alignment methods can only produce thin films or coatings. However, the high electric fields and long time required for alignments to establish over large distances may limit its practical applications for producing large-size composites. Instead, this method is best suited to small-size thin films with aligned conductive fillers especially for electronics.[183–185]

Electrophoretic deposition (EPD). The electric field induced alignment discussed above was observed only for conductive GNPs and dielectric BNNS because their electrically neutral surface could be polarized by electric fields. GO, MoS₂ or Ti₃C₂T_x with surface charges cannot be polarized, but instead move towards the electrode with the opposite charge in a phenomenon called the ‘electrophoresis’ and deposit on the electrode surface (Figure 9d).[186] Such a process is known as EPD. Depending on the shape of substrate on which 2D nanosheets deposit, the morphology of the final assembly can be different. In most cases, flat substrates are used as electrodes, leading to 2D films with well-aligned 2D nanosheets on the substrate surface.[187–190] Conductive substrates with other shapes, such as 1D carbon fibers [191] and 3D Ni foam [192], could also work as electrodes, facilitating GO coating on their surface. The film thickness deposited on the substrate can be precisely controlled, and its quality depends on many factors, such as the size and electric charge of 2D nanosheets, the concentration of solution, the type of solvents, the voltage of electric field and the deposition

time. Various 2D nanosheets including functionalized rGO,[187] $\text{Ti}_3\text{C}_2\text{T}_x$, [188,189] and MoS_2 [190] with surface charges were assembled into aligned 2D films using EPD. Polymer nanocomposites were also fabricated either through one-step EPD using 2D nanosheet/polymer colloids [193–195] or by depositing 2D nanosheets and polymer layers in sequence [196]. The EPD technique is more attractive for large-scale production of uniformly thick, large-size 2D films than other methods, such as VAF and tape casting, thanks to its highly tunable deposition kinetics. Therefore, transparent rGO/polyetherimide (PEI) composite films containing only 20 nm thick rGO layers were fabricated by controlling the voltage and the deposition time (Figure 9e-f)[196]. The EPD technique was also employed for producing thin films on flexible or complex substrates made from polyethylene terephthalate (PET)[195], carbon fibers[191] and Ni foams[192]. However, there are some limitations: (i) the technique can only be applied to 2D nanofillers or their polymer mixtures with surface charges in low-viscosity colloidal suspensions; and (ii) the substrate must be electrically conductive.

4.2.3. Magnetic field assisted assembly

Magnetic field induced alignment. Magnetic fields are effective in manipulating the orientation of anisotropic magnetic particles.[197] The magnetostatic energy arising from the anisotropic magnetic susceptibility drives the alignment of anisotropic particles in a magnetic field.[198] GO LCs were aligned along the direction of magnetic fields, although a strong magnetic field (0.25 T) and a long exposure time (~ 5 h) were required to overcome the weak magnetism of GO sheets.[68] A common strategy to improve their alignment under magnetic fields is to functionalize 2D nanosheets with magnetic materials, such as superparamagnetic iron oxide (Fe_3O_4) nanoparticles. Functionalized rGO sheets with attached Fe_3O_4 nanoparticles significantly reduced the magnetic field required for alignment, so that the magnetic fields generated by common rare-earth magnets were sufficient.[199] 2D

nanosheets including GNPs[200,201] and BNNSs[202–205] were functionalized and aligned in a range of polymers using such a strategy. Depending on the position of magnets, the 2D nanosheets can be aligned horizontally or vertically (Figure 10a, left). A horizontal magnetic field led to in-plane alignment of Fe₃O₄-functionalized GNPs in an epoxy matrix (Figure 10b),[201] while the application of a vertical field resulted in aligned *h*-BN platelets in silicone along the transverse direction (Figure 10c).[199]

Magnetic field modulated spatial distribution. In addition to orientation, the magnetic field can also control the distribution of magnetically functionalized 2D nanofillers in nanocomposites (Figure 10a, right). By placing Ni or Co templates with predefined shapes, such as Ni wires in a mesh pattern, on permanent magnets, a virtual mold was created to attract magnetized rGO (m-rGO) sheets around the templates, leading to locally concentrated m-rGO sheets in the composite (Figure 10d). Such a capability to control the spatial distribution of 2D materials cannot be realized using electric or mechanical fields. By locally confining the conductive fillers while maintaining the global conductive network in nanocomposites, this method provides a conceptually new approach for fabricating conductive and transparent polymer composites.[199] The magnetic field can be generated in a cost effective manner without the constraint of electrodes, and thus the fabrication process has the potential to be scaled up for industrial applications. Nevertheless, the functionalization of 2D nanosheets with magnetic particles is required to increase their responsiveness to magnetic fields, inevitably adding extra steps.

4.3. Template directed assembly

4.3.1. Dynamic ice templating

Dynamic ice templating, also known as directional freeze-casting, is a technique that uses growing ice crystals as templates to assemble colloidal particles in an aqueous solution into a 3D macroscopic network with a controlled morphology. Depending on the growth direction

of ice crystals, this strategy can be broadly categorized into unidirectional and bidirectional freeze-castings, which are discussed in the following.

Unidirectional freeze-casting (UFC). The UFC technique was first developed for the assembly of ceramic microplatelets inspired by the formation of sea ice.[206] It involved a cold metal finger whose temperature was controlled by a liquid nitrogen bath and a ring heater (Figure 11a) with the aqueous slurry of ceramic particles placed on top. As such, a constant temperature gradient was established in the slurry to drive the unidirectional growth of ice crystals, entrapping ceramic particles between the vertical ice lamellae (Figure 11b).[206] After freezing, the ice lamellae were removed by freeze-drying, producing a porous structure with morphologies replicating the ice template. A range of 2D nanosheets, such as GO/rGO,[207–212] BNNSs,[213–215] $\text{Ti}_3\text{C}_2\text{T}_x$ [216] and their hybrids,[216,217] were assembled into composites by two typical routes (Figure 11c), namely, (i) the *in-situ* method in which 2D nanosheets and a polymer resin or monomer are first mixed in an aqueous medium followed by freeze-casting; and (ii) the *ex-situ* method in which the aqueous dispersion containing 2D nanosheets is first freeze-casted into porous scaffolds followed by infiltration of a liquid polymer. The *in-situ* method was used to produce both porous composites with ultralow densities[207] and compact films with layer-structured 2D nanofillers through a subsequent compression process.[211] On the other hand, the *ex-situ* approach generally yielded an anisotropic aerogel consisting of 2D nanosheets alone, followed by infiltrating the porous skeleton with a polymer, such as epoxy and polydimethylsiloxane (PDMS), to form solid composites with aligned 2D nanofillers.[208–210,213–217] For UFC, the suspension started freezing under a single temperature gradient, causing the nucleation of ice to occur randomly on the cold surface and thus inevitably creating randomly oriented, multiple small-size domains perpendicular to the ice growth direction (Figure 11d).[206] Therefore, alignment was achieved only along the ice growth

direction (Figure 11e), while the morphology transverse to it is irregular as a consequence of the random nucleation of ice crystals on the cold plate (Figure 11f).[210]

Bidirectional freeze-casting (BFC). To better control the morphology with an almost perfectly aligned structure, controlled nucleation of ice crystals is critical. Therefore, a BFC technique was developed by placing a PDMS wedge on the cold surface, introducing dual temperature gradients so that the nucleation of ice crystals could be tailored along two preferred directions (Figure 11g).[218] A typical morphology of porous rGO/PU nanocomposites made by BFC is shown in Figure 11h-j.[219] Arising from the dual temperature gradients, highly lamellar rGO/PU walls were created when ice crystals grew along two orthogonal directions (Figure 11h). These lamellae were partly bridged by rGO/PU ligaments in the transverse direction (Figure 11i) owing to the entrapment of rGO and PU by the rapid solidification front.[210,211] In contrast to UFC which yields randomly dispersed sheets perpendicular to the freezing direction (Figure 11f), large domains of highly-aligned lamellae with long-range orders were achieved in two directions by BFC (Figure 11j). The lamellae were compressed transversely to form solid composites.[219,220] These composites containing a combination of 2D hybrid nanofillers mimic the brick-and-mortar structure of nacre, imparting many unique mechanical and functional properties which are discussed in Section 5.[219–223] The directions of two temperature gradients in the BFC approach are not necessarily orthogonal, but can also be along the axial and radial directions in a cylindrical container.[222] In the cylindrical configuration, the ice crystals grow from the periphery towards the center of the cylinder, creating an aerogel containing vertically aligned and radially converging nanofiller walls.

Morphology control. The precise control of aligned structures by freeze-casting relies on a few parameters, including the size of 2D fillers,[206,212] the freezing temperature,[223] and the addition of anti-freezing reagents.[225] If the particle size is too small, they may not be

entrapped by the moving water-ice front.[206] As such, ULGO led to much better alignment and properties of unidirectional GAs (UGAs) than their small GO (SGO) counterparts.[212] Moreover, binders are usually required to maintain the structural integrity of the aerogels prepared using 2D nanosheets with much smaller lateral sizes than GO. For example, PVA[213], PU[219], sodium carboxymethylcellulose[215] or GO sheets[217] were used as binders for BNNS aerogels. The freezing temperature controls the freezing kinetics of ice, determining the wall thickness and pore size. With decreasing freezing temperature from -40 to -120 °C, the wall in a BNNS aerogel became thinner with reduced pore sizes thanks to the larger number of ice nuclei at lower temperatures.[223] Another way to control the freezing kinetics is to add antifreezes such as ethanol to inhibit ice crystal growth. It was found that the addition of an optimized amount of ethanol into the rGO aqueous dispersion led to better alignment during UFC.[226] Similarly, an effort was made to precisely control the pore size of the 3D porous network by varying the type and concentration of ions in the aqueous solution.[225] It is suggested that ions with a high charge density, such as F^- , preferred to stay at the ice-water interface, inhibiting the growth of ice crystals and therefore leading to smaller pore sizes. On the contrary, the addition of ions of a low charge density, such as I^- , led to larger pore sizes because these ions tended to be integrated within ice crystals without hindering their growth.[225]

The majority of ice templating studies to fabricate nanocomposites has focused on constructing 3D macroscale assemblies using 2D nanosheets followed by infiltration of polymers. Recently, a reverse process was proposed to fabricate synthetic nacre that replicates the structure and chemical composition of natural nacre.[227] A 3D laminated chitosan (CS) matrix was first made based on BFC of a CS precursor solution. Then the aragonite nanocrystals were precipitated from a solution containing calcium bicarbonate to mineralize the predesigned matrix. The synthetic nacre was finally obtained after hot pressing

at 80 °C, which showed a toughness comparable to its natural counterparts with similar toughening mechanisms. This unique approach achieved an extremely high content of inorganic fillers in the polymer matrix, which can be very promising to produce nanocomposites with high 2D nanosheet contents.

4.3.2. Template-directed CVD

As mentioned in Section 2.2, 2D materials, such as graphene,[60,61] BNNS[62–64] and some TMDs like MoS₂ and WS₂, [10,11] can be grown on Cu, Ni and SiO₂ substrates using the CVD technique with high crystallinities and large lateral dimensions.[13] While the excellent qualities of CVD-grown 2D materials deserve their applications as fillers for nanocomposites, one of the biggest challenges is to transfer these materials from substrates to polymer matrices. There are two main strategies, namely, (i) assembling polymers with 2D materials on substrates followed by removal of substrates; and (ii) removing substrates to obtain freestanding 2D materials followed by infiltration or incorporation of polymers. Depending on the shape of templates on which 2D materials grow and the strategy used to incorporate 2D materials into the matrices, polymer nanocomposites with different morphologies and filler arrangements can be achieved.

2D templates. 2D templates, such as Cu foils and SiO₂/Si wafers, are the most viable substrates for the growth of continuous 2D materials with large areas, high quality and controlled thicknesses. The lateral dimensions of CVD-grown 2D materials, such as graphene and BNNS, can be made in the order of tens of centimeters[60,64], sufficient to span the whole dimension of bulk composites. Due to planar structures of 2D materials, one intuitive way for fabricating composites is to laminate them alternately with polymer films,[228–232] similar to the laminating process widely used in conventional fiber composite production (Figure 12a). Specifically, the 2D material grown on a substrate was first coated with a polymer solution through spin coating[230,232] or stacked with polymer films by hot

pressing.[229] Then, the substrate, commonly Cu foil, was etched using FeCl_3/HCl solution, producing a freestanding 2D filler/polymer thin film. These films were subsequently stacked layer by layer, yielding a thicker nanocomposite laminate containing distinctly separated, highly aligned 2D nanofillers which had semi-infinite lateral sizes covering the whole dimension of composite components. Using this simple processing technique, graphene/poly(methyl methacrylate) (PMMA) [230,232] and BNNS/PEI [229] laminates with thicknesses of a few micrometers were obtained. A cut-and-stack process was developed to increase the laminate thickness, with its scale rising exponentially with each stacking step.[228] A similar approach was recently reported by folding the initial graphene/PC film several times to expedite the lamination process.[231] Excellent mechanical properties [231], electrical conductivities [228] and dielectric properties [229] were achieved for the nanocomposite laminates made from a small amount of 2D nanofillers. Nonetheless, the lamination approach is difficult to scale up when thicker composites are preferred. In addition, the maximum contents of 2D nanofillers used in the composites were often limited to less than 1 wt %, inevitably producing much thicker polymer layers than the 2D nanofiller.

3D templates. Alternative to 2D templates, 3D templates have been employed in the form of metal foams and meshes as versatile substrates for CVD growth of 3D architectures. 3D graphene foams (GF) were first grown on Ni foam templates by Cheng and colleagues (Figure 12b).[25] Using methane gas (CH_4) as the carbon source, carbon was deposited onto the Ni foam at 1000 °C to obtain Ni-graphene foam upon cooling. After coating a protective PMMA layer, the Ni foam was etched out using a mixture of FeCl_3 and HCl . A freestanding GF was finally obtained by dissolving PMMA in hot acetone. The GF had a highly porous structure with extremely low density of $\sim 1.3 \text{ mg/cm}^3$ and interconnected graphene struts consisting of mono- to few-layer graphene walls (Figure 12c).[233] In addition to GFs, h-BN foams (BNFs) were also grown similarly on Ni foam templates using borazane ($\text{H}_3\text{N-BH}_3$) as

the precursor,[234,235] or on graphite foams using B_2O_3 precursor for carbothermal CVD.[236,237] Liquid polymers can be easily infiltrated into the pores or dip-coated on the strut walls, either before or after etching of metal templates to form nanocomposites. For example, the epoxy resin was first filtrated into the Ni-GF structure followed by etching of Ni foam, yielding a porous GF/epoxy nanocomposite with a pore volume of ~19 vol % replicating the hollow graphene struts (Figure 12d).[233] Alternatively, epoxy was directly infiltrated into the freestanding GF, producing solid nanocomposites with dense graphene struts (Figure 12e).[30] In addition to epoxy, other common polymers including PMMA[234], PDMS[235,238,239] and polymeric phase change materials (PCMs)[240,241] were also used as the matrix of solid nanocomposites reinforced with GFs or BNFs. Unlike the solid or semi-solid nanocomposites prepared by polymer infiltration, dip-coating of polymer solutions onto the foams gave rise to highly porous composite structures with porosities of up to 90 %. These porous composites were useful in energy attenuation applications, such as mechanical [242] or sound damping [243] and electromagnetic interference (EMI) shielding.[244,245]

In addition to Ni foams, Ni meshes with interwoven structures also served as templates for CVD growth of graphene woven fabrics (GWFs).[246] Similar to GFs, the freestanding GWFs were lightweight and contained well-defined orthogonally interwoven graphene tubes (Figure 12f).[246,247] Nanocomposites were made by either infiltrating polymer into the Ni-GWF structure followed by etching of Ni meshes[247] (Figure 12g), or simply embedding freestanding GWFs onto a half-cured polymer film, such as PDMS[31,246,248,249] (Figure 12h). The most distinctive features of planar GWFs are their flexibility and well-defined mesh structure, making them particularly suitable for flexible strain sensing applications.[31,246,248,249]

High-density 3D templates for high filler contents. Similar to 2D templates, the maximum content of 2D nanofillers attainable in nanocomposites using common 3D Ni foams or Ni

woven fabrics is less than 1 wt % owing to the intrinsically large pore volume in the templates and thin layer of 2D materials. Such a low loading of 2D nanofillers severely limits the potential performance of nanocomposites expected from the excellent, inherent characteristics of 2D materials. Therefore, high-density GFs or BNFs are highly desired to increase the overall filler contents. Although compressing freestanding GFs or BNFs was a straightforward way to increase their densities,[250] the 3D structures collapsed completely under compression, leading to fragmented 3D networks and the loss of desired cellular architecture. Instead of increasing the densities of freestanding GFs and BNFs, the direct growth of graphene or BN on high-density 3D templates is a plausible alternative. For example, several layers of Ni foams were stacked and compressed to a multilayer Ni web with significantly reduced pore sizes, which served as the template to grow a multilayer graphene web (MGW) having an ultrahigh density ten times that of the common GF.[30] Unlike the macroscopically isotropic GF structure, the MGW consisted of in-plane oriented graphene struts which were densely packed through the thickness direction. The ultrahigh-density MGW was infiltrated with epoxy, giving rise to a high graphene content of 8.3 wt % in the final composite. High-density Ni templates were also prepared by cold pressing Ni powders into a highly dense coupon.[251] GFs grown on such coupons yielded filler content as high as 32 wt % in the epoxy composite. A similar strategy was adopted to grow BNFs on high-density carbon nanorod networks using a B_2O_3 vapor precursor, leading to densely interconnected BN networks in the BNFs.[237] The high-density BNFs were immersed in a PMMA solution to fabricate porous nanocomposites with ~ 50 wt% BN. Unlike the conventional dispersion techniques which inevitably cause filler agglomeration at high filler contents, the exceptionally high graphene or BN contents achieved in these composites did not sacrifice excellent filler dispersion as a result of the inherently interconnected networks of GFs or BNFs, effectuating unprecedented mechanical and functional properties, including

modulus, strength and fracture toughness,[30,251] electrical and thermal conductivities [30,237] and dielectric properties.[237]

4.3.3. Polymer templating

Polymer foams/sponges are alternative templates for the 3D assembly of 2D nanosheets. Polymer templating provides a more versatile and cost-effective solution to assembling 2D nanosheets into 3D macroscopic monoliths than CVD-based metal templating. The most popular polymer foams include PU [252–255] and melamine [256–258], both of which are commercially available. Nanocomposites are fabricated by simple dip coating of polymer foams into a solution containing 2D nanofillers, such as graphene [257], GO sheets [252–254,258] and BNNSs [256]. These fillers are attached onto the surface of polymer struts (Figure 13a) to form porous nanocomposites after drying whose structure resemble the original polymer foams (Figure 13b). Unlike the metal template which must be completely etched out in order to infiltrate polymers, the polymer templates do not need such a removal process as they can provide mechanical support and elasticity to the final porous composites.[258] It can be said, thus, that polymer templating is a simple, versatile and fast technique to produce porous nanocomposites, which finds a range of applications as oil/organic absorbers,[253,254,257] flexible sensors,[252] and elastic conductors.[253] Nonetheless, it is impossible to control the pore sizes by simple dip coating, as they are determined by the inherent pores in the polymer foams. To rectify this problem, the ice templating technique was supplemented when the PU foam was dipped into GO solution, generating a hierarchical porous structure with highly aligned pores in the framework of commercial PU foam skeletons (Figure 13c-d).[255] More precise control of porous structures could be achieved using custom-made polymer templates. A 3D printed acrylonitrile butadiene styrene (ABS) template with precisely controlled arrays of hexagonal prisms was immersed into GO solution, which was freeze-dried, reduced and demolded to

yield a graphene honeycomb (GHC) structure inversely replicating that of the ABS template (Figure 13e)[259]. The GHC featured a long-range ordered honeycomb consisting of porous graphene walls (Figure 13f), and was coated with PDMS to form a porous nanocomposite. The unique honeycomb structure sustained large tensile and flexural strains with little variation in electrical conductivity, making the GHC/PDMS composites promising for elastic conductor applications.

Besides polymer foams, polymer microspheres can also serve as templates for the assembly of 2D nanosheets. Negatively-charged BNNSs [260] and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets [261] were self-assembled onto the surface of positively-charged polystyrene (PS) microspheres aided by electrostatic interactions in a solution (Figure 13g). After drying, the 2D nanosheet-coated PS microspheres were further hot-pressed and cured to produce solid composites with inherently interconnected 2D nanosheets within the PS matrix (Figure 13h).

Polymer templating can be a simple and cost-effective alternative to CVD-based templating when porous composite structures are desired. In addition, the polymer templates can be custom-designed and precisely manufactured using 3D printing, which is not applicable to ice or CVD-based templating. However, there are very limited polymer foams available commercially for use as the templates.

4.3.4. Interfacial templating

2D GO sheets are an amphiphile consisting of hydrophilic edges with attached carboxyl groups and hydrophobic basal planes containing aromatic islands and epoxy/hydroxyl groups.[70,262,263] The amphiphilic properties of GO sheets enabled them to act like surfactants,[263] making liquid-gas, liquid-liquid and liquid-solid interfaces ideal templates for their assemblies into 2D films or 3D aerogels depending on the nature of interfaces.

The Langmuir–Blodgett (LB) method is a liquid-air interface assembly technique.[264] In a typical process,[265] GO sheets were first dispersed in volatile solvents such as

water/methanol mixtures and the mixture was spread dropwise onto the water surface in a LB trough (Figure 14a). GO sheets self-assembled at the water-air interface as the solvent evaporated, forming a monolayer on the water surface. Two moving barriers were used to precisely control the surface pressure and achieve the desired packing density of GO sheets. Finally, the monolayer of GO sheets was transferred to a substrate by pulling it vertically from the trough. The substrate could be rigid silicon, glass, quartz or flexible PET, but had to be hydrophilic with surface treatment[266]. The quality of GO LB films can be controlled by several parameters, including the size of GO sheets, the surface pressure and the pulling speed during dip coating. It is shown that SGO sheets of 1 – 3 μm in lateral size tended to overlap with each other under a high surface pressure, while ULGO sheets of 50 – 200 μm in size tended to form a highly wrinkled structure[267]. ULGO sheets outperformed their small size counterparts in terms of sheet resistance after thermal reduction without much sacrifice in transparency, making them ideal candidates for transparent conductive films[267,268].

Amphiphilic GO sheets were also assembled into 3D networks in water-oil [269–272] or water-organic [273] emulsions using the liquid-liquid interfaces as soft templates. Oil- or organic-water emulsions could be stabilized by GO sheets through their self-assemblies at the oil-water or organic-water interfaces, forming Pickering emulsions containing GO-wrapped oil or organic droplets (Figure 14b).[263] Upon removal of liquid phases through evaporation [273] or freeze-casting[272], 3D GO aerogels with spherical pores resembling the shape of droplets were obtained (Figure 14c). Analogously, air bubbles were also introduced in a surfactant solution, in which GO sheets could also be assembled at the liquid-air interfaces to form a 3D aerogel after freeze-drying.[274] These 3D GO aerogels could then be reduced to GAs and infiltrated with polymers to fabricate composites.

The interfacial soft templating offers a cost-effective alternative to hard templating methods, such as CVD-based and polymer templating, to build 3D porous networks using 2D building

blocks. However, only surfactant-like GO sheets could be effectively assembled using interfacial soft templating, which is not applicable to other 2D materials without the amphiphilicity as in GO.

2D nanofillers can also be assembled at liquid-solid interfaces using the layer-by-layer (LbL) assembly method, as shown in Figure 14d.[2] Dilute solutions of 2D nanofillers with surface charges are first deposited onto a substrate with proper surface treatments, allowing sufficient attractive forces between the substrate and 2D nanofillers for strong adhesion upon solvent evaporation. Polymer molecules with opposite charges are subsequently deposited onto the existing 2D nanofiller layer driven by electrostatic interactions. Such alternating depositions of oppositely charged 2D nanofillers and polymers are repeated to form multilayer composite films with highly aligned structures.[21] GO sheets with abundant hydroxyl and carboxyl functional groups are negatively charged and thus can be assembled with positively charged polymers such as PVA, PEI, and polyaniline (PANI) using various techniques including spin-coating, spray-coating, and LB techniques.[275] Other 2D nanofillers, such as BNNS, MoS₂ and Ti₃C₂T_x, [276–282] can also be laminated with polymers driven by various attractive forces like electrostatic interactions, hydrogen bonding and vdW forces. Owing to the secondary nature of these interactions, the composite films prepared by the LbL method have relatively weak bonding between the 2D nanofiller and polymer layers. Further crosslinking processes are necessary to form strong covalent bonds between the layers so as to improve the mechanical properties of the films.[283] The each layer thickness and the morphology of composite films prepared by the LbL assembly can be controlled with nanometer precision and uniformity over large areas, which cannot be achieved by other film forming techniques, such as VAF and tape casting. Nevertheless, this method is time-consuming to operate, and therefore is not amenable to producing bulk composites with large thicknesses.

4.4. 3D printing

3D printing is the collective designation of a large class of additive manufacturing techniques which allows digital design and precise construction of complex 3D bulk structures from ink-based soft materials. It has been most widely used commercially on rapid prototyping from a range of polymers, including thermoplastics, thermosets and elastomers, thanks to its capability of converting 3D computer-based designs to real prototypes with efficiency and accuracy. The intriguing prospect of building complex 3D structures becomes the impetus to developing new 2D nanosheets or 2D nanofiller/polymer inks, which can be printed into multifunctional 3D structures offering both the excellent properties of 2D nanofillers and the specifically tailored structures. The advances in solution processing of 2D materials technologically enable new printable inks to contain pure 2D nanosheets with suitable rheological behaviors. Alternatively, these 2D nanosheets can act as functional fillers in the existing printable polymers. Depending on the viscosities of the inks, the 3D printing techniques can be divided into two broad categories, namely, droplet-based and filament-based approaches.[284] A comprehensive review of all 3D printing techniques is beyond the scope of this paper, and they have already been covered in a number of reviews.[284–288] In the following, we focus mainly on two techniques, which are most widely used for 3D printing of 2D nanosheets.

4.4.1. Inkjet printing

Inkjet printing is a droplet-based 3D printing technique. The inks for inkjet printing are prepared using solution exfoliated 2D nanosheets, such as graphene[289–293], GO[294,295], MoS₂[292,296,297], BNNSs[292], and Ti₃C₂T_x[298], in various solvents. In a typical process, printable inks are ejected from the printhead one droplet at a time and continuously deposit on a flat substrate in a predefined pattern, as shown in Figure 15a. The most important parameters controlling the droplet formation include the viscosity (μ), density (ρ) and surface tension (γ) of the ink, the nozzle diameter (d), as well as the droplet velocity (v). These

parameters have to be carefully tuned to achieve a stable droplet formation, which is characterized by a dimensionless figure of merit[284], $Z = (\rho\gamma d)^{1/2}/\mu$. Ideally, Z should vary in the range between 1 and 14:[297] a low Z prevents the droplet formation owing to a high viscosity while a high Z leads to droplet splashing when printed on a substrate. Most water-based solvent systems had low viscosities, leading to a high Z of ~ 40 for a common nozzle diameter of $\sim 20\ \mu\text{m}$. Therefore, either binder molecules or other higher-viscosity solvents were needed for proper formulation of 2D nanofiller-based inks.[297,298] Once the ink droplets reach the substrate, they dry out through the evaporation of solvents, leaving a thin film pattern containing only 2D nanofillers. The thickness of the final thin film is determined by the number of printing passes. To achieve homogeneous and uniform films, the wetting and drying of droplets on a particular substrate must be optimized to avoid the ‘coffee-ring’ effect.[291,298] Several strategies have been devised to mitigate the coffee-ring effect, including: (i) increasing the viscosity of solvents by adding binder molecules or using high viscosity solvents;[298] (ii) reducing the surface tension of the ink by adding surfactants[297] or stabilizing polymers;[290] (iii) unpinning the contact line by adding solvents having different contact angles with the substrate.[289] Conductive 2D nanofillers, such as graphene and $\text{Ti}_3\text{C}_2\text{T}_x$, were inkjet printed on flexible or transparent substrates to form highly conductive films with complex patterns. They were employed as various components, such as electrodes[290,298], transistors[291] and resistors[289] in emerging flexible electronics. Due to the planar nature of 2D nanofillers, the printed films exhibited layered structures (Figure 15b), giving rise to high in-plane electrical conductivities and EMI shielding capabilities[298]. The inkjet printing is also a promising technique for fabricating vdW heterostructures combining 2D nanosheets with very different properties. For example, electrically conductive graphene and semiconducting MoS_2 or WS_2 were inkjet printed to form a heterostructure with graphene as electrode and MoS_2 or WS_2 as active material for all-printed photodetectors

(Figure 15c).[293,297] Overall, the capabilities to customize patterns and to print in large-scale on a variety of substrates make inkjet printing a promising technique for fabricating flexible and transparent electronics at a low cost. However, inks with a relatively low viscosity of 2 – 20 mPa s are required to ensure stable droplet formation and avoid clogging of printheads, meaning that the inkjet printing is difficult to handle highly concentrated polymers, 2D nanofiller/polymer composite solutions or solutions containing large-size 2D nanofillers.[284] Furthermore, only 2D patterns with film thicknesses in micrometer scales can be obtained.

4.4.2. Direct ink writing (DIW)

DIW is a filament-based 3D printing technique in which viscoelastic materials are ejected from the printhead in the form of continuous filaments and deposited on the substrates layer by layer with a predefined pattern of each layer (Figure 15d). Inks with much higher viscosity ($10^2 - 10^6$ mPa s depending on the shear rate) were used in DIW than for inkjet, making it possible for highly viscous polymer inks containing functional fillers to be employed.[26] For high-aspect ratio 2D nanofillers, one particular advantage of DIW is that alignment along the printing direction can be naturally achieved by the shear flow developed in the nozzle. For example, 3D printed BNNS/PVA filaments showed aligned BNNSs along the longitudinal direction (Figure 15e),[299] offering the 3D printed filaments with anisotropic properties. In addition, the final products obtained from DIW can exhibit complex 3D architectures: for example, BNNS/poly(lactic-co-glycolic acid) inks were printed into complex shapes resembling a lumbar spine and a double helix, as shown in Figure 15f.[300] One of the most crucial elements for successful DIW is the development of 2D nanosheet inks with proper rheological properties. Several criteria must be met for the ink, namely, (i) low viscosity and shear modulus at a high shear rate so that the ink can flow through the printhead nozzles; (ii) high modulus at a low shear rate so that the ink can maintain the shape after deposition; and

(iii) good dispersion and homogeneity to prevent clogging of nozzles. To achieve proper rheological properties of 2D nanosheet inks satisfying the above, several strategies have been proposed. One approach is to increase the loading of 2D nanosheets in the inks to achieve the viscoelastic properties required for DIW. For example, GO aqueous solutions with concentrations up to 80 mg/mL were used as inks to print 3D horseshoe-shaped heaters[301]. More commonly, different additives were added to the 2D nanosheet inks to tune their rheological properties. GO aqueous inks became more printable after adding silica nanoparticles[34,302] or Ca^+ ions[303] with better rheological properties (Figure 15g), and various 3D aerogels such as microlattices and honeycombs were obtained by DIW after removing the water by freeze-drying (Figure 15h-i). The DIW technique offers more precise control over macroscopic structures and therefore can produce more complex and tailored GA structures than other techniques, such as self-assembly/gelation of GO suspensions and ice-templating.

4.5. Economic viability of different processing techniques

The economic viability of a processing technique is an important consideration for cost-effective industrial applications. Therefore, the overall economic viability of different processing techniques in terms of their costs and the resulting qualities of composites are assessed for commercial applications. The costs for different assembly strategies including LC phase assisted self-assembly, external field assisted assembly, template directed assembly and 3D printing are compared in Figure 16. The spontaneous LC phase formation of 2D nanofillers during the solution casting and sol-gel process enables various ordered structures including 1D fibers, 2D films and 3D structures.[305] The cost of LC phase assisted self-assembly is relatively low compared with template assisted self-assembly and 3D printing because of the low-temperature solution processing conditions. This makes the process commercially viable for producing composites with ordered structures. The external field

assisted assembly has advantages over the LC self-assembly in realizing long-range orders in composites, especially for those 2D nanofillers unable to form LC phases. The assembly technique can also produce composites at higher production rates and lower costs than the other methods used to achieve long-range ordered structures. The main advantages of mechanical force-assisted assembly such as tape casting and VAF are their simplicity and low cost to produce highly aligned films. The wet spinning of fibers usually involves spinning extrusion process, requiring a higher cost than tape casting and VAF.[306] The electric or magnetic field assisted assembly can be used to produce bulk composites with controlled alignment or spatial distribution, but the whole process requires a high electric power, making it expensive to operate. For the template assisted self-assembly, the operational cost usually depends the template materials. For example, ice templating can be a green, efficient and low-cost approach.[210] Although the ice templating technique is yet to be commercialized, several characteristics make it promising for large-scale application. First, the process is simple and do not need complicated equipment or setup. Therefore, the cost for scale up of the freeze casting setup is minimum.[307,308] Second, the freeze-drying technique is already widely used in the food industry. Therefore, controlling the freezing parameters, such as temperature and freezing rate, is relatively easy.[309] Third, once the freezing parameters are carefully controlled, the reproducibility in terms of sample morphology can be guaranteed even after the process is scaled up.[309] Interfacial templating techniques, such as L-B and LbL assemblies, are suitable for the fabrication of ultrathin films with a high degree of structural uniformity in alignment and film thickness.[268] However, the interfacial templating approaches are usually very time-consuming with low efficiencies, inevitably increasing the cost.[267,310] Metal templates are usually used for CVD growth of 2D nanofillers and the main drawback of CVD method is its high cost.[310] In addition to the processing cost needed to remove metal templates, CVD requires a high temperature, high

vacuum and continuous gas flow, significantly limiting their applications for large-scale production.[311] Driven by the superior qualities of CVD-grown 2D nanofillers, nonetheless, a cost-effective roll-to-roll process is under development, which can reduce the prohibitively high cost of CVD.[85] Although inkjet printing of 2D nanofillers is suitable for electronic and optoelectronic applications without additional etching or transfer procedures, the cost of instruments for printing large devices can be relatively high for practical applications.[9] The cost for 3D printing may be reduced using a DIW technology, which is structurally more stable and can be useful for larger scale applications than inject printing.[312]

5. Fundamental properties of 2D nanosheets/polymer composites

One important goal of rational assembly is to translate the excellent mechanical and functional properties of 2D nanosheets into their polymer nanocomposites. The excellent mechanical properties of 2D materials (Table 2) make them ideal candidates for reinforcing polymer composites. Unfortunately, composites made from conventional techniques exhibit far inferior strengths and moduli than the predictions based on the rule of mixtures (ROM) equations. It is also commonly observed that the modulus is enhanced at the expense of reduced strength and toughness.[1] Moreover, the functional properties, such as electrical and thermal conductivities, can only be drastically improved with high filler loadings by forming effective percolation networks, which in turn lead to even worse mechanical properties of the composites than the neat polymer matrix acting alone because of the detrimental agglomeration of nanofillers. The compromises between stiffness and strength, functional properties and mechanical robustness inevitably hinder practical applications of polymer composites made from 2D nanofillers. The rational assemblies of 2D nanosheets reconcile these trade-offs by tailoring the multiscale structures of 2D fillers in composites. In this section, we correlate multiscale structures to fundamental properties of 2D nanofiller/polymer

composites in order to identify important material and assembly parameters in determining various properties of composites.

5.1. Mechanical properties

5.1.1. Elastic modulus

Given the intriguing modulus of graphene (~1 TPa), it is the most widely studied 2D nanofiller for mechanical reinforcement. The modulus increase, ΔE , of composites was assessed by plotting $\Delta E = E - E_m$ as a function of graphene content, where E and E_m are the elastic moduli of composite and matrix, respectively, as shown in Figure 17a. To correlate the moduli with microstructures of composites, the corresponding SEM images of composites containing different types of graphene fillers are shown in Figure 17b. To achieve a high Young's modulus, important material parameters across different length scales must be controlled by rational assemblies. At the macroscale, the orientation of graphene plays an important role. Highly aligned rGO/PU composites (Figure 17, i) made by LC self-assembly [143] presented more prominent rises in modulus than their randomly dispersed counterparts (grey circles, Figure 17a)[313–315]. Due to the unique anisotropic structure of rGO sheets, the alignment along the loading direction in bulk composites maximized their load-bearing capabilities. Such alignment of dispersed rGO sheets were achieved by LC self-assembly [83,143,316] and flow-assisted VAF [170,171]. Nonetheless, these dispersed rGO sheets were discontinuous within the matrix similar to short fibers in conventional composites.[317] Their load-bearing capabilities were therefore significantly affected by their lateral dimensions and those with small sizes were generally poor load bearers in the composites. As such, continuous networks of high-aspect-ratio graphene sheets are desired to achieve a higher reinforcement efficiency. Indeed, it is proven that the epoxy composites with interconnected GA (Figure 17, ii) [29] and UGA (Figure 17, iii) networks [212] exhibited higher modulus enhancements than the aligned rGO/PU composite counterpart (Figure 17, i).

The benefit of high aspect ratios can be rationalized by the modified Halpin-Tsai model.[143,318] The Young's modulus of highly-aligned graphene/polymer composites along the alignment direction, $E_{\parallel}$, is given by:

$$E_{\parallel} = \left[\frac{1+2/3\alpha\eta_{\parallel}V_f}{1-\eta_{\parallel}V_f} \right] E_m, \text{ where } \eta_{\parallel} = \frac{E_f/E_m-1}{E_f/E_m+2/3\alpha}. \quad (2)$$

In Equation (2), E_f and E_m are the Young's moduli of rGO and epoxy, respectively, V_f is the filler volume fraction and α is the aspect ratio of graphene. Assuming a modulus of 250 GPa for rGO,[103] a higher α led to a higher modulus enhancement of composite (grey dashed line, Figure 17a). Notably, the moduli of GA and UGA/epoxy composites along the alignment direction approached the theoretical values predicted by the Halpin-Tsai model at a low rGO content, which was very close to the upper limit of the increase predicted by the ROM for rGO/epoxy composites (blue solid line, Figure 17a). Such impressive improvements were attributed to the high aspect ratios of rGO sheets and interconnected GA and UGA structures, in addition to their excellent alignment (Figure 17b, ii and iii). With increasing graphene content, the enhancement in modulus became saturated and deviated from the theoretical predictions, due probably to increasing thicknesses of rGO walls which led to interlayer slippage with reduced load-carrying capabilities.

At the microscale, the defects and functional groups present in graphene sheets also affected the modulus of composites. The CVD-grown graphene exhibited a much higher modulus of up to 500 GPa than rGO sheets (250 GPa) thanks to its high-quality crystal structure.[97,98,116] Such an inherently high modulus translated to a high modulus of composite containing CVD-grown graphene sheets. Highly-aligned CVD-grown graphene/PC composites made by layer stacking (Figure 17b, iv) showed impressive modulus enhancements at ultralow graphene contents, approaching the theoretical limit predicted by the ROM.[228] Both the 3D GF/epoxy[233] and GWF/epoxy[247] composites presented

higher modulus increases than the 3D GA and UGA counterparts assembled from rGO sheets. In particular, the GF/epoxy composites showed an increase approaching the upper limit predicted by the ROM [233], similar to the aligned graphene/PC composites. This remarkable outcome arose from the seamlessly interconnected graphene networks spanning the whole dimensions of the composite (Figure 17b, v), allowing the loads to be carried mainly by the GF structure. With increasing graphene content, the modulus slightly decreased relative to the upper limit prediction because of the interlayer slippage as the thickness of graphene layers increased.

To summarize, the elastic modulus of composites can be improved close to the theoretical upper limit at low graphene contents through rational assemblies of 2D graphene by controlling various material parameters at different length scales, including microscopic defects and functional groups and macroscopic aspect ratios, alignment and interconnection. 2D and 3D CVD-grown graphene with negligible intrinsic defects and interconnected structures are the most effective in improving the modulus of bulk composites. Nevertheless, additional modulus increases at high graphene contents are challenging in light of the slippage between the multilayer graphene with reduced load-bearing capabilities.

5.1.2. Strength and fracture toughness

The modulus of polymer nanocomposites can be easily improved by incorporating fillers, but translating the excellent strength and fracture toughness of graphene into composites are relatively more challenging as these properties are highly sensitive to defects in the nanofillers. For the composites with randomly dispersed rGO sheets, the modulus increase was often accompanied by reductions in strength and fracture toughness (grey circles, Figure 18a and b)[319,320]. The undermined strength and fracture toughness arose mainly from the inevitable agglomeration especially at high filler contents because of the drastically increased viscosities of polymers beyond processing capabilities with increasing rGO loading.[1] To

eliminate the issue of dispersion, one effective strategy was to first assemble 2D graphene sheets into a well-defined, porous 3D architecture through self-assembly or template-directed assembly. The high porosity in the pre-dispersed 3D fillers allowed infiltration of liquid epoxy resins to produce 3D graphene/polymer composites with both strength and fracture toughness improved by increasing graphene loading.

Strength. For 3D graphene/epoxy composites, the strengths were not compromised by the improved elastic moduli, as shown in Figure 18a. For GAs and UGAs fabricated by LC assisted self-assembly and UFC from ULGO sheets, the improvements in flexural strength of their composites were rather moderate with only about 10 % higher than solid epoxy.[29,212] GFs and GWFs grown by CVD led to higher enhancements in strength of composites than those of 3D graphene structure assembled with rGO sheets. Although the GWF/epoxy composites showed lower absolute values due to their hollow tubes, the rise in tensile strength was higher at 28 %.[247] A maximum strength was obtained with 0.2 wt% GFs, which is 38 % higher than solid epoxy.[233]

Several factors are deemed critical to concurrent improving strength and modulus, not the improvement of one property at the expense of the other. Firstly, the excellent dispersion arising from the predefined 3D graphene structures eliminate the adverse stress concentrations which are common for randomly dispersed nanofillers.[1] Secondly, at the microscopic level, the large lateral dimensions and high aspect ratios of graphene favor an effective interfacial load transfer. For the UGA made from SGO sheets with a mean area of $1.1 \mu\text{m}^2$, the flexural strength of the composites decreased slightly while the modulus increased, in contrast to both enhanced strength and modulus of the UGA composites made from ULGO with a mean area of $1596 \mu\text{m}^2$ (Figure 18a). The effect of lateral size can also be explained by the critical size of $\sim 3 \mu\text{m}$ required for an effective stress transfer between graphene and the polymer matrix according to the strain maps obtained from Raman

spectroscopy and the shear lag theory (Figure 18c).[317] Ideally, a size larger than 10 times the critical value, i.e. $\sim 30\ \mu\text{m}$, is required for most effective reinforcement. As such, large-size sheets with high aspect ratios are preferred for efficient strengthening. Thirdly, the interconnected high-quality graphene networks contribute to improved strengths. Both GFs and GWFs prepared by template-directed CVD had much higher quality graphene networks than GAs and UGAs, offering higher reinforcing efficiencies. It is also noted that the GWF/epoxy composites showed even higher elongations before fracture than the neat epoxy, while the other composites exhibited somewhat constant or reduced fracture strains (Figure 18a, dashed lines). The orthogonally aligned graphene tubes in GWFs functioned as strong and tough fibers, increasing the fracture strains when loaded in these two directions.[247]

It should be noted that the improvements in composite strength were still lower than the predictions from the ROM. This can be understood by the fact that neither rGO nor CVD-grown graphene were able to form strong interfacial bonds with the epoxy matrix because of the lack of reactive functional groups on their surfaces.[29,212,233,247] The interfacial bond strength between the pristine graphene and polymer matrix was determined to be only $\sim 1\ \text{MPa}$ according to the Raman spectroscopy mapping.[317] This value is much lower than the typical interfacial bond strengths, 20-40 MPa, of carbon fiber/polymer interfaces. This means that functionalization of rGO or CVD-grown graphene is required to improve the strength of composites. Nevertheless, a compromise must be made between the interfacial bond strength and the inherent strength of graphene as chemical functionalization would inevitably lower the strength of graphene through defect creation.

Fracture toughness. Fracture resistance is more relevance and crucial for practical engineering applications than strength, and it is characterized by the fracture toughness. Similar to strength, 3D graphene structures had improved fracture toughness of composites with increasing modulus through their well dispersed and interconnected rGO or graphene

networks (Figure 18b). Unlike the moderate improvements in strength, the fracture toughness exhibited more prominent improvements with the addition of 3D graphene structures. The solid GA/epoxy and UGA/epoxy composites gave rise to about 60 % enhancements against solid epoxy.[29,212] Porous epoxy showed 15 to 30 % higher fracture toughness values than their solid counterparts, due to the additional toughening mechanisms brought by the well dispersed and oriented pores.[233,247] GFs and GWFs yielded even higher fracture toughness of composites than the GA and UGA counterparts, achieving remarkable 70 to 80 % augmentations against solid epoxy.[233,247]

The interconnected cellular graphene structures imparted unique toughening mechanisms responsible for the highly improved fracture toughness of epoxy composites (Figure 18d). GA/epoxy solid composites showed rough, stair-like fracture surfaces when cracks were deflected by aligned GO layers (Figure 18d, i), leading to huge dissipation of energy and thus improved fracture toughness by about 60 %.[29] Similarly, UGAs effectively blunted and deflected the crack tips along the interfaces between rGO and epoxy, as indicated by the rough fracture surfaces consisting of smooth epoxy regions of 20 - 30 μm in size separated by the rGO networks (Figure 18b, ii)[212]. Interestingly, the porous GF/epoxy structure had a higher resistance to fracture than the solid counterparts, as evidenced by the rough fracture surface with protruding blocks separated by triangular-shaped pores (Figure 18b, iii).[233] These pores offered additional toughening mechanisms by effectively deflecting the crack paths, leading to 70 % increase in fracture toughness against the solid epoxy.[233] To maximize the effect of pores, the GWFs/epoxy composites containing hollow graphene tubes were placed such that the crack propagated along the direction 45° to the orthogonal direction. The hollow graphene tubes (Figure 18b, iv) deflected the cracks away from the plane of maximum stress to that of minimum stress, requiring much higher energies for the cracks to propagate.[247]

5.2. Transport properties

Polymer composites possess unique advantages of low density, low-temperature processability and structural flexibility against metals and ceramics, thus are considered favorable materials for emerging multifunctional applications. Nevertheless, the critical functional properties, including electrical conductivity, thermal conductivity and dielectric properties, of most polymer matrices are much inferior to their metal and ceramic counterparts. Thanks to the excellent characteristics of 2D nanofillers that can compensate the limitations of polymers, they can alter the overall functional properties of polymer composites, consequently facilitating their unparalleled multifunctional applications.

5.2.1. Percolation theory

Many of the functional properties of composites including electrical conductivity, dielectric constant and thermal conductivity are dictated by the phenomenon known as the percolation. As shown in Figure 19a, the percolation occurs at a critical filler content where 2D nanofillers form interconnected networks spanning the whole dimension of the matrix such that the transport of electrons or phonons via the interconnected networks involving only the 2D nanofillers and their interfaces prevails. Such a critical content in volume percent (vol %) is defined as the percolation threshold, V_c . Due to the formation of effective transport paths, the physical properties of the composite, P , change rapidly near V_c following a scaling law:[321]

$$P \propto |V - V_c|^\mu, \quad (3)$$

where V is the volume fraction of 2D nanofillers and μ is a critical exponent. For electrical and thermal transport properties, the electron tunneling and much lower interface thermal resistance between the adjacent 2D nanofillers facilitate rapid increases in electrical and thermal conductivities near the percolation threshold.[322,323] For dielectric constant, a

surge occurs prior to the percolation threshold, while a significant drop is observed owing to the dielectric relaxation associated with the conductive networks.[324,325]

Electrical percolation is the most commonly observed. The percolation threshold depends on the geometry, dispersion and orientation of fillers in the matrix. The effect of percolation threshold can be explained based on the interparticle distance (IPD) model.[322,326] For fillers with 2D in-plane orientation, the percolation threshold is given by[322]

$$V_{c_2D} = \frac{2\pi D^2 t}{(D+D_{IP})^3}, \quad (4)$$

and for fillers with 3D orientation,

$$V_{c_3D} = \frac{27\pi D^2 t}{4(D+D_{IP})^3}, \quad (5)$$

where D and t are the diameter and thickness of circular 2D fillers, respectively, and D_{IP} is the average interparticle distance between the adjacent 2D sheets. The percolation thresholds (V_c) measured of different composites containing 2D aligned,[144,181,210,212,228] 3D interconnected[29,258] and randomly dispersed[322] graphene are plotted against the reciprocal of aspect ratio ($1/\alpha = t/D$) in Figure 19b, together with the predictions from the IPD model (dashed lines). The experimental V_c values for the randomly dispersed GNPs or rGO sheets are much higher than the predictions based on both the 2D and 3D model. This observation reflects the filler agglomeration associated with the processing difficulties arising from the high viscosities with high-aspect-ratio fillers. In contrast, 3D interconnected graphene structures [29,258] allowed excellent dispersion of nanofillers even with much higher aspect ratios. This results in sharp drop in percolation threshold with increasing aspect ratio, in agreement with the predictions based on the 3D IPD model. 2D aligned graphene in the matrix yields lower percolation thresholds along the alignment direction than those of 3D architectures. As the aspect ratio increased, highly aligned CVD-grown graphene in PC [228] achieved an ultralow percolation threshold of remarkable 0.003 vol % thanks to the semi-

infinite size of graphene. Other 2D nanosheets such as $\text{Ti}_3\text{C}_2\text{T}_x$ showed a much higher percolation threshold than graphene because of their much lower aspect ratios limited by the relatively small lateral dimensions.[261,324]

Percolation of fillers is essential to endowing composites with excellent functional properties, such as high electrical conductivity, high thermal conductivity and high dielectric constant. Depending on specific applications, either an ultralow or a high percolation threshold is required. An ultralow percolation threshold is highly desired for applications requiring excellent transport properties, such as highly electrically or thermally conductive composites. Well dispersed 2D nanofillers with high aspect ratios and high degrees of alignment contribute to an ultralow percolation threshold. On the other hand, a high percolation threshold is often needed to maintain the insulating nature of composites with an appreciably high filler content, such as the case of high-dielectric constant (high- k) materials for capacitive energy storage applications. In other words, desired functional properties of composites can be achieved if the percolation of 2D nanofillers is controlled through various rational assembly techniques.

5.2.2. Electrical conductivity

Electrically conductive composites are finding emerging applications in many technological fields as sensors, elastic conductors and flexible EMI shielding materials. As most polymer matrices are insulating, a percolated network of conductive 2D nanofillers, such as graphene and $\text{Ti}_3\text{C}_2\text{T}_x$, is required to make composites electrically conducting. According to percolation theory,[321] the electrical conductivity of a composite, σ , near the percolation threshold, V_c , is given by

$$\sigma = \sigma_0(V_f - V_c)^s, \quad (6)$$

where σ_0 is the electrical conductivity and V_f is the volume fraction of nanofillers, and s is a conductivity exponent. The percolation theory suggests a drastic increase in electrical

conductivity near the percolation threshold, transforming the composite from insulating to conductive. The electrical conductivities of polymer composites containing highly aligned or 3D networks of 2D nanosheets with filler contents spanning almost three orders of magnitude are compared in Figure 20a and their fabrication methods are tabulated in Figure 20b. The comparison identifies several important factors affecting electrical conductivities of composites. Firstly, CVD-grown graphene either in the form of 2D aligned layers [228,230] (hollow circles) or 3D structures such as GWF[247], GF[233] and MGW[30] (solid circles) are the most effective fillers amongst all. The effectiveness arises from the nanoscale mechanism of almost defect-free graphene sheets produced by the CVD process (Figure 20c, i), leading to exceptionally high electrical conductivities of over 1 S cm^{-1} at low graphene contents of less than 1 wt %.[228,230,233] Secondly, the polymer composites containing 3D interconnected networks (solid symbols) of graphene, rGO or $\text{Ti}_3\text{C}_2\text{T}_x$ generally show higher electrical conductivities than the 2D aligned counterparts (hollow symbols) at similar filler loadings. This can be attributed to the microscale mechanism of inherently interconnected networks (Figure 20c, ii) which facilitate electron transfer through tunneling or Ohmic contacts. Such networks of CVD-grown graphene at a high loading of 8.3 wt % improved the electrical conductivity to an exceptional value of 50 S cm^{-1} .[30] While rGO sheets with more defects or functional groups are inferior to CVD-grown graphene, they can be assembled to form ultralow-density UGAs with unidirectional alignment through UFC (solid triangles)[209,210]. The epoxy nanocomposites prepared using these UGAs delivered an ultralow percolation threshold of 0.007 vol % along the alignment direction[210]. Other rGO networks made by polymer templating[258] or sol-gel process[29] showed lower electrical conductivities resulting from more isotropic structures. Other than the graphene family, 3D $\text{Ti}_3\text{C}_2\text{T}_x$ networks in a PS matrix [261] also presented a high electrical conductivity of 10 S cm^{-1} . Thirdly, high filler contents of more than 10 wt % were achieved in the form of aligned

structure by VAF (Figure 20c, iii)[27,161,170] or compaction of aerogels made from BFC.[220] Such a macroscopic mechanism of high filler contents led to ultrahigh electrical conductivities of composites approaching those of rGO [70] and $\text{Ti}_3\text{C}_2\text{T}_x$ papers [27] , *i.e.*, 1390 and 4665 S cm^{-1} , respectively.

5.2.3. Dielectric properties

Polymer nanocomposites with a high relative permittivity or dielectric constant (k) are potential candidates for a number of applications, such as EMI shielding, capacitive energy storage and electroactive actuators, thanks to their lightweight, flexibility and mechanical robustness. The k values of most engineering polymers are in the range of 2 – 3, which are too low for practical applications. While some ferroelectric polymers, such as PVDF and its copolymers, exhibit higher k values of up to ~ 50 , a further rise in k is necessary by adding high- k or conductive fillers. The dielectric constants measured of composites containing different types of fillers at 1 kHz are compared in Figure 21a. Traditionally, high- k ferroelectric ceramics such as BaTiO_3 are added to polymer matrices to form high- k composites. Nevertheless, a large amount of ceramic fillers over 50 vol % only brought about a moderate k of ~ 70 , and the brittle nature of ceramics deteriorated the mechanical properties and flexibilities of polymer composites.[327] Conductive fillers, such as metal particles [328,329], CNTs [330] and conductive 2D nanofillers, [114,211,219,324,325,331] were shown to be more effective than dielectric ceramics. The k value of a composite containing conductive fillers can be predicted from the percolation theory:[321]

$$k \propto k_0 |V_f - V_c|^{-q}, \quad (7)$$

where k_0 is the dielectric constant of matrix, V_f is the volume fraction of nanofillers, and q is an exponent having a theoretical value close to 1. q is normally fitted with experimental data and varies depending on the aspect ratio of nanofillers. A larger aspect ratio was found to result in a higher q value.[330] According to Equation (7), a large increase in k is expected as

the nanofiller content increases closely to the percolation threshold. Therefore, apart from the inherent conductivity of nanofillers, the k value of a composite largely depends on the geometric features of conductive fillers, including the shape, aspect ratio and orientation, as they determine the percolation threshold. Regarding the effect of shape, it is clear from Figure 21a that 2D nanofillers, including rGO,[114,211,219,331] GNP[325] and $\text{Ti}_3\text{C}_2\text{T}_x$ [324], outperformed 1D CNTs and 0D Ni nanoparticles, achieving higher k values at lower filler loadings. Among different geometric features, the aspect ratio and alignment played a key role. Although $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets remarkably increased the k value of a poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) composite to over 10^5 , such an improvement was only possible at a high filler content of 7 vol % due to their small lateral sizes of less than 1 μm and thus relatively low aspect ratios.[324] GNPs with large lateral sizes of 25 μm delivered a giant k value of over 10^7 at a much lower filler loading of 2.3 vol % than the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, thanks to GNP's much higher aspect ratio of $\sim 10^3$. [325] rGO sheets with aspect ratios of over 10^4 were even more effective with extremely low filler loadings of less than 1 vol % than GNPs and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The k value of PVDF increased from ~ 20 to over 140 with only 0.08 vol % rGO nanosheets, and a massive k of 7500 was reaped at an rGO loading of merely 0.4 vol %.[331] These comparisons signify the importance of aspect ratio in determining the dielectric properties. A high aspect ratio effectively decreases the percolation threshold, leading to a rapid increase in k at a low filler loading. In addition to a high aspect ratio, the alignment of 2D fillers in the polymer matrix also contributes to a high k of composites. Ultra-large rGO sheets with aspect ratios over 10^4 could self-align in an epoxy matrix, giving rise to a k of ~ 15000 with only 1.6 vol % of rGO.[114] Porous composites containing highly aligned rGO/PVA walls fabricated by UFC showed a high k of 5720 at only 0.17 vol % of rGO.[211]

The ultrahigh k of conductive 2D nanofiller/polymer composites can be understood by considering the aligned layers as micro-capacitors, as shown in Figure 21c.[324] Under an external electric field, the charge carriers migrate and accumulate at the conductor/insulator interfaces according to the Maxwell-Wagner-Sillars (MWS) effect.[114] The interfacial polarization introduced between the polar polymer molecules and the nanofillers (Figure 21c) facilitated the formation of nano- or micro-capacitors which consist of two conductive fillers with a thin insulating polymer layer placed in-between, contributing to a sharp increase in k near the percolation threshold of fillers. In addition, the functional groups present on the surface of rGO and $\text{Ti}_3\text{C}_2\text{T}_x$ sheets were able to form hydrogen bonds with polar polymer molecules, which introduced dipoles at the interface leading to additional interfacial polarization (Figure 21d).[324] Further increasing the filler content beyond the percolation threshold generates more capacitors, effectively increasing k by at least a few orders of magnitude. Meanwhile, more conductive pathways are created through either the tunneling or the Ohmic contact between the adjacent 2D nanofillers, resulting in dielectric relaxation. When the filler content increases far beyond the percolation threshold, the dielectric relaxation prevails eventually over the micro-capacitor effect, leading to a gradual reduction in k of the composite.[324,325]

The increase in dielectric constant is always accompanied by a surge in dielectric loss. As shown in Figure 21b, the dielectric losses of composites containing 1D CNTs [332] and 2D $\text{Ti}_3\text{C}_2\text{T}_x$ sheets,[324] rGO [331,333,334] and GNPs [325,335] increased by a few orders of magnitude as k increased because of the formation of percolative networks of conductive nanofillers. Conductive 2D nanosheet/polymer composites with high k and high loss values can be used for EMI shielding applications, which is discussed in detail in Section 6.2.1.[114,336] On the other hand, it is challenging to achieve a low loss while maintaining a high k because of their conflicting requirements pertaining to percolation. Many efforts have

been made to mitigate the increase in dielectric loss of composites for their potential applications as dielectric capacitors. One effective strategy is to block the electron tunneling by introducing insulating barriers on the surface of conductive fillers.[337] For example, polymer barriers were introduced between the layered rGO walls of UGAs through UFC. The electrical leakage in the transverse direction was suppressed to a low loss of 0.076 while maintaining a high k of over 1000.[211] Adding 2D BNNSs in the polymer barriers further moderated the dielectric losses thanks to the highly insulating nature of BN. Both solution processed BNNSs[7,33] and CVD-grown *h*-BN films [229] or foams [237] were highly effective in suppressing the dielectric loss of engineering polymers, such as PEI, PC, polyaramid and cross-linked benzocyclobutene (*c*-BCB), to less than 0.01. For ferroelectric polymers like P(VDF-TrFE-CFE), the addition of BNNSs effectively suppress their losses to 0.03 – 0.04 while maintaining a high k of 40.[338] BNNSs were also used as insulating layers between rGO layers in highly aligned rGO/PU composites (Figure 21e), leading to a high k of over 1000 with a loss of less than 0.1.[219] The high k and low loss of BN and BN-graphene hybrid composites make them promising as dielectric capacitors for electrical energy storage applications, which is discussed in Section 6.3.1.

5.2.4. Thermal conductivity

Polymer composites with high thermal conductivities are increasingly important for thermal management applications. Most polymers have low thermal conductivities of 0.1 to 0.3 Wm⁻¹K⁻¹, which are too low to efficiently dissipate the excessive heat generated in high power density devices, such as consumer electronics and batteries. 2D nanosheets, such as graphene and BNNSs, with high in-plane thermal conductivities are ideal fillers for fabricating composites with high thermal conductivities. The phenomenon of thermal percolation is not as apparent as in electrical percolation because of the much smaller differences in thermal conductivity ($\kappa_f/\kappa_m = 10^4$) between the conductive fillers and polymer matrices than those in

electrical conductivity ($\sigma_f/\sigma_m = 10^{15}$). As such, the thermal percolation threshold was found to be much higher than the electrical percolation threshold for the same 2D nanofiller/polymer composite.[339] Nonetheless, the formation of percolated networks allows the phonon transport through adjacent 2D nanosheets, exhibiting much lower thermal resistances than those at the 2D nanofiller/polymer interfaces. This also means that the thermal conductivities of composites can be substantially improved using 3D foams or aerogels as fillers. The 3D graphene or BNNS structures show clear advantages over the randomly dispersed counterparts in improving the thermal conductivities of composites, especially at low filler contents of less than 10 vol %, as shown in Figure 22a. At a low graphene content of 4.6 vol %, the thermal conductivity of an epoxy composite reached $8.8 \text{ Wm}^{-1}\text{K}^{-1}$ by reinforcing a high-density GF as the filler,[30] which is much higher than $1 - 2 \text{ Wm}^{-1}\text{K}^{-1}$ achieved by dispersed rGO or GNP sheets at a similar filler loading. When the filler content further increases, the advantage of 3D fillers diminishes owing to the formation of percolated networks for randomly dispersed fillers. Nevertheless, the 3D structure prepared with better dispersed graphene or BNNSs is preferred against the directly dispersed nanosheets for higher mechanical properties of the composites. Among different 3D foams and aerogels, GFs and BNFs made by template-directed CVD (blue symbols in Figure 22a) are more effective in improving the thermal conductivities of composites than aerogels made by polymer- or ice-templating. The thermal conductivities of graphene walls in CVD-grown GFs were as high as $1000 \text{ Wm}^{-1}\text{K}^{-1}$ thanks to the unspoiled pristine crystal structures and seamlessly interconnected conductive networks [340].

To deliver exceptional thermal conductivities, a high filler loading is required similar to electrical conductivity. Highly aligned rGO and BNNSs with high filler contents of over 40 vol % should be able to deliver much higher thermal conductivities than 3D GFs and BNFs. In addition, to achieve a high thermal conductivity of GO/polymer composites, high

temperature annealing is often necessary to mitigate the adverse phonon scattering by functional groups and defects on GO sheets. Thermal reduction of neat GO films without a polymer matrix at temperatures over 2000 °C led to a significant reduction in O/C ratio,[105] imparting ultrahigh thermal conductivities of up to $\sim 1200 \text{ Wm}^{-1}\text{K}^{-1}$ along the alignment direction (red circles in Figure 22a).[104,105,341] Heat-treatment of a CVD-grown graphene film at 2800 °C gave rise to nearly perfect crystallinity, resulting in an exceptionally high thermal conductivity of $2292 \text{ Wm}^{-1}\text{K}^{-1}$ (orange circle in Figure 22a),[28] approaching the value of suspended graphene sheet (dashed line in Figure 22a). In comparison, rGO papers reduced using HI solution showed a lower thermal conductivity of $\sim 500 \text{ Wm}^{-1}\text{K}^{-1}$ because of the residual functional groups and defects.[106] In addition to neat rGO and graphene films, composite films containing highly aligned 2D nanosheets, such as BNNSs and GNPs, made by VAF [159,342] or external field-induced alignment [146,182,204,343] also showed anisotropic thermal conductivities with relatively high in-plane values.

The design strategies developed to achieve high thermal conductivities of composites across different length scales are summarized in Figure 22b. At the nanoscale, the CVD technique and high-temperature annealing guarantee intact crystal structures. The graphene film treated at 2800 °C exhibited nearly perfect crystallinity (Figure 22c) with lower Raman I_D/I_G ratios (Figure 22d) than that annealed at 400 °C (Figure 22e and f). Such integral crystal structures with few phonon scattering sites led to extremely high intrinsic thermal conductivities of graphene film. At the microscale, the interconnection between 2D nanosheets allows phonon transport across their interfaces with highly matched phonon vibrational frequencies (Figure 22g) because of their identical structures, generating a much lower interfacial resistance than through the 2D nanofiller/polymer interfaces. Meanwhile, the multilayer structures are crucial to reducing the phonon energy damping by the surrounding polymer [122] because the thermal conductivities of monolayer graphene and *h*-BN sheets were much reduced once

embedded in the polymer matrix (see Section 3.2.3).[95,120,121] At the macroscale, extending these stacked nanosheets into continuous 2D aligned or 3D interconnected networks by various rational assembly techniques can minimize the phonon scattering at the 2D nanofiller/polymer interfaces. This was partly attested by the fact that the thermal conductivities of the composites fabricated using the aligned or interconnected graphene networks were well fitted by the ROM without taking into account the interfacial thermal resistance.[240] Moreover, high filler contents of over 40 vol % can be achieved with 2D aligned structures, leading to exceptional thermal conductivities approaching that of pristine graphene.

5.2.5. Mass transport properties

Mass transport properties are commonly characterized by the permeability of various masses, such as gas molecules and ions, through composite membranes. Defect-free monolayer graphene and other 2D nanofillers are impermeable to many gas molecules and ions, making them ideal to improve the barrier properties or offer selective molecular transport capabilities of polymer films.[350–353] The addition of 2D nanofillers alters the molecular transport pathways by creating tortuous pathways for gas or liquid molecules to diffuse in the matrix and thus reducing their permeabilities through composites (Figure 23a and b). The permeability of composites depends largely on the volume fraction, aspect ratio and orientation of 2D nanofillers in addition to the intrinsic permeabilities of matrix materials. The permeability values normalized by that of the neat matrix, P_c/P_o , for composites containing aligned [143,354] and randomly-oriented [355,356] GO or rGO sheets are compared in Figure 23c. The relative permeabilities decreased consistently with increasing filler contents. The rGO and GO sheets aligned against the permeation direction led to lower permeabilities to gases than randomly oriented counterparts because of more tortuous paths

for gas molecules to transport through layered structures. The experimental data agree well with theoretical predictions from the Nielsen model:[353]

$$\frac{P_c}{P_o} = \frac{1-V_f}{1+\frac{2}{3}\alpha V_f(S+\frac{1}{2})}, \quad (8)$$

where V_f is the volume fraction, α is the aspect ratio, and $S = \frac{1}{2}\langle 3 \cos^2 \theta - 1 \rangle$ is the orientation parameter. Randomly-oriented 2D nanofillers correspond to $S = 0$ while those of highly aligned yield $S = 1$. Both the experimental and theoretical results suggest that the excellent barrier properties of 2D nanofillers can be better translated into composites when they are aligned in the matrix. Therefore, the composite films are normally synthesized by simple LC self-assembly or LbL assembly, generating stacked 2D nanofillers with interlayer channels for mass transport.[143,354,357,358] Such brick-and-mortar arrangements maximize the diffusing path of molecules, leading to lower permeabilities of composites than those containing randomly-oriented fillers. Another important parameter determining the permeability is the aspect ratio. The Nielsen model (Equation 8) signifies that 2D nanofillers with higher aspect ratios lead to lower permeabilities of composites because of the increased diffusing path lengths. The significance of aspect ratio is also confirmed by the experimental study where GNPs with high aspect ratios ($\alpha = 1500$) gave rise to 10 % lower permeabilities of polypropylene (PP) composites against O_2 than those with low aspect ratios ($\alpha = 100$).[359] Other 2D nanofillers such as BNNS and MoS_2 were also used to reduce the permeabilities of various gases, including H_2 , O_2 , and H_2O , by fabricating composite films.[360–362]

The selectivity is an important mass transport property that measures the membrane's ability to allow specific gases or ions to pass through while blocking others in an environment containing mixed gases or solutions. Membranes with both high selectivity and high permeability towards certain gases or ions are essential for molecular separation applications. There are two types of selective mass transport channels, namely, (i) interlayer channels formed between 2D nanofillers (Figure 23d) and (ii) porous channels because of the pores in

the 2D nanofillers (Figure 23f). 2D nanosheets including GO, MoS₂ and Ti₃C₂T_x were stacked using VAF to form ultrathin membranes with nanosized interlayer channels for selective transport of molecules and ions.[164,166,363–365] These ultrathin membranes are formed seldom freestanding and need to be supported on a substrate for practical applications. The 2D nanofillers were also added to polymer matrices to produce freestanding composite membranes to mitigate the common trade-offs between the permeability and selectivity of polymer membranes.[350,351] The permeability and selectivity performance of these membranes depends on the size and structure of nanochannels formed between the adjacent 2D nanofillers. These characteristics were tailored by controlling the size of 2D sheet [365], interlayer crosslinker [366,367], and surface chemistry [166,169,368,369]. In particular, functionalization of 2D nanosheets with chemical groups or crosslinking agents having high affinity to target gases significantly enhanced the selectivity while simultaneously improving the permeability.[367–370] For example, PEG- and PEI-functionalized GO sheets were used to construct selective gas transport channels with high CO₂ affinity in a commercial Pebax matrix for separating CO₂ from N₂ and CH₄, as shown in Figure 23d.[368] The ethylene oxide groups in PEG and amine groups in PEI improved the solubility and reactivity of CO₂ in the composite membrane by absorbing and reacting with CO₂, respectively, leading to concurrently enhanced CO₂ permeability and CO₂/N₂ selectivity, exceeding the theoretical upper bound for polymer membranes (Figure 23e).

In addition to interlayer channels, selective mass transport can also be realized through nanosized pores on 2D nanofillers (Figure 23f).[371] The filtration of gases or ions are determined by their molecular shape and size relative to the pores, such that smaller molecules can be effectively separated from larger ones. Artificial pores were created by defects, etching or ion bombardment on graphene and GO sheets for gas or ion separation membranes.[372,373] However, the size and uniformity of these pores were difficult to

control, making industrial applications using porous graphene or GO sheets in polymer membranes rather challenging. The 2D MOF nanosheet having intrinsic pores with a well-defined pore structure and size (Figure 23g and h) is an emerging, highly selective separation membrane that discreetly allowed the species with sizes smaller than the pore diameters to pass through while rejecting the larger ones.[352,374] The consistent pore sizes and shapes in 2D MOF enabled precise transport of target molecules through the composite films when they were aligned in the matrix, giving rise to high selectivities.[375–377] Moreover, a large number of 2D MOF nanosheets were either exfoliated from the layered MOF, similarly to other 2D nanofillers, or synthesized from metal ions and organic ligands using a bottom-up approach to create diverse pore sizes and shapes. Therefore, it is possible to tailor the mass transport of various gases, liquids and ions for myriad molecular sieving applications,[41] as discussed in Section 6.4.

6. Toward multifunctional applications

6.1. Challenges to multifunctional applications

The rational assembly of 2D nanosheets into 2D aligned and 3D interconnected structures allows effective translation of excellent mechanical and functional properties of 2D nanosheets to their polymer composites. Nonetheless, the emerging applications of nanocomposites pose more stringent requirements on their multifunctionalities. The first challenge is to achieve desired functional characteristics without deteriorating the mechanical properties. Conventional synthesis techniques require the addition of appreciable amount of 2D fillers in order to form percolation and therefore achieve improved functional properties. However, high filler loadings are often deleterious to mechanical properties because of potential filler agglomeration. In contrast, the mechanical properties of composites containing 2D aligned or 3D interconnected 2D nanofillers are not compromised for the benefit of functional properties even at high filler loadings because of their inherently

excellent dispersion attribute.[30] The second challenge is that the composites should retain more than one desired functional characteristics for many emerging applications. These properties are occasionally achieved in the same composite: for example, high electrical and thermal conductivities are obtained in graphene/polymer composites. However, properties of mutually exclusive natures are often required. One telling example is the high dielectric constant and low dielectric loss, which are usually mutually exclusive in composites but highly desired for applications like electroactive actuators and electrical energy storage.[7] This conflicting condition compels rigorous design of 2D nanofillers and even calls for contradictory microstructures in terms of their percolation and distribution in order to achieve desired multifunctionalities. Intriguingly, a combination of mutually exclusive properties can also be achieved in the same composite through the rational design and assembly of 2D nanofillers and accurate control of their orientation, concentration, distribution and interconnection. In this section, we demonstrate how rationally assembled structures can be best utilized to impart multifunctional properties, especially those mutually exclusive, and how these properties pertain to many emerging fields, such as flexible electronics, energy storage, conversion and harvesting.

6.2. Flexible electronics

6.2.1. EMI shielding

Electromagnetic waves emitted by electronic devices can potentially interfere with and cause malfunction in other devices. Therefore, protection of electronics from unwanted EMI is of paramount importance to ensure their proper functions.[114,336] With the electronic devices being made thinner, lighter, more compact and in flexible forms, conventional EMI shielding materials such as metal foils are no longer suitable because of their high densities and lack of flexibility.[336] The highly conductive 2D nanofillers/polymer composites with high k are ideal alternatives for EMI shielding applications in emerging flexible electronics because of

their light weight, good processability and excellent flexibility. The EMI shielding mechanisms consist of three components, namely, (i) reflection, (ii) absorption and (iii) multiple reflection of the incident EM waves.[114] The capability of a material to reflect EM waves mainly depends on its electrical conductivity. A high electrical conductivity favors the reflection shielding component because of the interaction between the charge carriers and EM fields.[378] Meanwhile, the absorption of EM waves requires a high k and high dielectric loss of the shielding material.[244] Therefore, constructing a highly conductive network of 2D nanofillers in the composite is the primary goal towards high EMI shielding effectiveness (SE), as electrical conductivity contributes to both reflection and absorption of the EM waves. While the reflection and absorption of EM waves are mainly determined by the intrinsic properties of composites, the multiple reflection calls for a large surface area and abundant interfaces in the composites. The large surface area of 2D nanosheets containing functional groups provides countless interfaces to reflect EM waves internally, which can further enhance the EMI SE.[27]

Depending on the application scenarios, strategies to construct conductive networks differ. When the thickness of a EMI shielding material is a primary concern, highly aligned graphene, $\text{Ti}_3\text{C}_2\text{T}_x$ or $\text{Mo}_2\text{TiC}_2\text{T}_x$ thin films [27,105,165,379] and their polymer composites [27,114,380] made by LC assisted self-assembly or VAF are good candidates. The plot of EMI SE as a functional of thickness is shown in Figure 24a. Freestanding films can be made as thin as only a few microns, and usually less than 1mm. Yet such thin films show excellent in-plane electrical conductivities of 10^4 to 10^5 S m^{-1} as a result of their high orientation (Figure 24b), leading to excellent EMI SE ranging from 20 to 90 dB depending on their thickness. For a similar thickness, $\text{Ti}_3\text{C}_2\text{T}_x$ films show higher EMI SE than rGO or graphene films mainly ascribed to their higher electrical conductivities. The $\text{Ti}_3\text{C}_2\text{T}_x$ films [27,165] made by VAF exhibited electrical conductivities of $\sim 4 \times 10^5 \text{ S m}^{-1}$, which are approximately

four times those of graphene or rGO ($\sim 1 \times 10^5 \text{ S m}^{-1}$) made by CVD [379] or LC assisted self-alignment [105]. Compared to neat graphene or $\text{Ti}_3\text{C}_2\text{T}_x$ films, their polymer composites exhibit improved mechanical properties, but the electrical conductivity is diminished depending on the filler loading. The composites made with low molecular weight polymer matrices, such as SA, accommodated an extremely high loading up to 90 wt % of $\text{Ti}_3\text{C}_2\text{T}_x$, making the $\text{Ti}_3\text{C}_2\text{T}_x/\text{SA}$ composite almost as conductive as its neat freestanding film.[27] Therefore, the EMI SE of the composite was still high, reaching 57 dB at a thickness of only 8 μm . On the other hand, when common high molecular weight engineering polymers, such as epoxy [144] and PU [380] , were used, the increase in mechanical properties of the composites were often at the expense of reduced conductivity because of the low filler content, usually less than 10 wt %, that can be added in the composite. As such, the EMI SEs of rGO/epoxy[144] and rGO/PU[380] composites were lower than 40 dB even though they were thicker than the freestanding film. 3D porous composite foams have higher thicknesses but much lower densities than highly aligned composite films (Figure 24c). Therefore, these lightweight composite foams can be particularly useful for aerospace applications in which light weight is a primary concern. GFs made by CVD on Ni foam templates are commonly explored for EMI shielding applications due to their high electrical conductivities and porous structures. The very first attempt was made by incorporating PDMS into the GF structure, yielding a porous composite with a density of only 0.06 g cm^{-3} , which showed an EMI SE of 33 dB.[336] Further efforts were made to incorporate CNTs in the PDMS or replace PDMS with conductive polymers to further increase the conductivity.[244,245] A remarkable EMI SE of 91 dB was achieved by coating a conductive polymer, [poly\(3,4-ethylenedioxythiophene\) polystyrene sulfonate \(PEDOT: PSS\)](#), on the GF surface without compromising its inherently low density (Figure 24c).[244] Assembling $\text{Ti}_3\text{C}_2\text{T}_x$ sheets into a freestanding conductive network is challenging because of their small aspect ratios and thus

poor stability. As such, rGO sheets were used as binder to facilitate the formation of a freestanding $\text{Ti}_3\text{C}_2\text{T}_x/\text{rGO}$ aerogel by UFC. [216] The aerogel was impregnated with epoxy to form a conductive composite, leading to a high EMI SE of 56 dB. Alternatively, 3D $\text{Ti}_3\text{C}_2\text{T}_x$ networks were formed directly in a PS matrix by electrostatically assembling $\text{Ti}_3\text{C}_2\text{T}_x$ sheets on the surface of PS microspheres followed by hot pressing.[261] The solid composite showed an EMI SE of 62 dB.

While the high electrical conductivities can enable both reflection and absorption of EM waves, the absorption capabilities of highly aligned films and 3D networks of conductive fillers play a dominant role for EMI shielding of their polymer composites. Although part of the incident EM waves can be reflected on the surface thanks to the interaction with abundant charge carriers of conductive fillers, the majority of EM waves penetrates the surface into the internal structure of the aligned film or porous foam, as shown in Figure 24d and Figure 24e, respectively.[27,244] These surviving waves induced an EM field within the structure, polarizing dipoles thanks to the capacity associated with the high k . In particular, 2D nanofillers, such as rGO and $\text{Ti}_3\text{C}_2\text{T}_x$, with high electronegative functional groups (e.g., -F, -O-, -OH) were readily polarized with local dipoles between the basal plane, C or Ti, and functional groups.[27,244] These dipoles are polarized and relaxed under an alternating EM field created by the incident EM waves, leading to polarization losses that dissipate the EM energies. Meanwhile, the polarized electrons accumulate at the nanofiller/matrix interfaces can hop from one conductive filler to another by the tunneling effect under the EM field, inducing conduction losses which also dissipate the EM energies. Both the polarization and conduction losses arising from the high k values and high dielectric losses of composites are responsible for the dominant role of absorption as the major EMI shielding mechanism.

6.2.2. Flexible conductors and sensors

Transparent conductive films (TCFs). TCFs have been widely used in touch panels of modern electronics and transparent conductive electrodes of solar panels.[386] Indium tin oxide (ITO) has been the dominant material for long in the market. However, ITO is brittle making it difficult to use in emerging flexible or foldable displays. 2D nanosheets, such as graphene and MXene, with high electrical conductivities and optical transparency have been explored as flexible TCFs exploiting their durability and flexibility. The performance of TCFs is characterized by the conductivity ratio, σ_{DC}/σ_{opt} , where σ_{DC} is the electronic conductivity and σ_{opt} is the optical conductivity. A high conductivity ratio requires both a low sheet resistance and a high transmittance. To replace ITO, a sheet resistance lower than $100 \Omega \text{ sq}^{-1}$ and optical transmittance above 90 % across visible spectrum are required, corresponding to a σ_{DC}/σ_{opt} higher than 35.[387] Thin films of graphene, rGO, $\text{Ti}_3\text{C}_2\text{T}_x$, Ti_3CT_x , and V_2CT_x with different thicknesses can be deposited on flexible polymer substrates using techniques, such as spin-coating, spray-coating, L-B assembly, tape-casting, electrophoretic deposition, inkjet-printing and CVD.[311,388] For graphene, CVD-grown multilayer graphene films showed higher σ_{DC}/σ_{opt} than chemically derived rGO sheets, a reflection of their higher electrical conductivities.[387] Nevertheless, the maximum σ_{DC}/σ_{opt} achieved by CVD-grown graphene was ~ 11 ,[389] far short of the industry's standard of 35. Most recently, MXene films such as $\text{Ti}_3\text{C}_2\text{T}_x$, Ti_3CT_x , and V_2CT_x have been explored as TCFs by virtue of their extremely high electrical conductivities.[388] For example, $\text{Ti}_3\text{C}_2\text{T}_x$ thin films were prepared by spin-coating of precursor dispersion containing large-size $\text{Ti}_3\text{C}_2\text{T}_x$ sheets (Figure 25a-b).[111] After annealing at 200°C in vacuum, the film showed an outstanding electrical conductivity of 9880 S cm^{-1} , the highest value reported for MXene films thus far. Therefore, the $\text{Ti}_3\text{C}_2\text{T}_x$ film exhibited a lower sheet resistance than graphene-based conductive films at the same transmittance (Figure 25c), yielding a higher σ_{DC}/σ_{opt} of 15. Further improvements in σ_{DC}/σ_{opt} are still necessary for potential replacement of ITO

TCFs, which can be achieved by reducing the sheet resistance through several strategies, such as using 2D nanofillers with large lateral sizes, post treatments by chemical doping, and hybridization with conductive 1D nanofillers.[311,387,388] Large-size 2D nanofillers would reduce the number of junctions between adjacent sheets, leading to a lower inter-sheet resistance and thus a higher conductivity.[311,388] Chemical doping is an effective approach to increase the carrier concentration and hence lower the sheet resistance. Doping agents such as acids and halogenating reagents shift the Fermi level of graphene by forming charge transfer complexes for enhanced carrier concentrations.[390] For example, both the electrical conductivity and optical transparency of L-B assembled rGO films increased after treatment with HNO_3 and SOCl_2 . [267] Hybridization with other 1D conductive nanofillers, such as CNTs and Ag nanowires, has also demonstrated a reduction in inter-sheet resistance by minimizing the contact resistance between rGO sheets. For example, Ag nanowire and GO-Au nanoparticle solutions were sequentially spin-coated on a glass substrate to fabricate a hybrid film with an ultralow sheet resistance of $26 \, \Omega \, \text{sq}^{-1}$. Such a low sheet resistance gave rise to a high $\sigma_{\text{DC}}/\sigma_{\text{opt}}$ of 74,[311] surpassing that of commercial ITO film and thus promising for next-generation flexible TCFs.

Elastic conductors. Elastic conductors have received much attention for their applications as stretchable electrodes in wearable electronics and robots.[20] For such applications, the electrical conductivity of conductors should be constant under large deformations. Integrating highly conductive 2D nanosheets with elastomers can yield stretchable conductive composites. As the conductivity of composites is controlled by interconnected networks, proper structural design of 3D conductive networks is critical to allowing large strains before failure without changing the conductive pathways. Many patterns have been proposed to improve the stretchability of composites, such as wrinkles, meshes, coils, honeycombs and kirigami structures.[20] For example, a 3D graphene honeycomb panel was prepared by self-

assembly of GO sheets on a 3D-printed honeycomb template followed by thermal reduction and coating with PDMS (Figure 25d-f).[259] The honeycomb panel was sandwiched between two highly conductive GF/PDMS face sheets to serve as stretchable circuits in a stretchable LED display. The high conductivity and relatively small change in resistance with increasing strain enabled the graphene honeycomb panel to illuminate arrays of LED with a low voltage input (Figure 25g) and maintain the function under different types of deformation (Figure 25h).

Multifunctional wearable sensors. Piezoresistive sensors can detect strains by virtue of the changes in their electrical resistance. Contrary to the requirement for elastic conductors, sensor materials require large changes in resistance in response to tiny strains. Composite sensors made from conductive 2D nanosheets are able to detect various forms of deformation, including tension, shear, torsion, bending and pressure.[246,248,249] In particular, flexible nanocomposites are conformable to different shapes, making them ideal to be worn on different human body parts and serve as body motion sensors.[31] The change in resistance stems mainly from the altered inter-sheet distance which either promotes or discourages electron tunneling between the conductive sheets. Both 2D aligned and 3D structures of graphene and MXene composites were used for pressure and in-plane strain sensing. Highly sensitive pressure sensors were made from multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ sheets on a PI substrate.[391] The large interlayer distances between the aligned $\text{Ti}_3\text{C}_2\text{T}_x$ layers were reduced significantly by the applied pressure (Figure 25i-j), leading to increased conductivities and high gauge factors ranging from 94 to 180 under small strains of less than 1 %. Such a mechanism allowed the detection of tiny pressures down to 5 kPa with a fast response time and good stability (Figure 25k). While 2D films can serve as pressure sensors, 3D structures of graphene and $\text{Ti}_3\text{C}_2\text{T}_x$ with well-defined conductive networks are suitable for multidirectional strain sensing. Conductive 3D composite aerogels or foams made from $\text{Ti}_3\text{C}_2\text{T}_x$, graphene

and their hybrids were used as flexible strain sensors to detect both lateral strains and pressure.[209,238,252,274,392–394] To achieve high sensitivity to strain, the continuous conductive pathways were intentionally destroyed to allow a large change in contact resistance with only a subtle change in applied strain.[252,394] For example, a highly elastic strain sensor was produced based on fragmentized GF/PDMS composites,[394] which presented high sensitivity with a gauge factor of 29, much higher than those of the undamaged GF/PDMS counterparts. In addition, high stretchability of 70 % was also achieved, leading to effective sensing of both large human motions and small pressure changes brought by the pulse of radial artery. Nonetheless, most of these sensors are only capable of sensing the amplitude of strains or pressures but inept to differentiate their directions, limiting their applications to sensing only single-axis motions. For more complicated applications, such as medical diagnosis of movement disorders and artificial skins for soft robotics, highly sensitive multidirectional strain sensors are required to discriminate complex strain conditions. This usually requires highly anisotropic structures with well-defined alignment of conductive fillers. Therefore, 1D nanofillers such as metal nanowires,[395] CNTs[396] and carbon nanofibers[397] were commonly used for multidirectional sensing. For 2D nanofillers, GWFs in the form of orthogonally interwoven graphene tubes resembled the alignment of 1D fibers exhibited the ability to differentiate off-axis lateral strains (Figure 25l-m).[31] Further improvements of multidirectional sensing capabilities involved the development of sensors with decoupled resistance responses under multiple strain states, such as pressure-insensitive strain sensors.[398] Other sensing capabilities such as temperature,[399] humidity [400] and gas molecules [162] are useful addition to existing strain sensing, which can be achieved using 2D nanosheets, such as rGO [399,400] and $\text{Ti}_3\text{C}_2\text{T}_x$ [162]. However, integrating multiple sensing abilities in an identical sensory system is still a challenging task because discriminating the exact source of

resistance change under multiple stimuli is very difficult. Therefore, multiple sensors with decoupled sensing properties may be an alternative solution to complex sensing systems involving multiple sensing signals corresponding to specific external stimuli.

6.2.3. Thermal interface materials

The miniaturization of electronic components with high power densities has driven the development of multifunctional thermal interface materials (TIMs) for thermal management in electronics, light-emitting diodes and energy storage systems. The primary requirement for TIMs is the high thermal conductivity, but light weight, flexibility and good processability are some of other desired properties for emerging applications in wearable electronics. By virtue of the excellent thermal conductivity of graphene, only a small amount of graphene added into polymers can fulfill the requirement of thermal conductivity over $1 \text{ Wm}^{-1}\text{K}^{-1}$ for TIM applications[122,344]. However, the composites also become electrically conductive even with very low graphene contents,[322] resulting in short circuiting of electronic devices when the composites are applied directly as TIMs. Therefore, developing composites with high thermal conductivities but electrical insulation is critical for their practical applications. BNNSs are an excellent insulator[401] with a high thermal conductivity of over $300 \text{ Wm}^{-1}\text{K}^{-1}$,[402] making them ideally suited for TIM applications. To maximize the heat dissipation efficiency, highly aligned structures with high BNNS loadings are desired, which can be achieved by VAF[159,342], electrical[153,182] or magnetic[204] field induced alignment and directional freeze-casting[213,215,223] (see Section 5.2.4 for details). For example, highly aligned BNNS/PVDF composite fibers were fabricated by electrospinning.[153] The highly oriented nanofiber membranes were stacked and hot-pressed to form composite films (Figure 26a). At a high BNNS loading of 33 wt %, the percolation of BNNSs along the fiber direction was achieved (Figure 26a, i-iii), delivering an ultrahigh thermal conductivity of $10.4 \text{ Wm}^{-1}\text{K}^{-1}$ (Figure 26b). This value is four times that of randomly oriented BNNSs and twice that of hot-pressed one. The

enhanced thermal conductivity was accompanied by the simultaneously boosted electrical resistivity thanks to the insulating nature of BNNSs (Figure 26c). The in-plane alignment of BNNSs is particularly useful as lateral heat spreaders in electronics to avoid hot spots having high temperatures. Nonetheless, the thermal conductivity along the thickness direction was very poor ($\sim 0.5 \text{ Wm}^{-1}\text{K}^{-1}$, Figure 26b), making the heat dissipation from hot spots to heat sink less effective. To augment thermal conduction along the thickness direction, the use of directional freeze-casting yielding a vertically aligned structure was a viable solution.[213,215,223] Both UFC and BFC techniques were used to fabricate BN aerogels (Figure 26d-f), which were infiltrated with epoxy resin to form composites.[223] The bidirectionally aligned BNNSs in the form of long-range lamellar structure were more effective in dissipating heat than uniaxially aligned or randomly oriented BNNSs, as indicated by the faster rise in temperature when they were put on hot stages (Figure 26g-h). The bidirectional freeze-cast sample showed the highest thermal conductivity associated with the nacre-like lamellar walls which could conduct the heat along two orthogonal directions (Figure 26i). Such a vertically aligned structure is more effective than in-plane alignment as thermal interface materials to effectively dissipate the heat from a heat spot to heat sink. The thermal conductivities were further enhanced using hybrid fillers of rGO and BNNSs.[167,217] However, the electrically insulating properties were inevitably compromised due the conductive graphene.

6.3. Energy storage, conversion and harvesting

6.3.1. Electrical energy storage

Polymer dielectrics are essential components of power electronics to store electric energy electrostatically and can be charged/discharged rapidly by applying/removing the external electrical field with a high power density. They have higher breakdown strengths, lower densities, higher flexibility and better processability than conventional ceramic counterparts. However, the low energy densities and low temperature resistances of polymer dielectrics are

the major hindrance for their commercial applications especially at high temperatures, because of their low dielectric constants and low glass transition (T_g) or melting (T_m) temperatures. For example, the state-of-the-art biaxially oriented polypropylene (BOPP) has an energy density of $\sim 2 \text{ J cm}^{-3}$ with a maximum working temperature of $\sim 105^\circ\text{C}$. In electric vehicles (EVs), the underhood temperature can be as high as 140°C , requiring additional cooling systems for proper functioning of inverters made from BOPP. Such a solution is far from ideal, however, as it adds a redundant weight to EVs. For improved thermal stability, engineering polymers with high T_g , such as PI, PEI, and *c*-BCB, have been used. Nevertheless, their low thermal conductivities ranging $0.1 - 0.5 \text{ W m}^{-1}\text{K}^{-1}$ and low Young's moduli lower than 3 GPa , make them highly susceptible to thermal and electromechanical breakdown at high temperatures. Therefore, simultaneous achievements of a high dielectric constant, breakdown strength, thermal conductivity, Young's modulus and glass transition temperature for a composite are highly desired for high-temperature dielectric applications.

2D BNNSs with a high modulus, excellent breakdown strength, high thermal conductivity and exceptional thermal stability are ideal fillers for high-temperature dielectrics. A remarkable breakdown strength of $\sim 600 \text{ MV/m}$ was achieved by adding $\sim 11 \text{ wt } \%$ BNNS into PVDF, much higher than $\sim 350 \text{ MV/m}$ of the pure matrix.[338] Thermoset polymers show higher thermal stability than thermoplastic counterparts. The $\sim 10 \text{ }\mu\text{m}$ thick BNNS/*c*-BCB composite films made by simple solution casting followed by thermal curing exhibited excellent flexibility and semi-transparency (Figure 27a-d).[7] These films were able to maintain stable dielectric properties at high temperatures up to 250°C (Figure 27e-f).[7] The largely improved breakdown strength and high-temperature stability by incorporating BNNSs can be attributed to three ameliorating functional features: namely, (i) the high breakdown strength of filler itself to prevent leakage currents; (ii) the much improved mechanical properties to avoid electromechanical failure under high electric fields; and (iii) the enhanced

thermal conductivities to effectively dissipate the heat and prevent thermal failure. The alignment of 2D BNNSs further ameliorated the mechanical, dielectric and thermal properties. Highly aligned BNNS/polyaramid nanofiber (PANF) composites made by VAF (Figure 27g-i) showed a combination of desired properties including high dielectric stability at high temperatures, a high Young's modulus, a high thermal conductivity and excellent electrical insulation, surpassing those conventional polymer dielectrics (Figure 27j-l).[33] The highly aligned BNNSs with optimized interfacial interactions with PANF mediated the stress and phonon transfer in the plane direction while blocking the electrical breakdown in the transverse direction, contributing to excellent mechanical, thermal and dielectric properties. One of the major energy loss mechanisms for high temperature applications is the electrical conduction through the thermally activated charge carriers.[7] The tunneling current can induce significant Joule heating in the composite, causing thermal runaway and thus premature breakdown at a service temperature well below the T_g of polymers. To tackle this issue, sandwich structures made from BNNSs or their composites with a high breakdown strength as the face sheets and high- k or high- T_g polymers as cores were rationally designed.[229,403,404] For example, PEI was sandwiched between two CVD-grown h -BN sheets to form a tri-layer composite (Figure 28a-c).[229] The outer BNNS layer effectively blocked the charge injection from the electrodes into the film, maintaining a decent energy density of 1.2 J cm^{-3} even at 200°C , which was close to PEI's T_g of 217°C (Figure 28d). At such a high temperature, the sandwich-structured BN/PEI composites outperformed other engineering polymers and single layer BNNS/ c -BCB composites[7]. The only drawback of BNNS/polymer composites towards high-temperature dielectrics is their low dielectric constant of 2 – 3 at 1kHz, giving rise to low energy densities. Conductive 2D nanofillers, such as graphene and $\text{Ti}_3\text{C}_2\text{T}_x$, can effectively improve the dielectric constant of polymers, as discussed in Section 5.2.3. However, high dielectric constants are always accompanied by a

decline in breakdown strength because of the tunneling of electrons between the adjacent fillers under high electric fields. In view of the above, using hybrid fillers containing both conductive fillers and BNNSs can be a viable solution for promoting the energy density. Microlaminate composites containing alternating rGO/PU and BNNS/PU layers were constructed using the sequential BFC (Figure 28e). The rGO/PU layers provided high dielectric constants while the BNNS/PU layers contributed low dielectric losses and thus high breakdown strengths, synergistically delivering a maximum energy density of 22.7 J cm^{-3} (Figure 28f). The high energy density achieved in the microlaminate composites offered a novel strategy to design multifunctional dielectric materials for high-temperature dielectric applications.

6.3.2. Thermal energy storage

Polymeric PCMs, such as paraffin wax (PW) and PEG, are organic materials capable of storing and releasing thermal energies as latent heat during phase transition. Owing to their high latent heat of fusion, polymeric PCMs can achieve high energy densities for high-performance thermal energy storage in a number of applications, such as thermal management in electronics and batteries and solar-thermal energy harvesting.[405] However, they have two critical drawbacks which significantly limit their practical use, namely, (i) low thermal conductivities and (ii) poor stability upon melting.[405] In particular, the low thermal conductivities of PCMs, typically less than $1 \text{ W m}^{-1} \text{ K}^{-1}$, significantly reduce the heat transfer rate in the material, resulting in temperature gradients across PCMs and long thermal energy charging and discharging times.[240] Highly thermally conductive 3D graphene structures are an attractive solution to the aforementioned drawbacks exploiting the ultrahigh thermal conductivity of graphene and high porosity to hold PCMs.

Highly porous GAs assembled from GO or rGO sheets were infiltrated with PCMs which showed improved thermal conductivities and morphological stability.[406–408] In particular,

the highly aligned GA/PW composites made from UFC with ameliorating anisotropy (Figure 29a-c) possessed a remarkable thermal conductivity of $8.87 \text{ Wm}^{-1}\text{K}^{-1}$ along the alignment direction (Figure 29d) combined with high latent heat retention of over 98 % that of PW (Figure 29e). The GA/PW composites also showed excellent mechanical and thermal stability (Figure 29f), with stable latent heat and thermal conductivity even after 200 melt-solidification cycles (Figure 29g). The above attributes combined with high photothermal conversion efficiency of graphene meant that the temperature of GA/PW composites was effectively raised by simulated sunlight to induce phase transition so that the solar energy was converted to a thermal energy and stored in PW. The high thermal conductivity also contributed to shortened charging time. Therefore, the multifunctional properties of GA/PW composites make them ideal solar-thermal conversion and storage materials with high charging and discharging rates.

In contrast, graphene walls in GFs fabricated through template-directed CVD exhibited a much higher thermal conductivity of $\sim 1600 \text{ Wm}^{-1}\text{K}^{-1}$ than rGO walls in GAs.[340] The infiltration of PCMs, such as PW and erythritol, into the GFs carbonized at 3000°C yielded composites (Figure 29h-i) with thermal conductivities up to 18 times higher than those of pure PCMs.[240] The high thermal conductivity of GF/PCM composites facilitated faster heat transfer than in the pure PCM when one end of these materials was heated (Figure 29j-l). Furthering the thermal conductivity of the GF/PCM composite was made possible through (i) reducing the pore size of GFs by incorporating other carbon nanomaterials, such as CNTs [241,409] and graphene sheets [410], into the large pore spaces, or (ii) directly growing graphene on high-density Ni foams containing sintered Ni powder with particle diameters of tens of micrometers.[411] Such high-density templates produced high-density GFs with thermal conductivities as high as $16.3 \text{ Wm}^{-1}\text{K}^{-1}$,[411] making them promising candidates as

thermal energy storage devices for thermal management in electronics and electromechanical energy storage devices.[412]

6.3.3. Energy conversion and harvesting

Efficient conversion between different energy sources, such as solar, thermal and electrical energies, plays a vital role in the development of renewable and clean energy technologies. By virtue of their multifunctional properties, 2D nanomaterials are promising contenders for efficient energy conversion. Here, we introduce a few successful examples of 2D nanofiller composites developed for energy conversion.

Photothermal and electrothermal energy conversion. Thermal energies can be converted from solar energy through a photothermal process or electrical energy through Joule heating.[405] Combining the two processes will yield more efficient thermal energy conversion, which requires materials with both a high photothermal conversion efficiency and an excellent electrical conductivity for efficient Joule heating.[156] Among various 2D nanofillers, graphene and MXene are the two groups that can satisfy such requirements because of their high electrical conductivities and high light-to-heat conversion efficiencies.[413] Furthermore, their 3D assemblies with porous structures allow the infiltration of PCMs, facilitating thermal energy storage for more efficient heating and cooling applications. A myriad of graphene [156,414–418] and $\text{Ti}_3\text{C}_2\text{T}_x$ structures [419–421] in the forms of 1D fibers, 2D films and 3D aerogels or foams have been used as nanofillers in phase changing composites for effective photothermal and electrothermal energy conversion. For example, graphene aerogel fibers made by wet spinning and supercritical drying were infiltrated with PEG and coated with fluorocarbon resin to avoid leakage when PEG was melted (Figure 30a-c).[156] The composite fiber could be heated up to 40 °C at an external voltage of 30 V when it was bent to form a loop (Figure 30d). Meanwhile, the composite fibers were woven into fabrics to generate heat through solar illumination. The fabrics

reached a temperature of about 20 °C when illuminated under the simulated sunlight of 1-Sun intensity even in the extremely cold environment simulated by liquid nitrogen (Figure 30e). These smart fibers open up vast opportunities for personal thermal management by efficiently converting sunlight and electricity to heat.

Electrical energy harvesting from heat. While the conversion from electrical energies to heat can be done easily with Joule heating, the reverse process is not trivial and is relevant to energy harvesting as a high efficiency of heat-to-electricity conversion is required. Thermal energies can be converted to electricity through either the thermoelectric [422] or pyroelectric effects [35]. A thermoelectric material designed to harvest electrical energies from temperature gradients should have a high Seebeck coefficient (S), high electrical conductivity (σ), and low thermal conductivity (κ) in order to achieve a high figure of merit, $ZT = S^2\sigma/\kappa$. [423] Conductive polymers are emerging thermoelectric materials because of their high electrical conductivities, high flexibility and excellent processability. 2D nanofillers with high electrical conductivities or high Seebeck coefficients [424], like graphene, [425–429] $\text{Ti}_3\text{C}_2\text{T}_x$, [430] MoS_2 , [431] and MoSe_2 , [432] have been added to conductive polymers such as PANI and PEDOT: PSS to achieve further improved ZTs of composites. Unlike thermoelectric generators requiring sufficient temperature gradients, pyroelectric generators are able to harvest thermal oscillations which are almost everywhere in our daily life. Piezoelectric polymers such as PVDF have an intrinsic pyroelectric effect, in which continuous temperature oscillation generates spontaneous electron polarization and thus the electricity (Figure 31a). The output current is proportional to the pyroelectric coefficient of the material and the rate of temperature change with time. As such, structural design of pyroelectric materials with high heating and cooling rates is of paramount importance. Lee *et al.* [433] developed a tri-layer composite consisting of a poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) pyroelectric material sandwiched between two electrodes

(Figure 31b). The top electrode was a thin layer of CVD-grown graphene sheet with a high thermal conductivity, enabling fast heating and cooling of the pyroelectric P(VDF-TrFE) layer as ambient temperature changes. The bottom layer was a CNT/PDMS composite, serving as a flexible and stretchable substrate. Alternating voltages were generated when the ambient temperature changed by heating and cooling (Figure 31c). The P(VDF-TrFE) layer also had a piezoelectric effect, capable of generating electrical voltages of $\pm 0.75\text{V}$ from mechanical deformations, making the sandwich structure a hybrid generator (Figure 31c).[35,433] The flexible composites were attached at various human body parts (Figure 31d), verifying their potential applications as wearable electronics and robotics capable of electrical energy harvesting.

6.4. Molecular sieving

Thanks to their cost-effective synthesis, fast permeation and precise selectivity, composite membranes containing 2D nanofillers are emerging materials for molecular sieving, which find many applications such as barrier films [143,434], water filtration [148,166], recycling of organic solvents [365] and gas separation [163,164].

6.4.1. Barrier films

Flexible barrier films impermeable to gases, moistures and chemicals find useful applications in food and electronics industries.[143,434] Amongst different 2D nanofillers, graphene is impermeable to almost all gas molecules, including the smallest helium.[435] Therefore, graphene and its derivatives are extensively employed to reduce the permeability of composite films for barrier applications.[143,354–359] The barrier properties of composite films highly depend on the filler content and alignment of graphene, as discussed in Section 5.2.5.[143,354] To achieve a high filler content with excellent alignment, the LbL assembly technique was used to deposit GO sheets and PEI molecules alternately on a transparent PET substrate. GO loadings as high as 88 to 91 wt % were achieved in the GO/PEI

composites by controlling the layer thickness while a decent transparency was maintained when ten GO/PEI bilayers were coated (Figure 32a).[358] The highly-aligned GO sheets in the PEI matrix (Figure 32b) reduced the oxygen transmission rate (OTR) of composite films with increasing number of bilayers deposited (Figure 32c). The 90-nm-thick GO/PEI film with 30 bilayer coatings reduced the OTR by 97 % against the PET substrate. Such excellent gas barrier properties combined with potentially high electrical conductivities after reduction provide ample opportunities to design a single rGO/PEI film for serving as both transparent electrode and barrier film in flexible electronics. Other 2D nanofillers such as BNNS and MoS₂ were also used for barrier films against various gases, including H₂, O₂, and H₂O.[360–362] These 2D nanofillers delivered excellent gas barrier properties along with other functionalities not attainable using graphene. For example, the addition of BNNS in PET decreased the permeabilities of O₂ while retaining the optical transparency and electrically insulating properties of PET matrix, which are important attributes for barrier applications in flexible electronics to protect the displays from O₂ and moistures.[360,361]

6.4.2. Liquid and gas separation

The membrane-based liquid nanofiltration makes use of the selective permeance of small molecules or ions through a thin membrane impermeable to large species for effective separation based on molecular sizes. The liquid nanofiltration membranes made from 2D nanofillers, such as GO and MoS₂, have shown much better performance in water purification and desalination than polymer membranes.[148,166,365,434] Taking the most common GO nanofiltration membrane for example, the interlayer spacing between the adjacent GO sheets was ~ 0.9 nm,[311] which allowed frictionless transport of water molecules through the unfunctionalized regions but rejected unwanted solute ions/molecules by size exclusion, enabling excellent water permeability and ion/molecule selectivity for water desalination and purification.[436] However, these GO nanofiltration membranes suffer from swelling in

aqueous solutions with expanded interlayer spacing, reducing the rejection rate of solutes with deteriorated long-term stability.[437] Therefore, the composite membranes made by LbL assembly of GO and polymer layers were found more suitable for water purification especially under cross-flow conditions albeit the inevitable expansion of interlayer spacing were inefficient to reject monovalent ions (such as Na^+) for desalination.[438]

Gas separation is another important application of 2D nanofillers/polymer composite membranes to achieve selective mass transport for energy and environmental sustainability. For example, separating CO_2 from the biogas (60 to 70 vol % CH_4 and 30 to 40 vol % CO_2 mixture) is an essential step aimed to increase the heating values and thus energy efficiencies of biogas as a fuel source. Polymer membranes are good candidates for gas separation because of their low cost and high energy efficiency but their usefulness is limited by the trade-off between permeability and selectivity.[439] Nanofillers of different dimensions are therefore added to polymers to mitigate the trade-off by tailoring the mass transport properties of composite membranes.[440,441] A myriad of 2D nanofillers, including GO,[367–370] MoS_2 , [442,443] and $\text{Ti}_3\text{C}_2\text{T}_x$ [163,164], are of particular interests because of their high aspect ratios and excellent barrier properties.[350,352] 2D MOF nanosheets are emerging nanofillers for gas separation membranes with high permeabilities and selectivities [41,374]. The high aspect ratios similar to other 2D nanofillers combined with well-defined pore sizes and structures make 2D MOFs excellent candidates for precise gas separation.[377] The direct transport of small CO_2 molecules through the intrinsic pores of 2D MOF nanosheets and the tortuous diffusing paths of large CH_4 molecules through interlayer channels gave rise to simultaneously high permeability of CO_2 and high CO_2/CH_4 selectivity, as shown in Figure 32d.[444] Therefore, 2D MOF/polymer membranes have shown better gas separation performance than those with other 2D nanofillers even at lower MOF loadings because of the unique size exclusion mechanism facilitated by the well-defined pore sizes.

For example, 2D copper 1,4-benzenedicarboxylate nanosheets (ns-CuBDC) with a thickness of ~25 nm and lateral dimension of ~4 μm were synthesized using a bottom-up approach (Figure 32e).[375] The 2D ns-CuBDC were incorporated to a PI matrix to form a composite film after casting. The well dispersed 2D ns-CuBDC in the PI matrix occupied much larger volumes than the bulk CuBDC (b-CuBDC) crystals (Figure 32f and g), obtaining a higher CO_2/CH_4 selectivity than its b-CuBDC/PI counterpart (Figure 32h). Other types of 2D MOFs with diverse intrinsic pore sizes were also synthesized by either a bottom-up approach or top-down exfoliation as effective nanofillers in CO_2/CH_4 or H_2/CO_2 gas separation membranes.[445–447] The excellent gas separation performance of the 2D MOF/polymer composite membranes together with high porosities and large specific areas of MOFs also warrants their applications for selective gas sensing.[448]

7. Conclusion and perspectives

The booming 2D material family represented by graphene since the last decade brings about ample opportunities to create transformative composites with combined mechanical robustness and multifunctionalities. Despite myriad efforts in developing 2D nanofiller/polymer composites with various filler-matrix combinations, the long-standing question of how the excellent properties can be translated into their composites is still a major concern for practical applications of these composites. Recent advances in novel manufacturing techniques highlighted in this review open a new insight into rational assembly of 2D nanosheets and their composites across different length scales encompassing 2D material synthesis, interfacial design and 3D structure assembly. Such a holistic multiscale strategy enables controllable dispersion, interconnection, alignment and filler content of 2D nanosheets in a polymer matrix, which in turn lead to achieving targeted microstructures and desired properties of composites. The ultimate goals are twofold: namely, not only to fully translate the excellent properties of 2D nanosheets in their composite

structures, but also to transform the conventional composites into multifunctional ones which are not possible due to the mutually exclusive nature of some properties in a conventional sense. This requires a thorough understanding of the relationship between processing techniques, multiscale structures and the properties of composites.

In this review, we have identified several critical parameters determining the overall performance of composites across different length scales which can be controlled by different rational assembly techniques. At the nanoscale, the inherent properties of 2D nanosheets are determined by their anisotropic structures, defects and functionalization, as well as number of layers, which in turn are influenced by their synthesis techniques, including liquid phase exfoliation of bulk crystals and CVD growth on metal templates. At the microscale, different rational assembly techniques result in excellent dispersion and seamless interconnection of 2D nanofillers to form highly porous cellular structures, giving rise to tailored interfacial properties and percolative characteristics. At the macroscale, the alignment and filler content play crucial roles in determining the bulk properties of composites. The convergence of these multiscale parameters not only enables the translation of excellent properties of 2D nanosheets to composites but also synergistically creates multifunctional characteristics, especially those mutually exclusive in nature, without degrading important mechanical properties. Such multifunctionalities lead to novel applications in many emerging fields, including flexible electronics, energy storage, conversion and harvesting.

Despite considerable progress in exploring various 2D nanosheets for fabrication of composites with intriguing properties and multifunctionalities, many challenges remain to be addressed and possible solutions are proposed as follows.

- (i) The state-of-the-art mechanical properties of graphene composites are still far from on a par with conventional fiber reinforced composites. [As discussed in Section 5.1 and Figure 18, the strength of GF/epoxy composite was 130 MPa,](#)

which is much lower than the values of glass fiber or carbon fiber reinforced epoxy composites. A major issue is the meaningful filler contents that can be achieved in graphene composites are much lower than those found in fiber-reinforced composites. High-density 3D structures made by template-directed CVD (Section 4.3.2) [30] or 1D fibers prepared by wet spinning (Section 4.2.1) [341], similar to conventional carbon fiber reinforcements, can be promising routes to increase the graphene content in the composite. Instead of using 2D materials alone to reinforce the polymer matrix, another promising route is to use 3D structures as interleaves to strengthen the conventional fiber-reinforced laminate composites with much enhanced interlaminar fracture resistance. For example, GFs made by template-directed CVD as discussed in Section 4.3.2 were used as interleaves to significantly improve the interlaminar fracture energies and shear strengths thanks to the toughening by crack deflection and interfacial crack formation. [449]

- (ii) Apart from structural reinforcements, the major advantage of 2D nanofiller/polymer composites lies in their intriguing multifunctional properties. For many functional applications such as thermal interface materials discussed in Section 6.2.3, the limit is the properties at the 2D nanofiller/polymer interfaces which are much inferior to the intrinsic properties of 2D nanosheets. Proper functionalization of 2D nanosheets is therefore necessary to improve the interfacial adhesion with polymer resins without diminishing their intrinsic properties. Functionalization is particularly pertinent to rational assembly strategies using 2D nanofillers made by intercalation assisted exfoliation (Section 2.1.3) and CVD techniques (Sections 2.2 and 4.3.2) as these techniques usually yield pristine 2D nanofillers without functional groups. While both chemical and physical

functionalization have been developed for various 2D nanofillers, the challenge of achieving strong interfacial adhesion with matrices without affecting the intrinsic properties of 2D nanofillers still remains. While covalent functionalization can improve the interfacial coupling between otherwise hydrophobic 2D nanosheets and hydrophilic polymer resins, it inevitably deteriorates the inherent characteristics of 2D nanosheets through defect creation. Non-covalent functionalization through hydrogen bonds, π - π interactions and electrostatic interactions can be an alternative choice as they do not alter chemical structures of 2D nanosheets.[6,345,450] Novel strategies using non-covalent functionalization to further improve the interfacial adhesion between 2D nanofillers and polymer matrices may alleviate the trade-off between interfacial bonds and intrinsic properties of 2D nanofillers.

- (iii) A more rigorous understanding of the structure-property relationships especially at the nano- and microscales is required to allow better rational design of 2D nanosheet assembly techniques. As shown in Section 5, the mechanical and functional properties of composites still fall below the expectations from the excellent intrinsic properties of 2D nanofillers mainly because of existence of large interfacial volumes in the composites. Therefore, understanding the role of interfacial structures and properties toward bulk properties of composites is vital to achieve optimal design of composite structures. In view of the atomic- or nanoscale dimensions of interfaces, there are significant challenges to experimentally quantifying the interfacial properties, such as interfacial chemistry, interfacial adhesion mechanism, bond strength, electron tunneling mechanism and interfacial thermal resistance. Therefore, it is necessary to develop reliable micro- and nanoscopic characterization techniques to directly probe the interfacial

properties. The combination of *in-situ* testing approaches and multiscale computational methods may also provide a clearer insight into the correlation between the interfacial properties and bulk properties of composites.

- (iv) For multifunctional applications, the prevailing challenge is to achieve a combination of properties that are often contradictory to each other in the same composite, *e.g.*, high dielectric constant and low dielectric loss for capacitive energy storage applications (Section 6.3.1). This may require both more dedicated design of microstructures and selection of hybrid 2D fillers with distinctive functionalities and spatial arrangements to achieve heterogeneous structures at different length scales. For example, the rational arrangements of graphene and BNNS into alternately aligned layers have been demonstrated using the ice templating approach, as discussed in Section 4.3.1. The resulting sandwich composites possess simultaneously high dielectric constants, low dielectric losses and high thermal conductivities suitable for capacitive energy storage applications.[451] In addition to hybrid 2D nanofillers, holistic approaches involving multiple rational assembly strategies need to be developed, as presented in Section 4. A few recent successful attempts of combining ice templating with external force assisted assembly techniques, such as wet spinning [452] and tape casting [453], may shed light on novel structures that can be achieved for multifunctional applications using a combination of different approaches.

Addressing the abovementioned challenges will add competitive advantages of 2D nanosheets as composite fillers, enabling 2D nanofiller/polymer composites serious contenders for emerging multifunctional applications.

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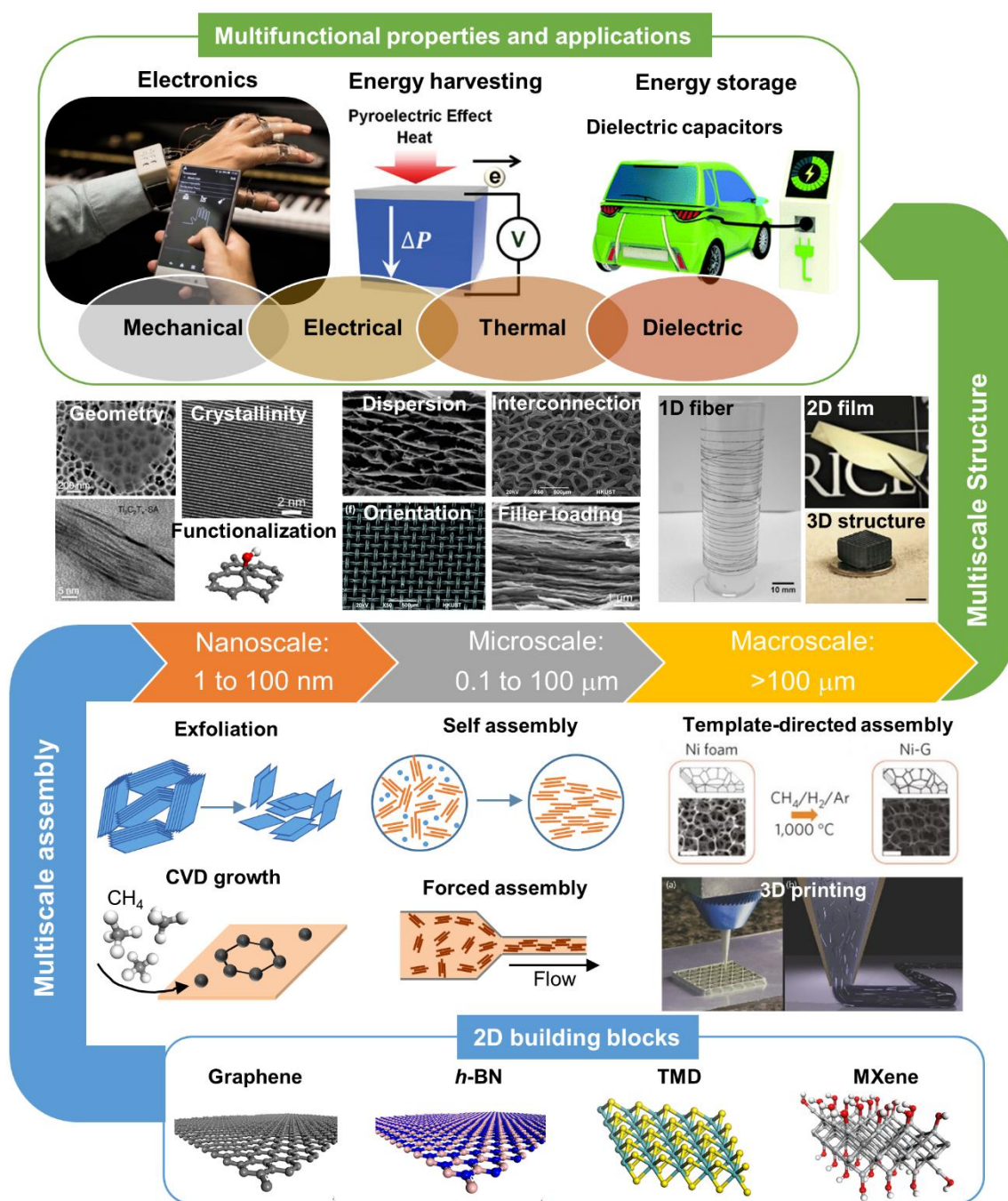


Figure 1. Relationships between multiscale assembly strategies, structural characteristics, properties and applications. 2D nanofillers are synthesized and assembled into 3D bulk composites by multiscale processing techniques, including exfoliation, chemical vapor deposition (CVD) growth, self-assembly, forced assembly, template-directed assembly and 3D printing. Different processing techniques lead to controllable structural features at different length scales, ultimately determining the multifunctional properties and applications

of composites. Schematics of template-directed assembly reproduced with permission from ref. [25]. Copyright 2011 Springer Nature. Schematics of 3D printing reproduced from ref. [26] with permission. Copyright 2014 Wiley-VCH. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) for geometry and filler loading reproduced with permission from ref. [27]. Copyright 2016 AAAS. TEM image for crystallinity reproduced with permission from ref. [28]. Copyright 2019 Wiley-VCH. SEM image for dispersion reproduced with permission from ref. [29] Copyright 2015 American Chemical Society. SEM image for interconnection reproduced with permission from ref. [30]. Copyright 2018 The Royal Society of Chemistry. SEM image for orientation reproduced with permission ref. [31]. Copyright 2017 The Royal Society of Chemistry. Photograph of 1D fiber reproduced with permission from ref. [32]. Copyright 2017 Wiley-VCH. Photograph of 2D film reproduced with permission from ref. [33]. Copyright 2019 Wiley-VCH. Photograph of 3D structure reproduced from ref. [34] under a Creative Commons CC BY license. Photograph of electronics reproduced with permission from ref. [31]. Copyright 2017 The Royal Society of Chemistry. Schematic of energy harvesting reproduced with permission from ref. [35]. Copyright 2019 Wiley-VCH. Schematic of energy storage reproduced with permission from ref. [36]. Copyright 2019 The Royal Society of Chemistry.

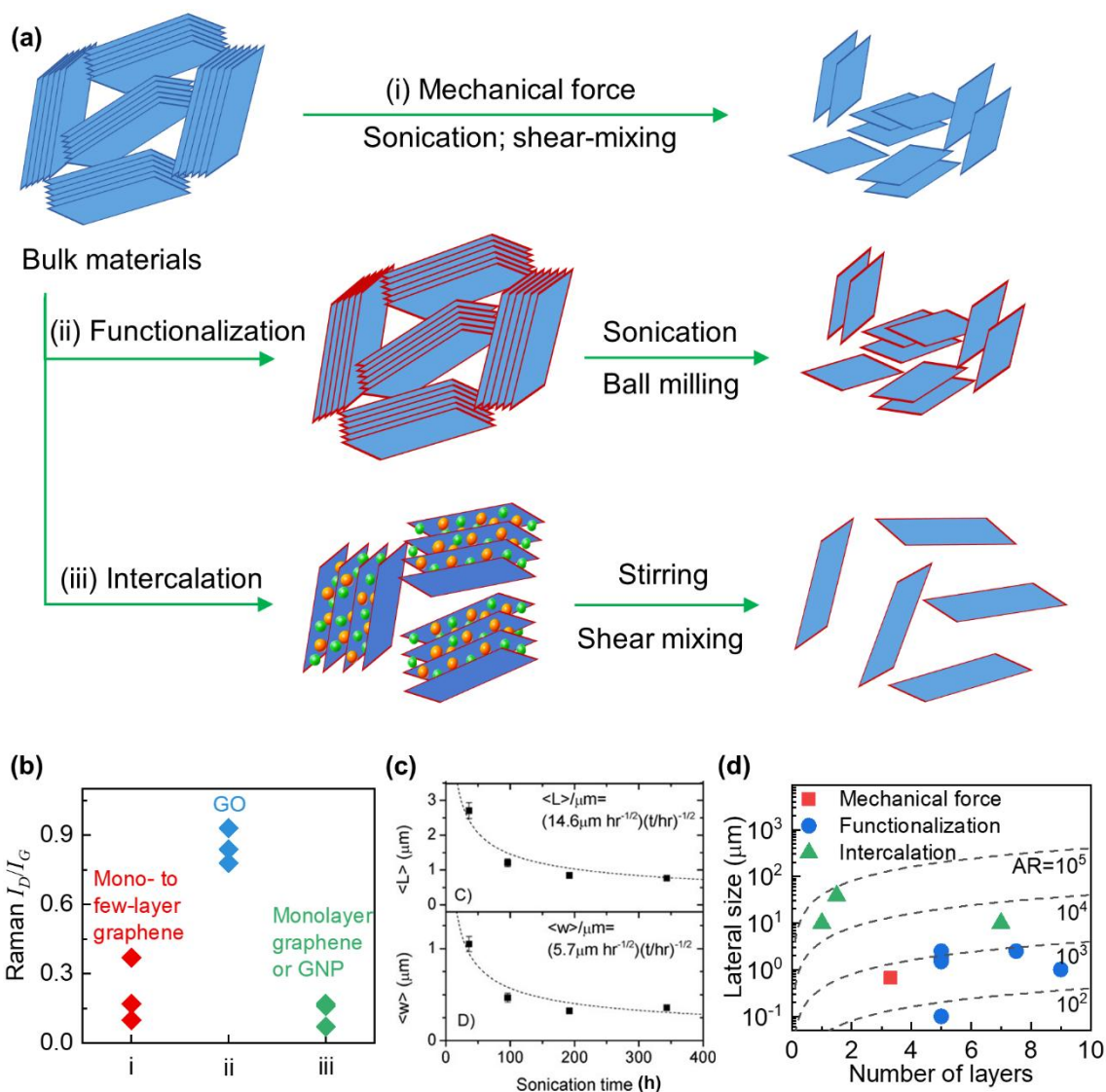


Figure 2. Solvent-based exfoliation techniques and their effects on the qualities of 2D fillers. (a) Schematics showing three types of solvent-based exfoliation techniques; (b) Raman D- to G-band intensity ratios of graphene, GO or GNP obtained using these techniques (i. assisted by mechanical force [37,38]; ii. functionalization-assisted [43,71,72]; and iii. intercalation-assisted [51–53]); (c) dependence of lateral dimensions of graphene sheets on sonication time. Reproduced with permission from ref. [65]. Copyright 2010 Wiley-VCH; and (d) effects of different exfoliation techniques on lateral dimensions, number of layers and aspect ratios of the resulting BNNSs (green triangles: refs. [51,52,56]; blue circles: refs. [44–49]; red squares: ref. [39]).

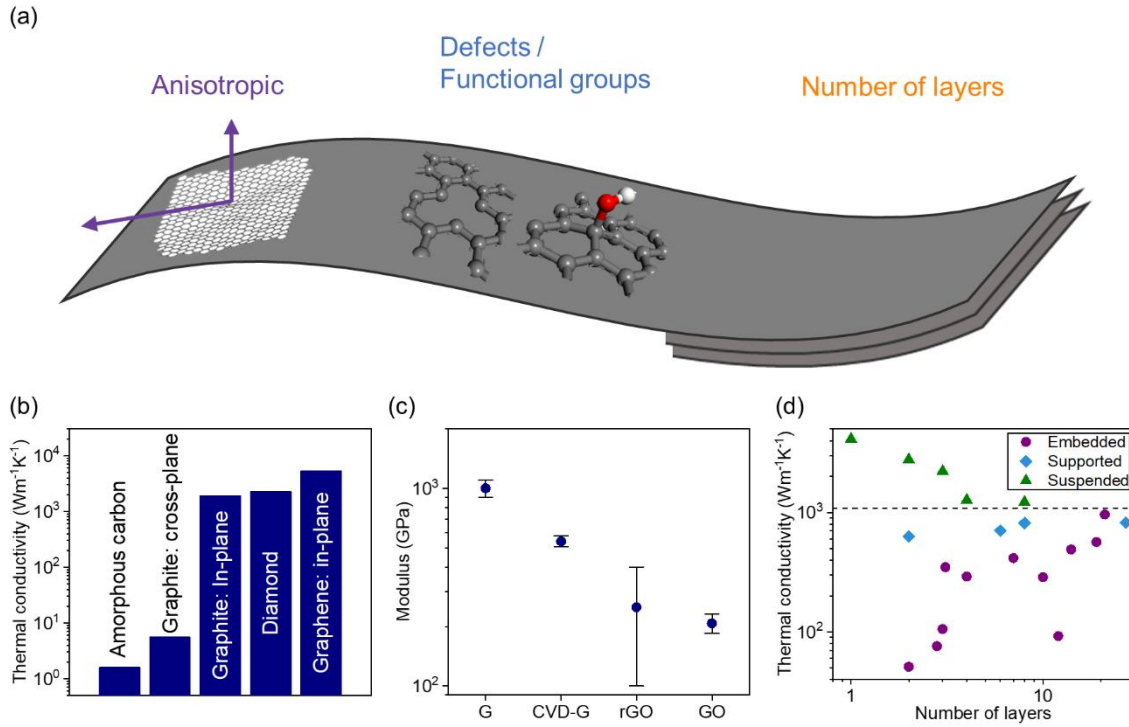


Figure 3. Extrinsic factors affecting the properties of 2D nanofillers. (a) Schematic showing important factors, including anisotropic structure, defects/functional groups and number of layers; (b) anisotropic thermal conductivities of graphene showing a few orders of magnitude difference between the in-plane and cross-plane values. Data obtained from refs. [94,113]; (c) effects of defects and functional groups on elastic moduli of different types of graphene: G (single-crystalline graphene) [86], CVD-G (CVD-grown graphene) [98], rGO [103] and GO [100]; and (d) effect of number of layers on thermal conductivities of suspended and supported graphene sheets (purple circles: graphene sheets embedded in SiO₂ layers;[124] blue diamonds: graphene sheets supported on SiO₂ substrate;[123] green triangles: suspended graphene sheets;[119] dashed line: natural graphite).

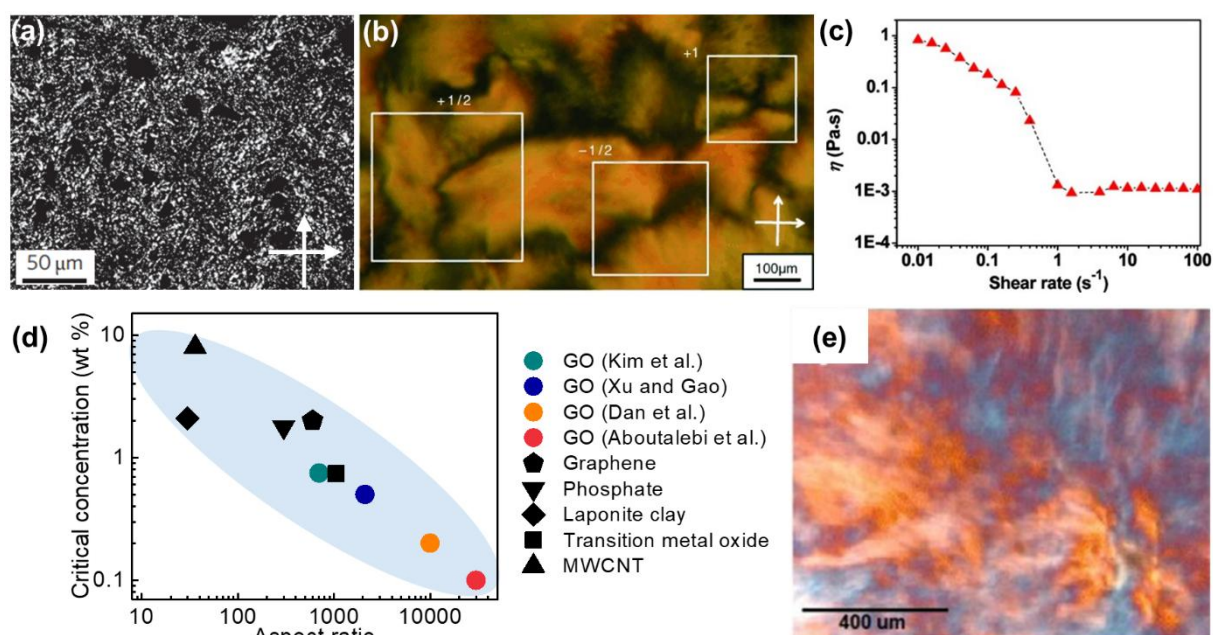


Figure 4. LCs of graphene and GO. (a) POM image of graphene in chlorosulfuric acid at a concentration of 20 mg mL⁻¹ showing LCs as indicated by the schlieren textures. Reproduced with permission from ref. [128]. Copyright 2010 Springer Nature; (b) POM image of GO in water showing nematic LCs. Reproduced with permission from ref. [68]. Copyright 2011 Wiley-VCH; (c) viscosity of GO solution as a function of shear rate. Reproduced with permission from ref. [69]. Copyright 2011 American Chemical Society; (d) critical concentrations for LC phase formation of 1D and 2D materials, including GO,[55,68,69,131] graphene,[128] phosphate,[133] clay,[125] transition metal oxide [134] and MWCNT [132], as a function of their aspect ratios; and (e) POM image of GO LCs in a water-borne epoxy. Reproduced with permission from ref. [83]. Copyright 2013 Elsevier.

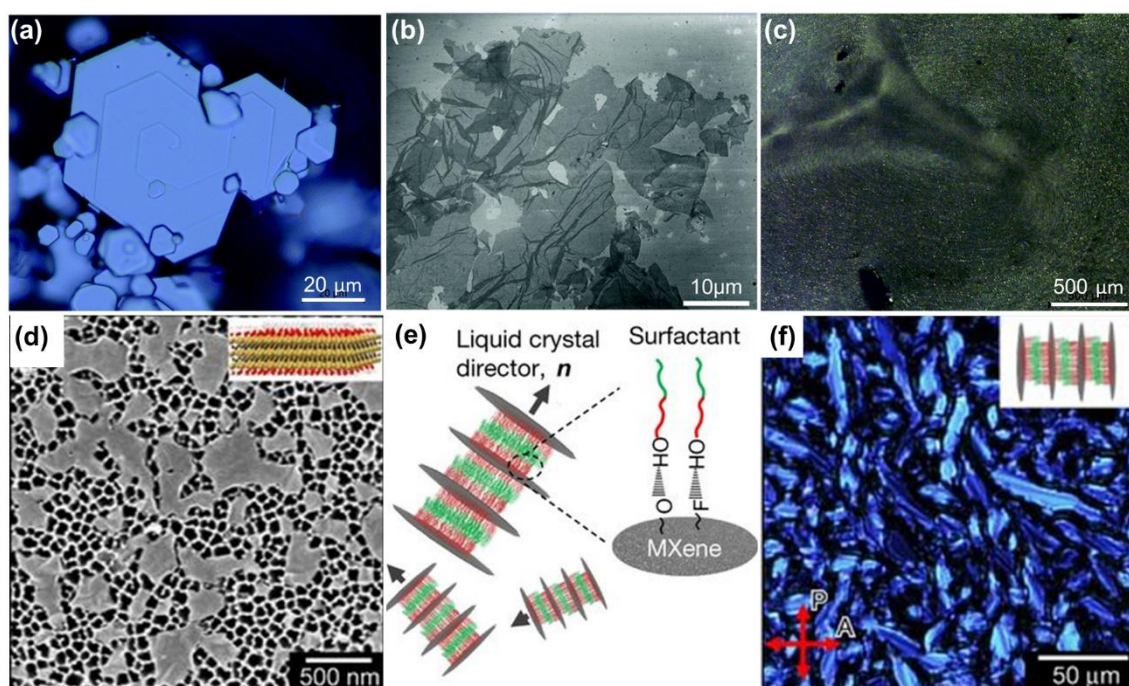


Figure 5. LCs of 2D nanosheets including (a-c) MoS_2 [141] and (d-f) $\text{Ti}_3\text{C}_2\text{T}_x$ [142] nanosheets. (a) Large MoS_2 bulk crystals as precursors for exfoliation of large-size MoS_2 nanosheets; (b) SEM image of exfoliated MoS_2 nanosheets with large lateral dimensions; (c) POM image of MoS_2 dispersion showing schlieren textures of nematic phase; (d) SEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets; (e) schematic of the LC formation facilitated by surfactant; and (f) POM image of $\text{Ti}_3\text{C}_2\text{T}_x$ dispersion aided by surfactant C_{12}E_6 showing fan-like textures of lamellar phase. (a-c) Reproduced with permission from ref. [141]. Copyright 2016 The Royal Society of Chemistry. (d-f) Reproduced with permission from ref. [142]. Copyright 2018 Springer Nature.

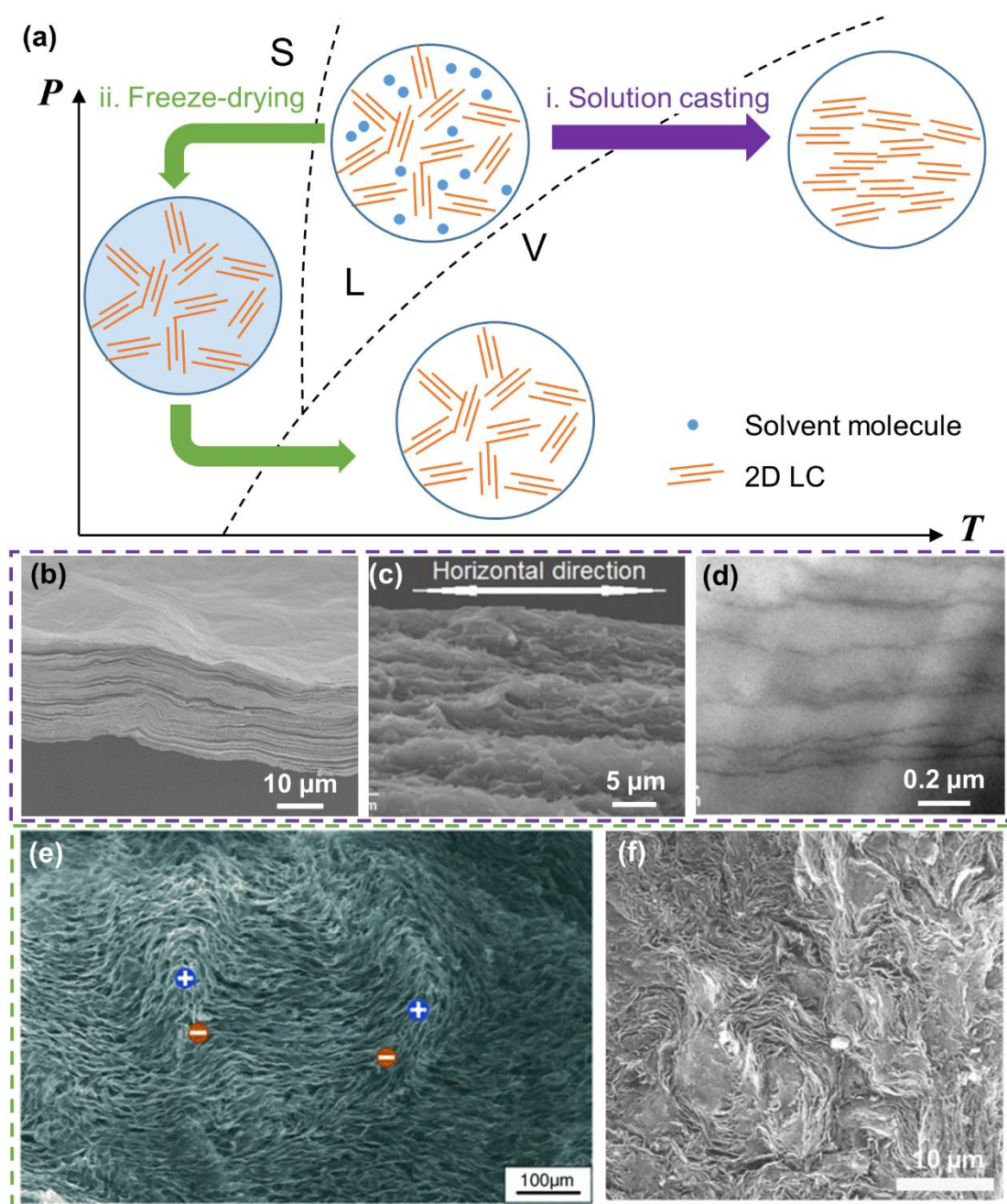


Figure 6. LC phase assisted self-assembly. (a) Pressure (P)-temperature (T) relationship with regard to two solvent removal processes for self-assembly of 2D LCs; (b) SEM image of self-aligned GO film. Reproduced with permission from ref. [55]. Copyright 2011 Wiley-VCH; (c) SEM and (d) TEM images of self-aligned GO sheets in an epoxy matrix. Reproduced with permission from ref. [83]. Copyright 2013 Elsevier; (e) SEM image of freeze-dried GO sheets with microstructure replicating textures of GO LCs (+ and – signs indicate $\pm 1/2$ disclinations in GO LCs). Reproduced with permission from ref. [68]. Copyright 2011 Wiley-

VCH; and (f) SEM image of freeze-dried $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets with more random orientations and smaller pore sizes than in GO counterparts. Reproduced with permission from ref. [142].
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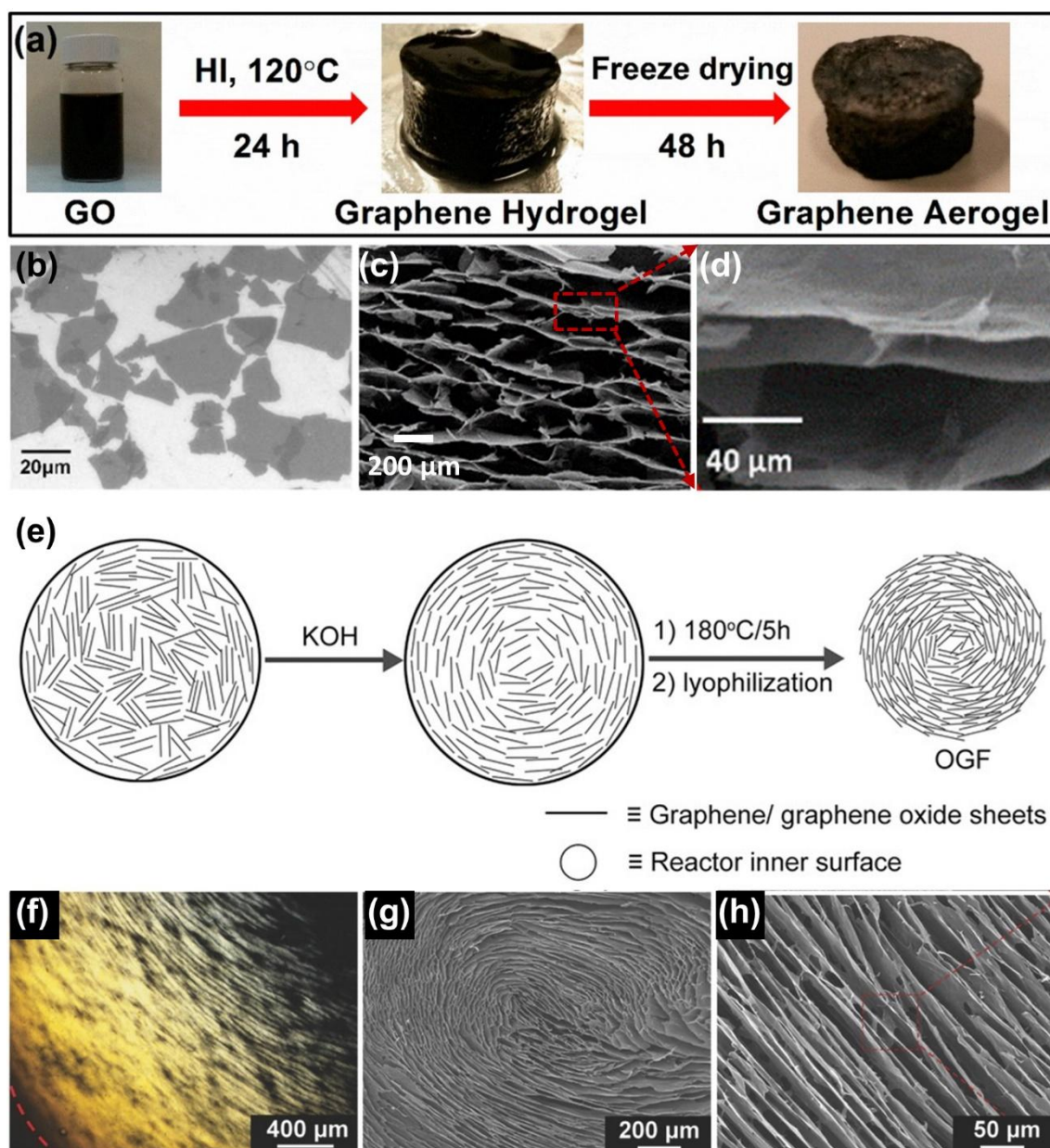


Figure 7. Sol-gel freeze-drying and morphology controls to achieve long-range orders by (a-d) using ULGO sheets[29] and (e-h) tuning the pH value[145]. (a) Fabrication of GA by sol-gel freeze-drying; SEM images of (b) ULGO sheets and (c-d) GAs; (e) fabrication of ordered GA by tuning the pH value; (f) POM of GO solution containing KOH in the vicinity of the inner surface of glass tube; and SEM images of ordered GA taken (g) from the inner core and

(h) close to the periphery. (a-d) Reproduced with permission from ref. [29]. Copyright 2015 American Chemical Society. (e-h) Reproduced with permission from ref. [145]. Copyright 2015 Wiley-VCH.

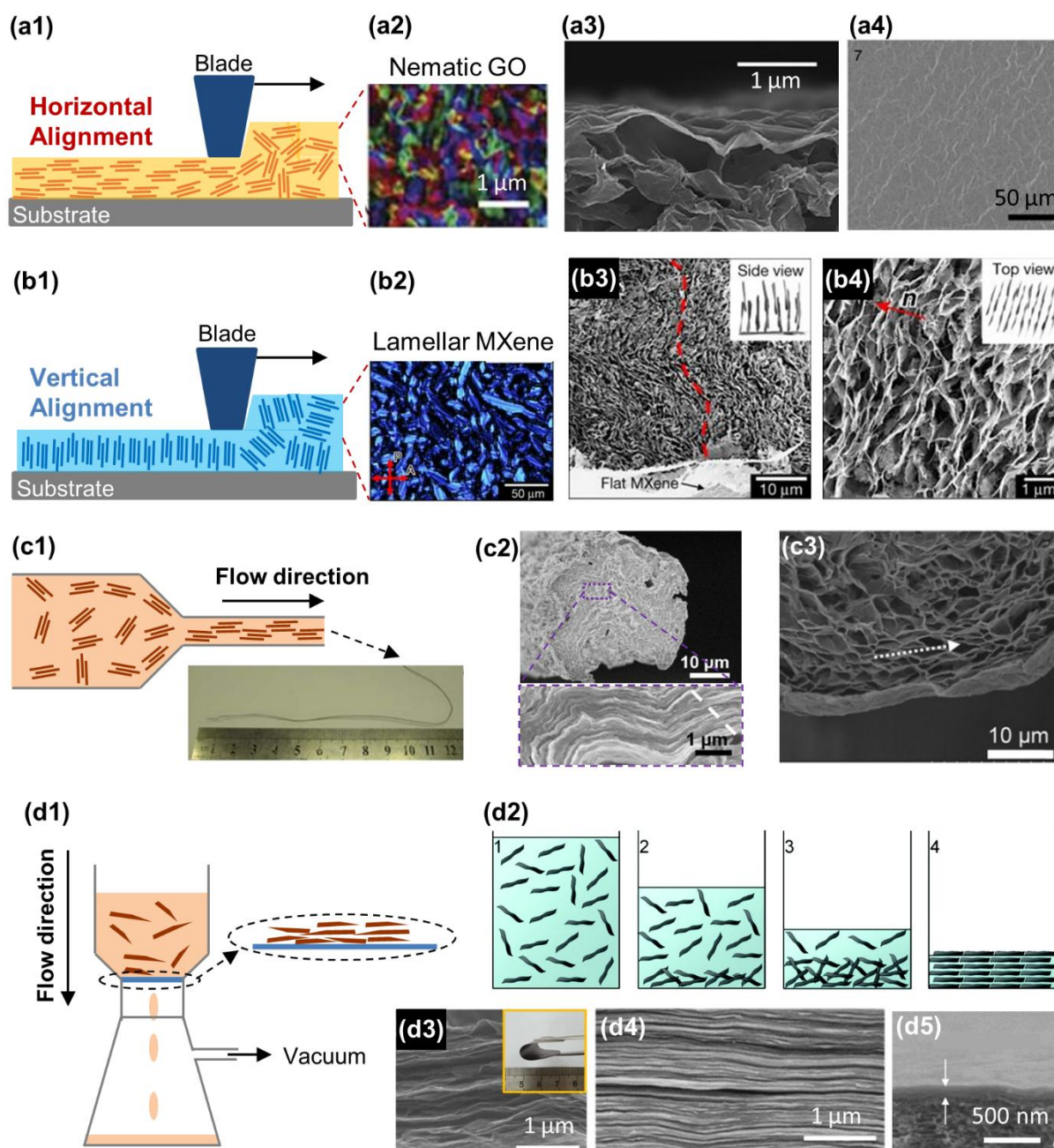


Figure 8. Mechanical force assisted assemblies with (a-b) shear fields and (c-d) flow fields. (a1) Schematic of tape casting of GO LCs; (a2) POM image of nematic LCs of GO;[148] (a3) cross-sectional and (a4) surface SEM images of horizontally aligned GO film.[148] (a2-a4)

Reproduced from ref. [148] under a Creative Commons CC BY license; (b1) schematic of tape casting of $\text{Ti}_3\text{C}_2\text{T}_x$ LCs; (b2) POM image of lamellar LCs of $\text{Ti}_3\text{C}_2\text{T}_x$ in the presence of surfactant;[142] (b3) side and (b4) top SEM images of vertically aligned $\text{Ti}_3\text{C}_2\text{T}_x$ film.[142] (b2-b4) Reproduced with permission from ref. [142]. Copyright 2018 Springer Nature; (c1) schematic of wet spinning with a photograph showing the wet-spun GO fiber;[155] [cross-sectional SEM images of wet-spun GO fibers dried by \(c2\) solvent evaporation \[140\] and \(c3\) freeze-drying \[155\]](#). (c1 and c3) Reproduced with permission from ref. [155]. Copyright 2012 American Chemical Society. (c2) Reproduced with permission from ref. [\[140\]](#). Copyright 2013 American Chemical Society; (d1) schematic of VAF; (d2) schematic of the assembly process of 2D nanosheets by VAF. Reproduced with permission from ref. [174]. Copyright 2011 American Chemical Society; (d3) cross-sectional SEM image of GO film made by VAF. Reproduced from ref. [164] under a Creative Commons CC BY license; (d4) SEM image showing highly-aligned GO paper made from ULGO sheets. Reproduced with permission from ref. [70]. Copyright 2012 American Chemical Society; [\(d5\) cross-sectional SEM image of ultrathin GO film supported on a porous substrate. Adapted with permission from ref. \[169\] under a Creative Commons CC BY license.](#)

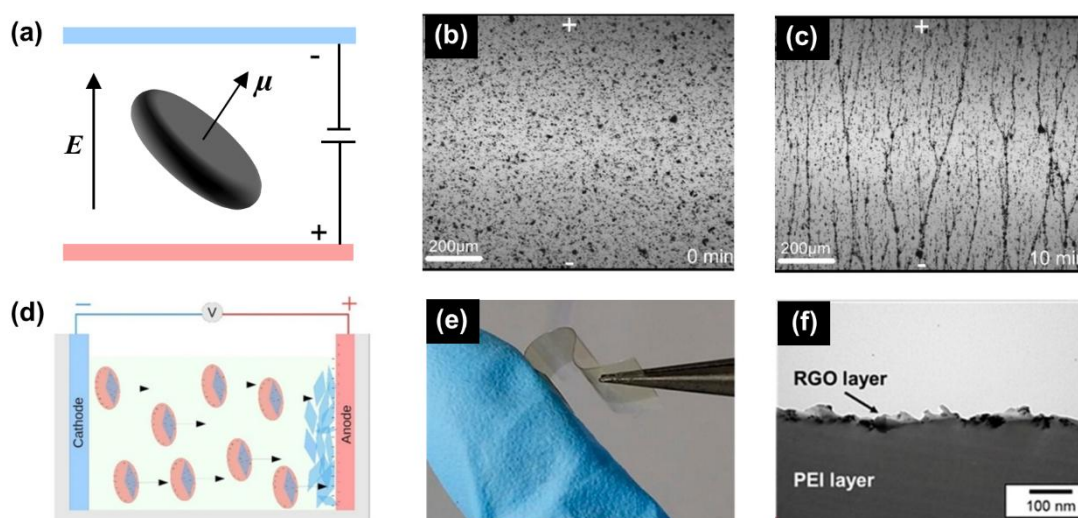


Figure 9. Electric field assisted assembly. (a) Schematic of the alignment of 2D fillers arising from the rotational torque induced by the dipole moment (μ) which is not aligned with the electric field (E); microscopy images showing the distribution of GNPs (b) before and (c) after applying the electric field. Reproduced from ref. [181] under a Creative Commons CC BY license; (d) schematic of EPD of 2D fillers under an electric field. Reproduced from ref. [188] under a Creative Commons CC BY-NC-ND license; and (e) photograph and (h) SEM image of rGO deposited on a flexible PET substrate using EPD. Reproduced with permission from ref. [196]. Copyright 2014 American Chemical Society.

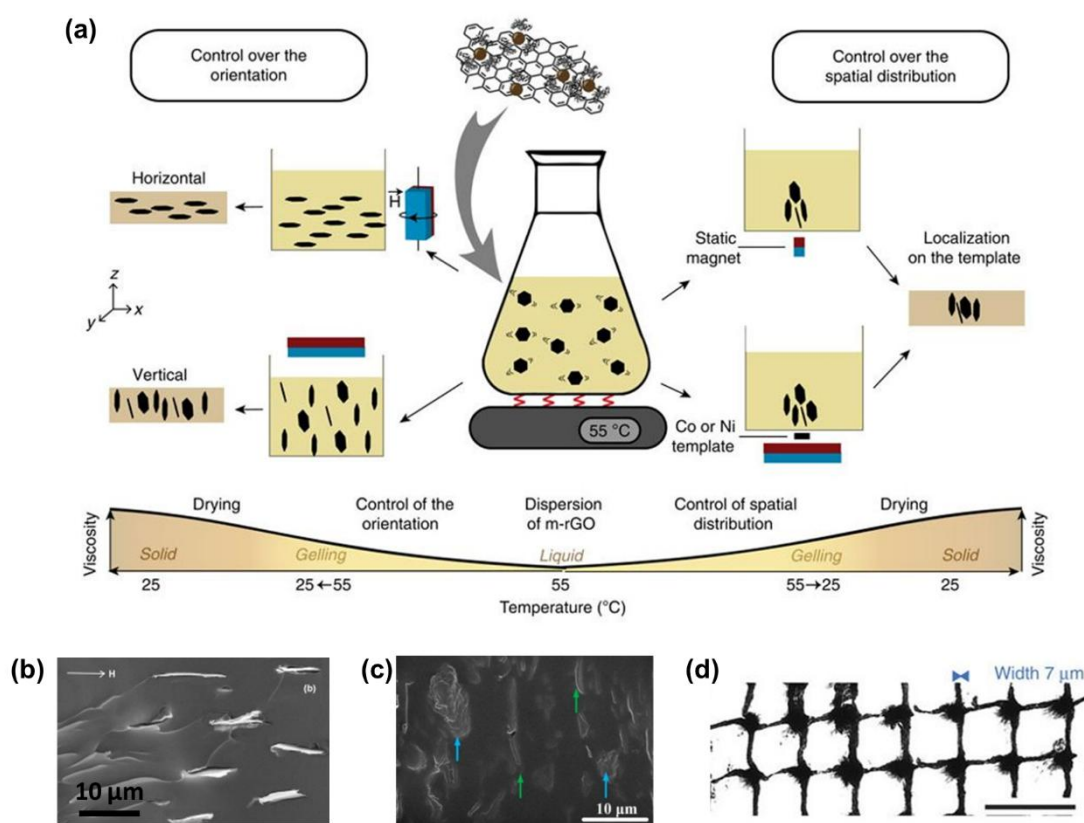


Figure 10. Magnetic field assisted assembly. (a) Schematic of magnetic field induced alignment and magnetic field modulated spatial orientation. Reproduced from ref. [199] under a Creative Commons CC BY license; (b) SEM image of in-plane oriented GNPs in epoxy matrix induced by the horizontal magnetic field. Reproduced with permission from ref. [201]. Copyright 2014 Elsevier; (c) SEM image of vertically aligned h-BN platelets in

silicone matrix as a result of vertical magnetic field. Reproduced with permission from ref. [205]. Copyright 2015 American Chemical Society; and (d) optical image of rGO assembled into a mesh pattern induced by localized magnetic fields (Scale bar: 100 μm). Reproduced from ref. [199] under a Creative Commons CC BY license.

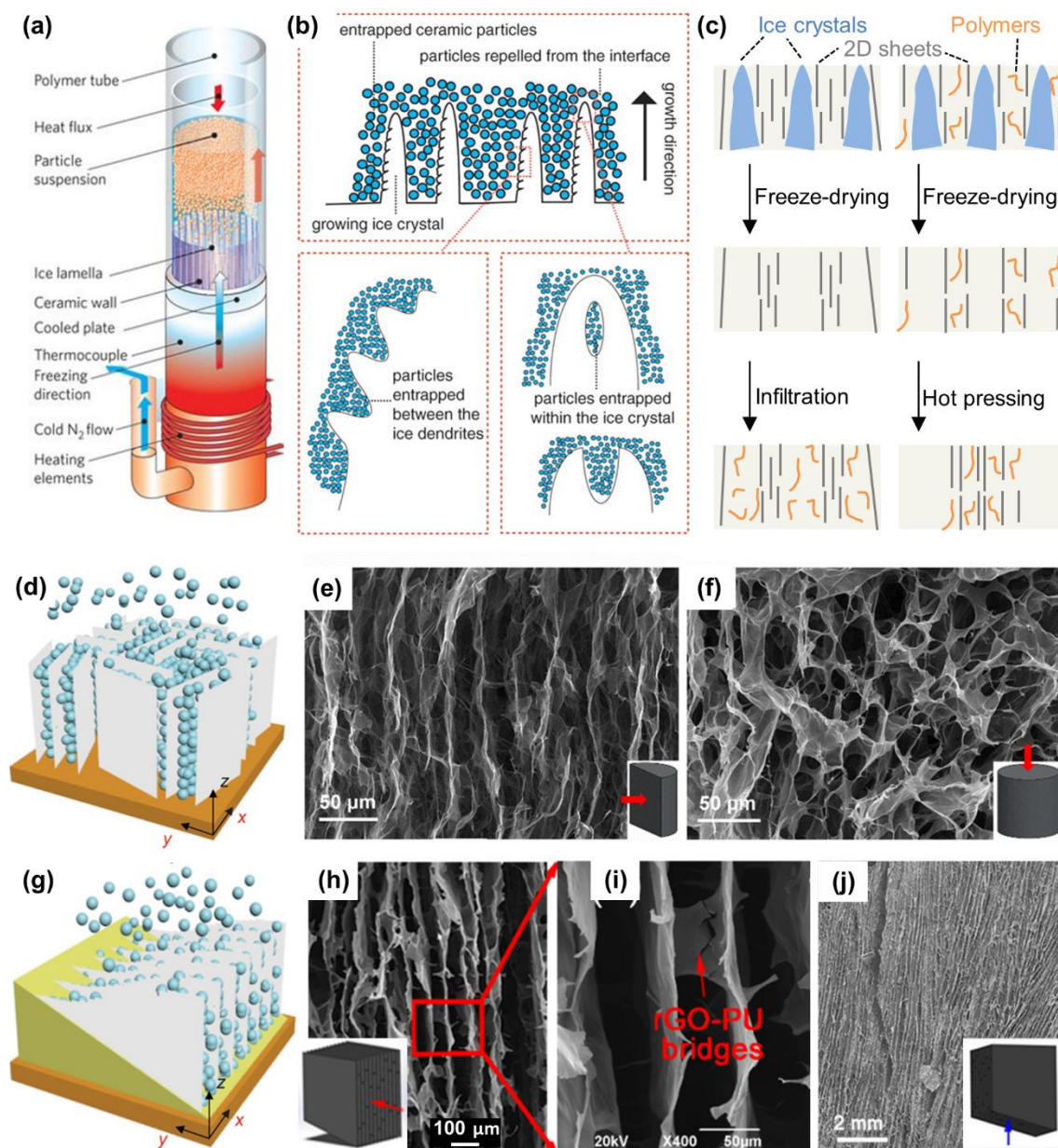


Figure 11. Dynamic ice templating. (a) Schematic of the setup for UFC of colloidal suspensions of 2D materials. Reproduced with permission from ref. [224]. Copyright 2014 Springer Nature; (b) schematics of the mechanisms for UFC. Reproduced with permission from ref. [206]. Copyright 2006 AAAS; (c) schematics of two routes for the fabrication of 2D

nanosheet/polymer composites through UFC; (d) schematic of the freezing process in UFC. Reproduced from ref. [218] under a Creative Commons CC BY-NC 4.0 license; SEM images of a GA made by UFC viewed from (e) the side and (f) the top. Reproduced with permission from ref. [210]. Copyright 2016 American Chemical Society; (g) schematic of the freezing process in BFC with a PDMS wedge on top of the cold surface. Reproduced from ref. [218] under a Creative Commons CC BY-NC 4.0 license; and SEM images of a rGO/PU composite aerogel made by BFC viewed from (h) the side (enlarged view in (i)) and (j) the top. Reproduced with permission from ref. [219]. Copyright 2018 American Chemical Society.

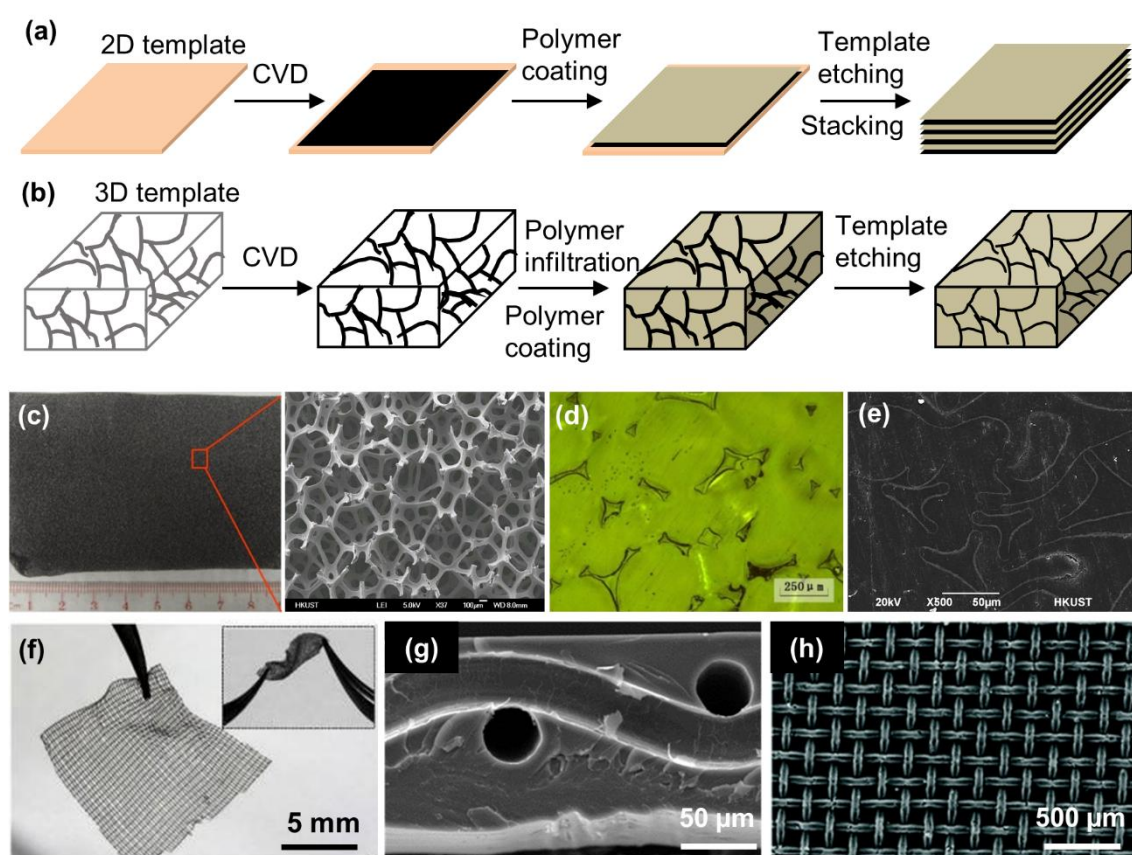


Figure 12. Template-directed CVD using (a) 2D templates and (b-h) 3D templates. (a) Schematic of the fabrication of laminate composite using 2D templates; (b) schematic of the fabrication of composite using 3D template; (c) photograph and SEM image of freestanding GF; (d) optical image of a porous GF/epoxy composite. (c-d) Reproduced with permission from ref. [233]. Copyright 2014, American Chemical Society; (e) SEM image of a solid

GF/epoxy composite. Reproduced with permission from ref. [30]. Copyright 2018 The Royal Society of Chemistry; (f) photograph of a flexible GWF. Reproduced from ref. [246] under a Creative Commons CC BY-NC-SA 3.0 license; (g) SEM image of porous GWF/epoxy composite. Reproduced with permission from ref. [247]. Copyright 2015 American Chemical Society; and (h) SEM image of GWF deposited on top of PDMS. Reproduced with permission from ref. [31]. Copyright 2017 The Royal Society of Chemistry.

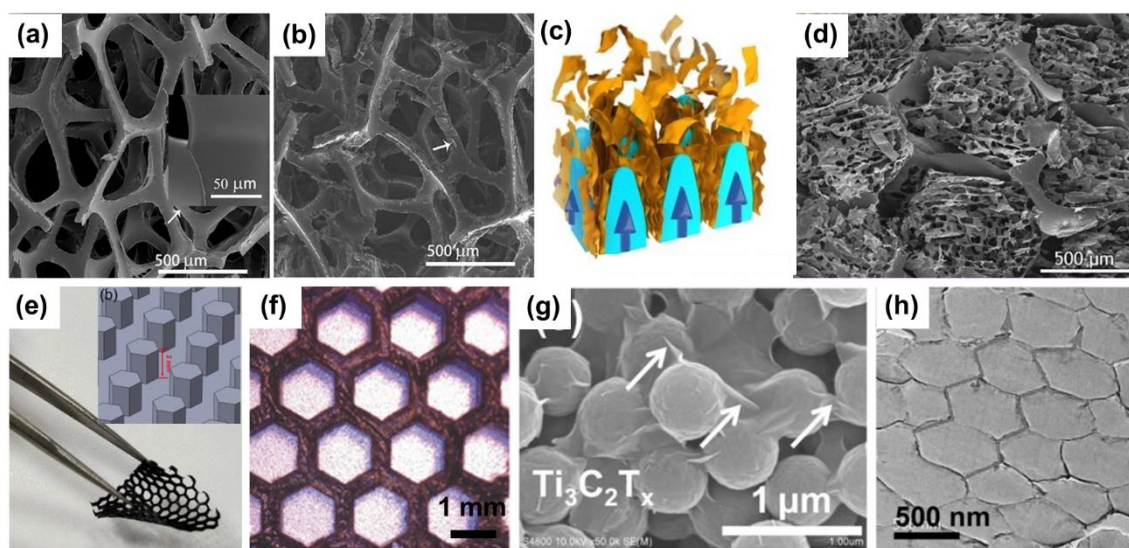


Figure 13. Polymer templating. SEM images of PU foam (a) before and (b) after dip-coating with GO sheets; Reproduced with permission from ref. [253]. Copyright 2013 Wiley-VCH; (c) schematic freeze-casting of GO in the PU foam network; (d) SEM image of hierarchical porous structure formed by GO aerogel in the PU foam skeleton. (c-d) Reproduced with permission from ref. [255] Copyright 2018 American Chemical Society; (e) photograph of GHC structure fabricated by freeze-casting in 3D printed ABS template (inset); (f) optical image of GHC. (e-f) Reproduced with permission from ref. [259]. Copyright 2018 Wiley-VCH; (g) SEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets assembled onto PS spheres driven by electrostatic interactions; and (h) TEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ /PS composite after hot pressing with interconnected $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (g-h) Reproduced with permission from ref. [261]. Copyright 2017 Wiley-VCH.

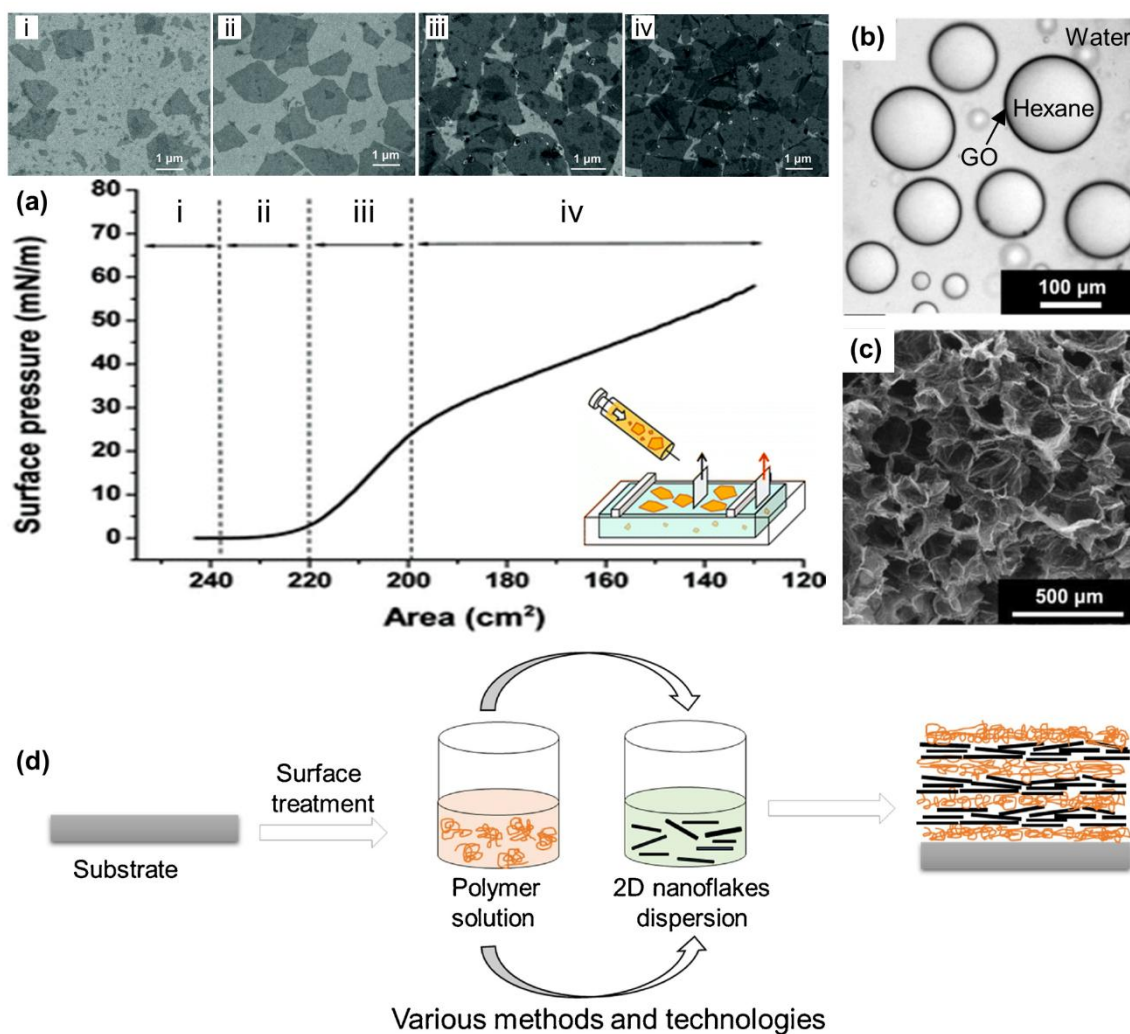


Figure 14. Interfacial templating at (a) the liquid-air, (b-c) liquid-liquid interfaces and (d) liquid-solid interfaces. (a) Surface pressures at different stages of compression and corresponding morphologies of GO sheets. Reproduced with permission from ref. [267]. Copyright 2011, American Chemical Society. The inset schematic shows the LB assembly process. Reproduced with permission from ref. [263]. Copyright 2010 American Chemical Society; (b) optical image of the emulsion consisting of GO wrapped hexane droplets in water; and (c) SEM image of GO aerogel after removing hexane and water. (b-c) Reproduced with permission from ref. [273]. Copyright 2014 Wiley-VCH. (d) Schematics of the LbL assembly method. Reproduced with permission from ref. [2]. Copyright 2018, Elsevier.

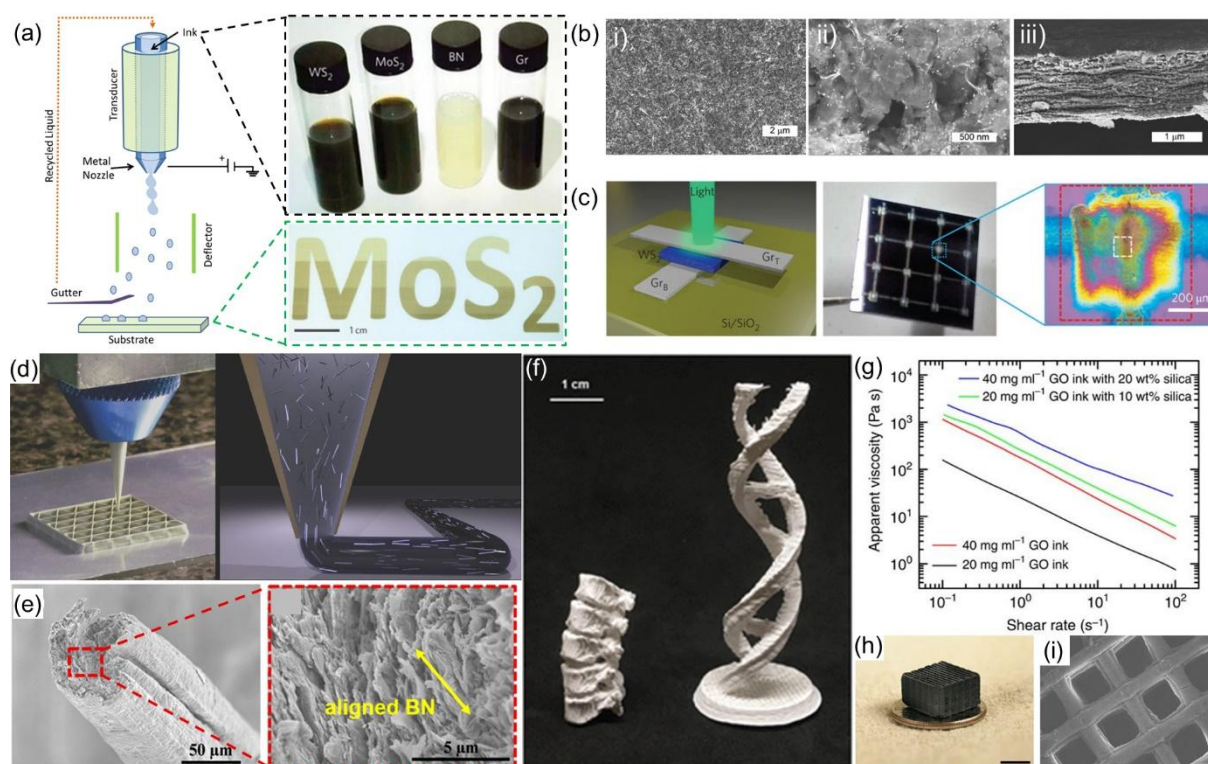


Figure 15. 3D printing techniques, including (a-c) inkjet printing and (d-i) direct ink writing (DIW). (a) Schematic of inkjet printing setup (left) [304] with photographs of different water-based 2D nanosheet inks (right top) and printed pattern using MoS₂ inks with increasing printing passes from top to bottom (right bottom). Photographs reproduced with permission from ref. [297]. Copyright 2017 Springer Nature; (b) SEM images of top view (i and ii) and cross-sectional view (iii) of inkjet-printed Ti₃C₂T_x inks on a PET substrate. Reproduced with permission from ref. [298]. Copyright 2018 Wiley-VCH; (c) schematic of an inkjet printed graphene/WS₂/graphene heterogeneous structure on a Si substrate as photodetector (left) and photograph of an inkjet printed array of heterogeneous structures (middle) with enlarged optical image of a structure (right). Reproduced with permission from ref. [297]. Copyright 2017 Springer Nature; (d) schematic of DIW process and alignment of high-aspect-ratio nanofillers induced by shear flow in the nozzle. Reproduced with permission from ref. [26]. Copyright 2014 Wiley-VCH; (e) SEM images of aligned BNNSs in PVA filaments during DIW. Reproduced with permission from ref. [299]. Copyright 2017 American Chemical Society; (f) complex 3D structures resembling lumbar spine and double helix fabricated by

DIW. Reproduced with permission from ref. [300]. Copyright 2018 American Chemical Society; (g) viscosities of GO inks with and without silica additives; and (h) photograph and (i) SEM image of a 3D printed graphene microlattice (scale bars: (h) 5 mm and (i) 200 μm). (g-i) Reproduced from ref. [34] under the Creative Commons CC BY license.

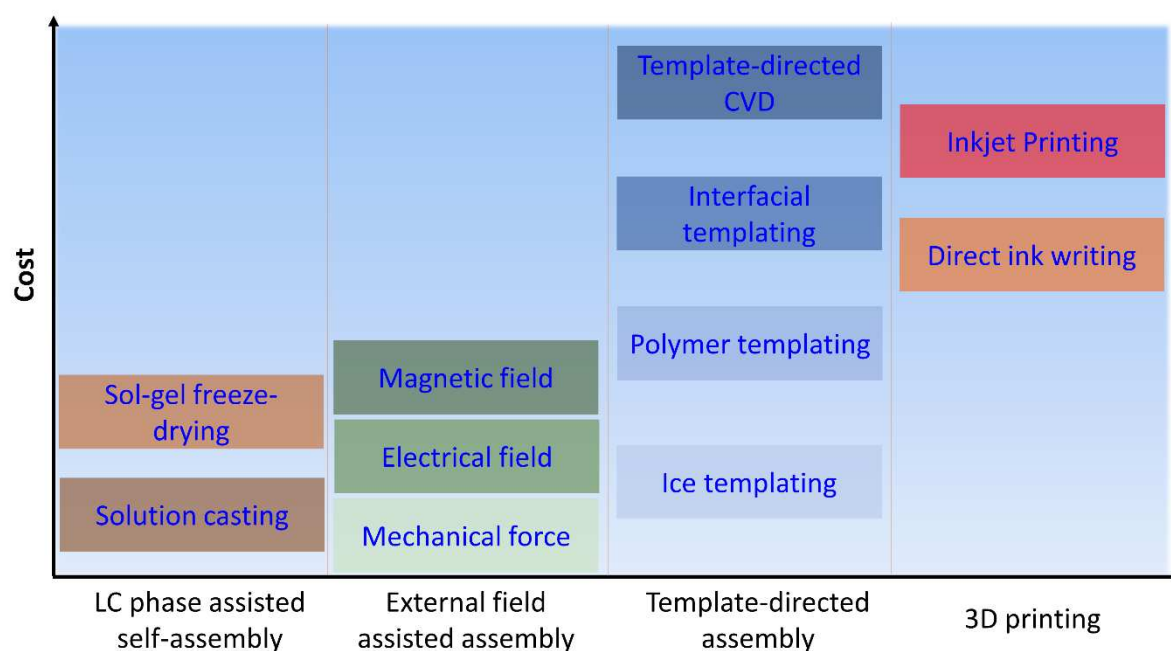


Figure 16. Cost comparison of different assembly techniques.

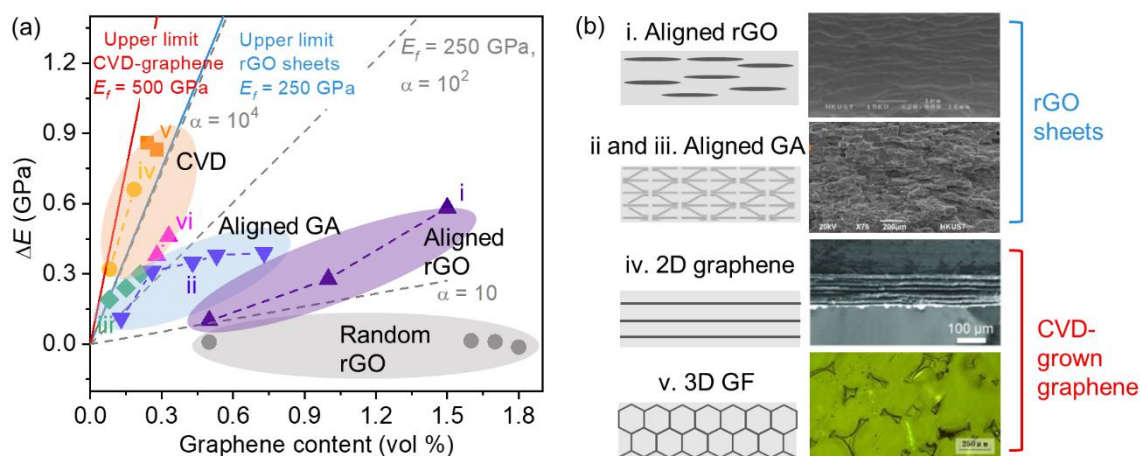


Figure 17. Improvements of elastic modulus of rationally assembled graphene/polymer composites. (a) Comparison of enhancements in modulus of graphene/polymer composites obtained by different rational assembly techniques (i. self-aligned rGO/PU;[143] ii.

GA/epoxy;[29] iii. UGA/epoxy;[212] iv. CVD-grown Graphene/PC;[228] v. GF/epoxy;[233] vi. GWF/epoxy[247]) with those of randomly dispersed rGO/polymer composites[313–315]. The dashed lines are the predictions based on the Halpin-Tsai model with different aspect ratios, α , and the blue and red solid lines are the predictions from the ROM. (b) Schematics and cross-sectional SEM images of graphene/polymer composites with different morphologies corresponding to those in (a). SEM image of aligned rGO reproduced with permission from ref. [143]. Copyright 2013 Elsevier. SEM image of aligned GA reproduced with permission from ref. [29]. Copyright 2015 American Chemical Society. SEM image of 2D graphene reproduced with permission from ref. [228]. Copyright 2016 AAAS. SEM image of 3D GF reproduced with permission from ref. [233]. Copyright 2014 American Chemical Society.

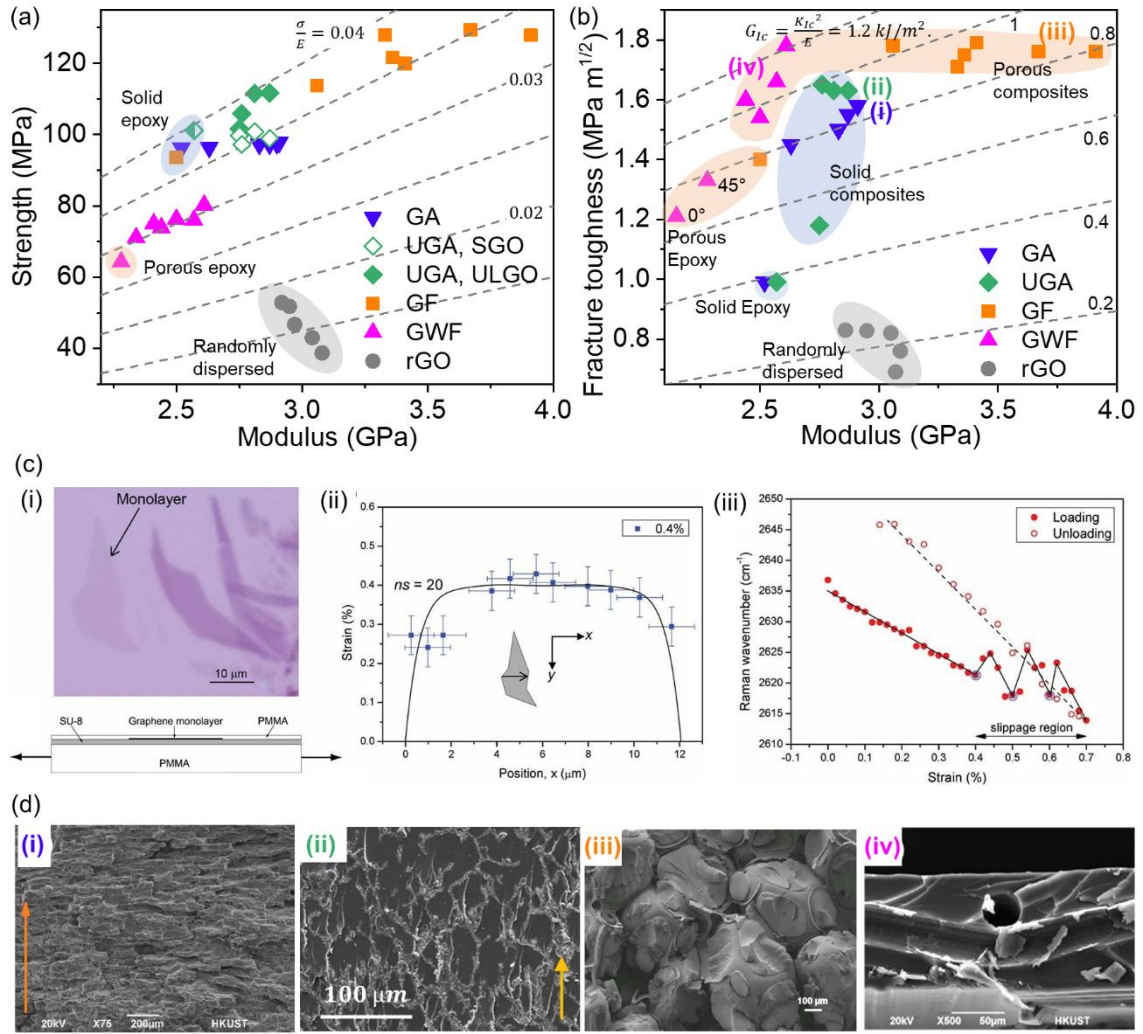


Figure 18. Strength and fracture toughness of 3D graphene/epoxy composites. Performance charts of (a) strength against modulus and (b) fracture toughness against modulus of 3D graphene/epoxy composites containing (i) GA,[29] (ii) UGA,[212] (iii) GF,[233] and (iv) GWF.[247] The grey circles represent randomly dispersed rGO/epoxy composites [319,320] for comparison. (c) Interfacial stress transfer between graphene and PMMA (i) characterized by the strain map in graphene sheets along the loading direction (ii) from Raman G' band shifts (iii). The fitting of experimental data with the shear-lag theory (solid line in (ii)) suggests a critical length of $\sim 3 \mu\text{m}$. Reproduced with permission from ref. [317]. Copyright 2010 Wiley-VCH. (d) Fracture surface morphologies of different 3D graphene/epoxy composites corresponding to the fracture toughness in (b). (i) Reproduced with permission

from ref. [29]. Copyright 2015 American Chemical Society. (ii) Reproduced with permission from ref. [212]. Copyright 2018 American Chemical Society. (iii) Reproduced with permission from ref. [233]. Copyright 2014 American Chemical Society. (iv) Reproduced with permission from ref. [247]. Copyright 2015 American Chemical Society.

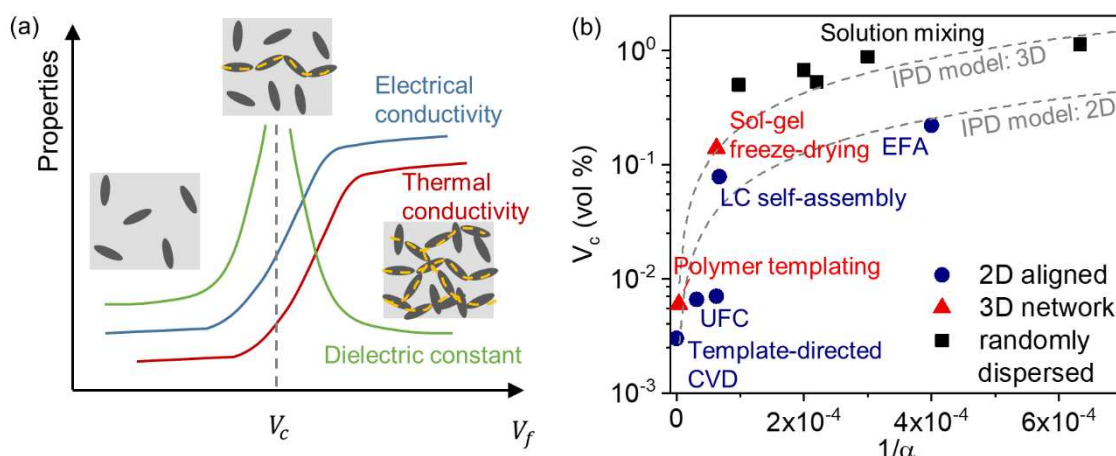


Figure 19. Percolation of 2D filler/polymer composites. (a) Schematic showing rapid changes in physical properties in the vicinity of percolation threshold, V_c ; (b) plot of percolation threshold as a function of reciprocal of aspect ratio (α) for graphene/polymer composites with different filler morphologies and distributions: randomly dispersed GNPs (black squares) made by simple mixing;[322] 2D aligned rGO or graphene sheets (blue circles) made by electric field assisted alignment (EFA),[181] LC self-assembly,[144] UFC,[210,212] and template-directed CVD;[228] and 3D rGO networks (red triangles) by sol-gel freeze-drying [29] and polymer templating [258]. The dashed lines are predictions based on the 2D and 3D IPD models given by Equations (4) and (5), respectively.

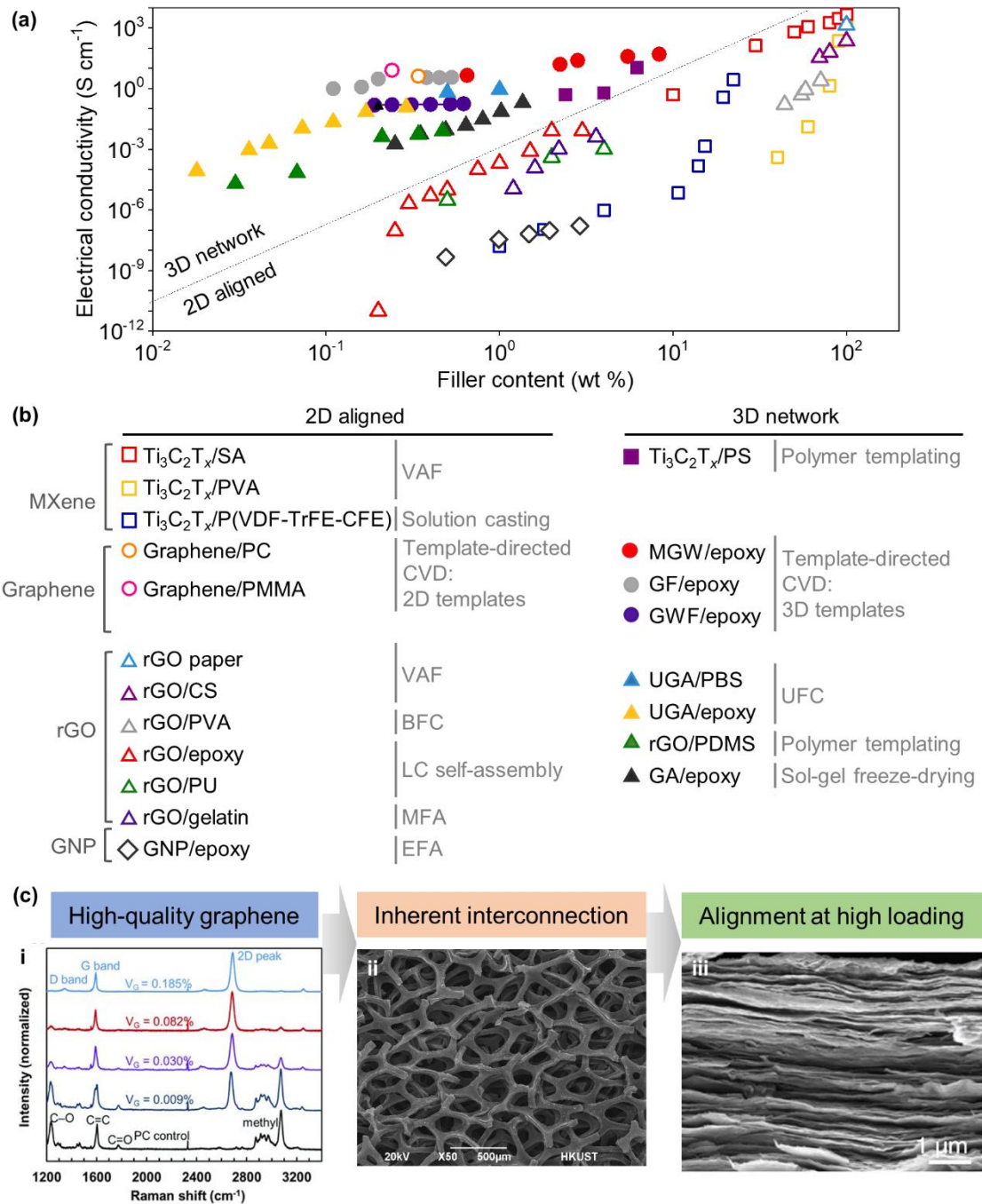


Figure 20. Electrical conductivities of 2D nanofiller/polymer composites. (a) Comparison of electrical conductivities between 2D nanofiller/polymer composites with different microscopic morphologies; (b) a list of 2D aligned and 3D network composites containing $\text{Ti}_3\text{C}_2\text{T}_x$ (2D[27,161,324] and 3D[261]), graphene (2D[228,230] and 3D[30,233,247]), rGO (2D[70,83,144,170,199,220] and 3D[29,209,210,258]) and GNP (2D[181]) for the data shown in (a) and their fabrication techniques; and (c) multiscale mechanisms for achieving

high electrical conductivities of composites: (i) Raman spectra of graphene/PC composites showing the nanoscale mechanism of high-quality graphene obtained by CVD; SEM images showing (ii) microscale mechanism of interconnected 3D graphene networks achieved by template-directed CVD and (iii) macroscale mechanism of high $\text{Ti}_3\text{C}_2\text{T}_x$ loadings (50 wt %) by forming highly aligned structures in a SA matrix *via* VAF. (i) Reproduced with permission from ref. [228]. Copyright 2016 AAAS. (ii) Reproduced with permission from ref. [30]. Copyright 2018 The Royal Society of Chemistry. (iii) Reproduced with permission from ref. [27]. Copyright 2016 AAAS.

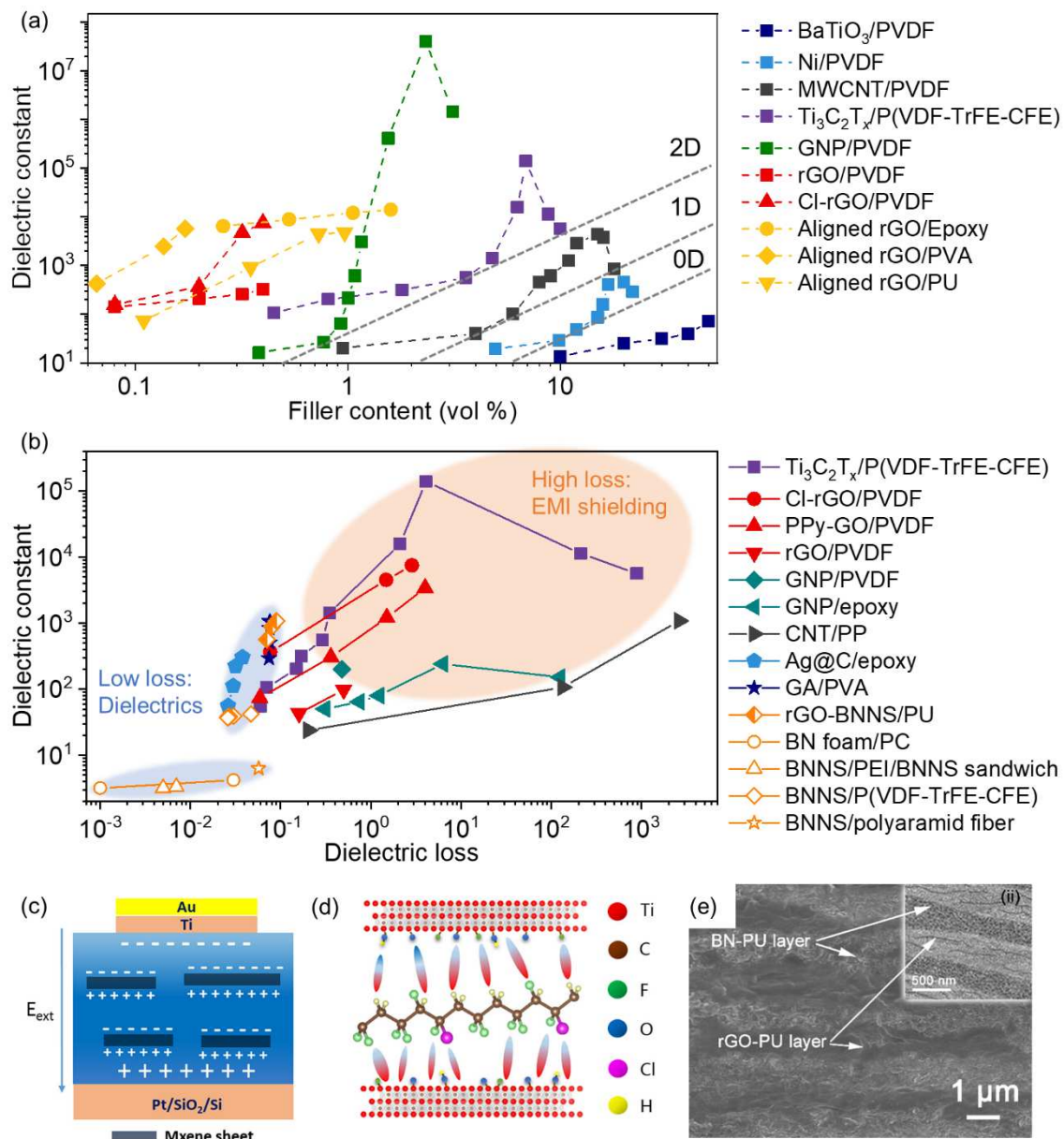


Figure 21. Dielectric properties of 2D nanofiller/polymer composites. (a) Comparison of dielectric constants of polymer composites containing ceramic fillers (BaTiO_3)[327], 0D conductive fillers (Ni nanoparticles[328]), 1D conductive fillers (CNTs[330]), and 2D conductive fillers ($\text{Ti}_3\text{C}_2\text{T}_x$,[324] GNP,[325] rGO,[331,333] aligned rGO[114,211,219]); (b) correlation between dielectric constant and dielectric loss for composites with different nanofillers, including conductive CNTs,[332] $\text{Ti}_3\text{C}_2\text{T}_x$,[324] rGO,[331,333,334] GNPs,[325,335] insulating BN,[7,33,229,237] and conductive fillers with insulating barriers [211,219,337]; schematics of (c) micro-capacitors formed between aligned conductive 2D nanosheets and (d) nanoscopic dipoles formed between functional groups (-F, -O-, -OH) on $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and polar polymer molecules. Reproduced with permission from ref. [324]. Copyright 2018 American Chemical Society; and (e) SEM and TEM images indicating aligned rGO/PU layers separated by BN/PU barriers. Reproduced with permission from ref. [219]. Copyright 2018 American Chemical Society.

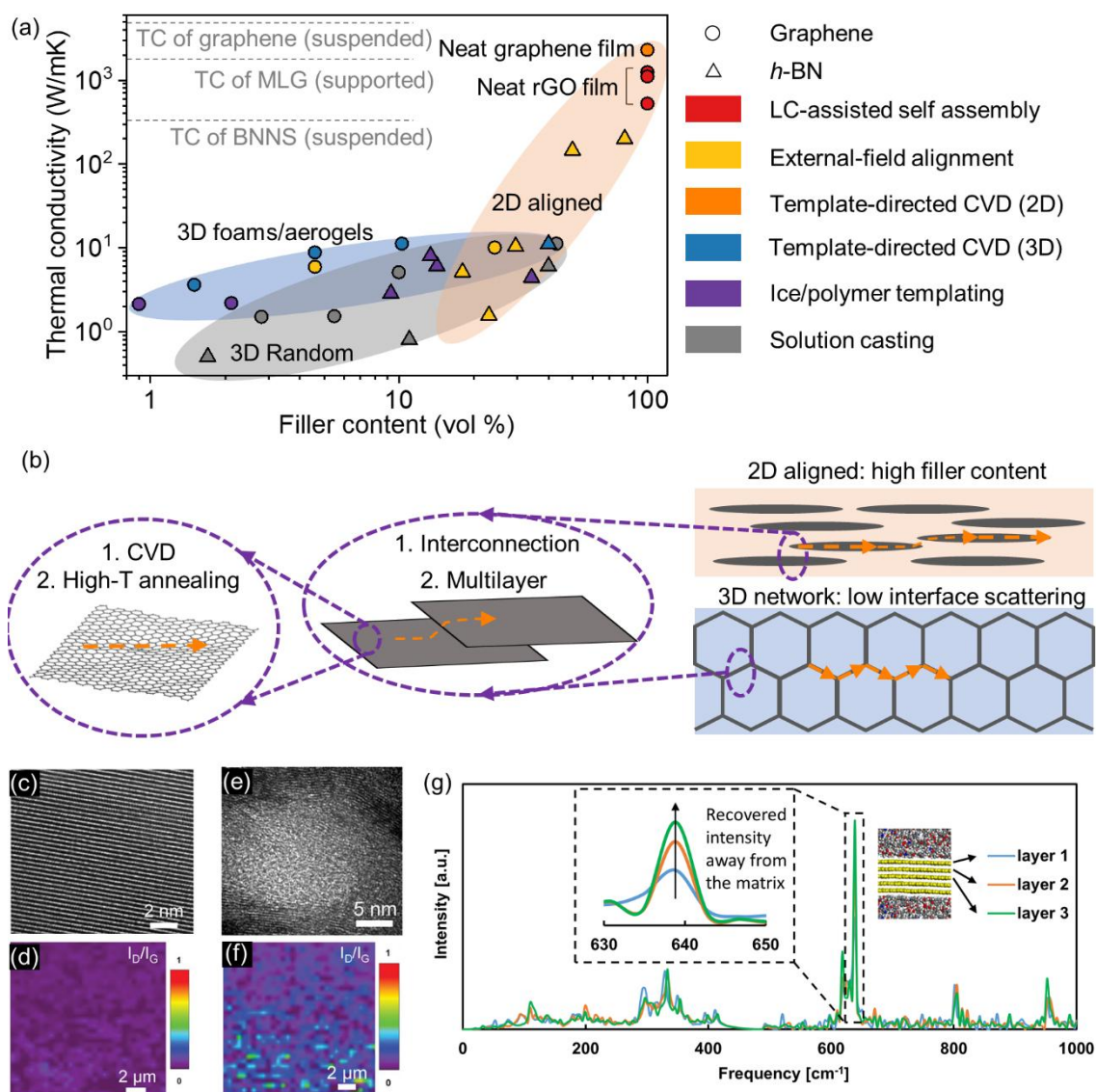


Figure 22. Thermal conductivities of neat 2D nanosheet films and 2D nanosheet/polymer nanocomposites. (a) Thermal conductivities of neat rGO/graphene films (red[104,105,341] and orange circles[28]) and polymer composites containing randomly dispersed graphene [122,339,344,345] or BNNSs [346], 3D graphene or BN foams/aerogels, [30,213,215,223,237,240,260,347–349] and 2D aligned graphene or BNNSs [106,146,153,159,182,204,342,343] prepared by various rational assembly techniques as a function of filler content; (b) schematic of the strategies devised to achieve high thermal conductivities of composites across different length scales; (c, e) TEM images and (d, f) Raman I_D/I_G intensity ratio maps for graphene films treated at 2800 and 400 °C. Reproduced

with permission from ref. [28]. Copyright 2019 Wiley-VCH; and (g) phonon vibrational spectra of different graphene layers showing matched frequencies with less power damping in the inner layers away from the polymer matrix. Reproduced with permission from ref. [122]. Copyright 2016 American Chemical Society.

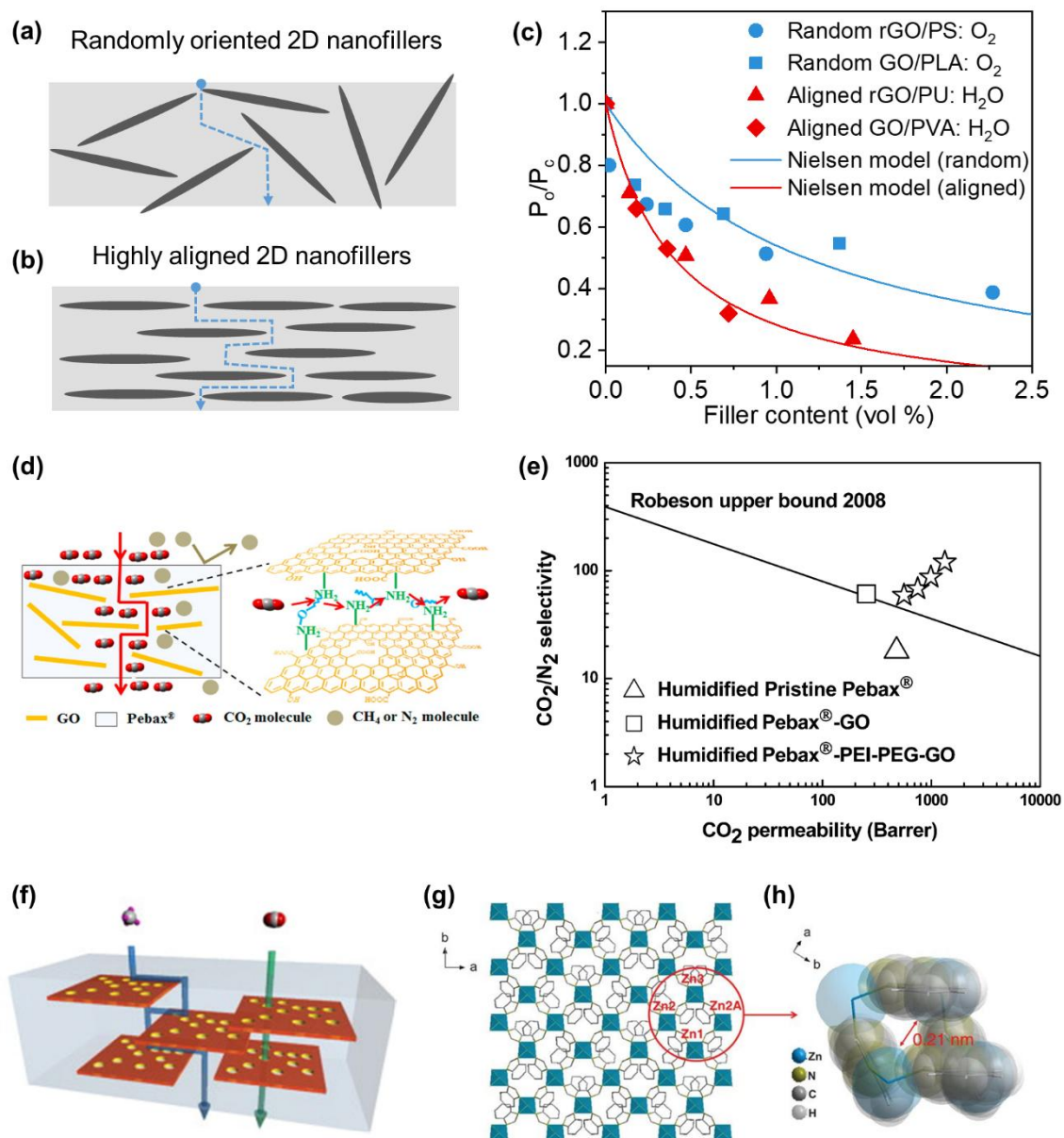


Figure 23. Mass transport properties of 2D nanofiller/polymer composites. Schematics of mass transport channels through (a) randomly-oriented and (b) aligned 2D nanofillers; (c) relative permeabilities of gas molecules through polymer composites containing aligned and randomly-oriented GO or rGO sheets; (d) schematics of selective transport of CO_2 molecules

through interlayer channels formed between functionalized GO sheets with high CO₂ affinities; (e) permeabilities of CO₂ and selectivities of CO₂/N₂ for functionalized GO sheets/Pebax composite membranes; schematics of (f) selective transport of CO₂ molecules through pores on 2D nanofillers, (g) molecular structure and (h) pore size of a Zn₂(bim)₄ MOF. (d) and (e) reproduced with permission from ref. [318]. Copyright 2015 American Chemical Society. (f) reproduced with permission from ref. [321]. Copyright 2013 Elsevier. (g) and (h) reproduced with permission from ref. [327]. Copyright 2014 AAAS.

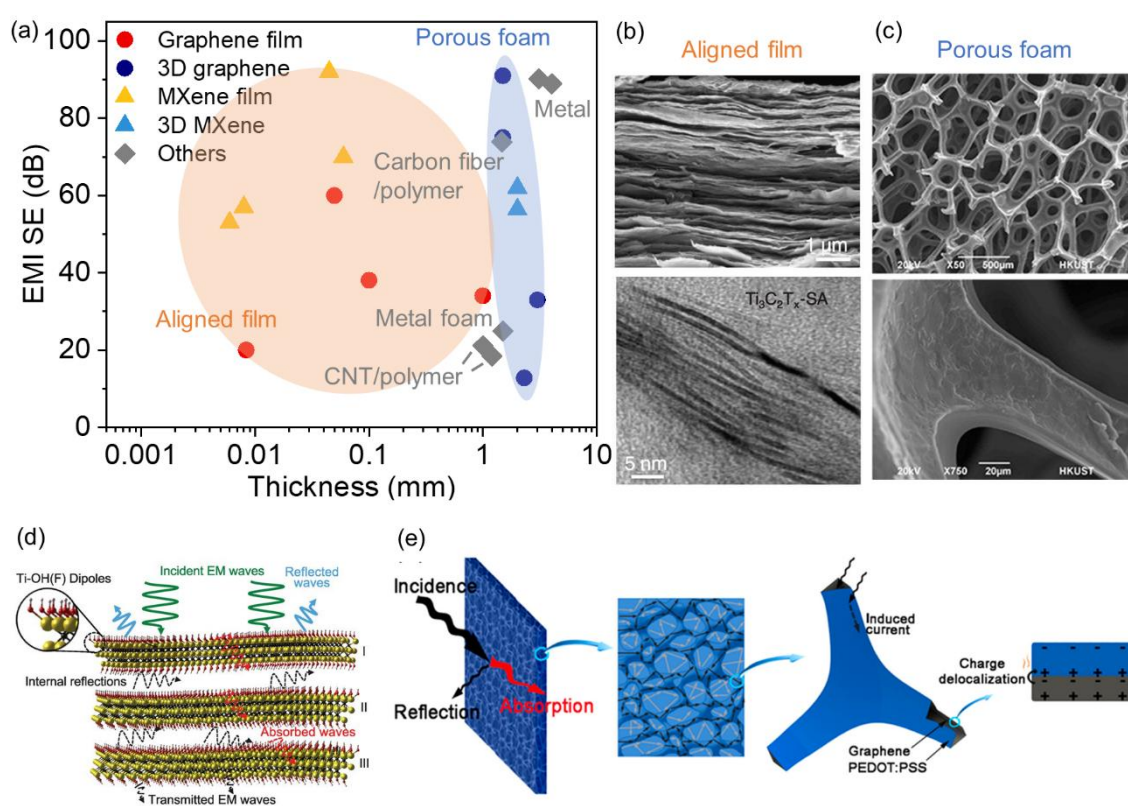


Figure 24. Graphene and Ti₃C₂T_x-based aligned films and porous foams for EMI shielding applications. (a) Comparison of EMI SEs of graphene and Ti₃C₂T_x-based films/foams with other widely used materials. Each symbol represents a category of materials: aligned graphene [379]/rGO [105] or composite films [114,380] (red circles); aligned Ti₃C₂T_x or composite films [27,165] (yellow triangles); porous graphene [244,245,336] or rGO [381] composite foams (dark blue circles); porous Ti₃C₂T_x composite foams [216,261] (blue

triangles); other materials including metal foils,[382] metal foams,[383] carbon fiber/polymer [382] and CNT/polymer composites [384,385] (Gray diamonds). (b) SEM and TEM images of aligned $\text{Ti}_3\text{C}_2\text{T}_x/\text{SA}$ composite films; (c) SEM images of porous GF/PEDOT:PSS foams; and EMI shielding mechanisms of (d) aligned films and (e) porous foams. (b) and (d) reproduced with permission from ref. [27]. Copyright 2016 AAAS. (c) and (e) reproduced with permission from ref. [244]. Copyright 2017 American Chemical Society.

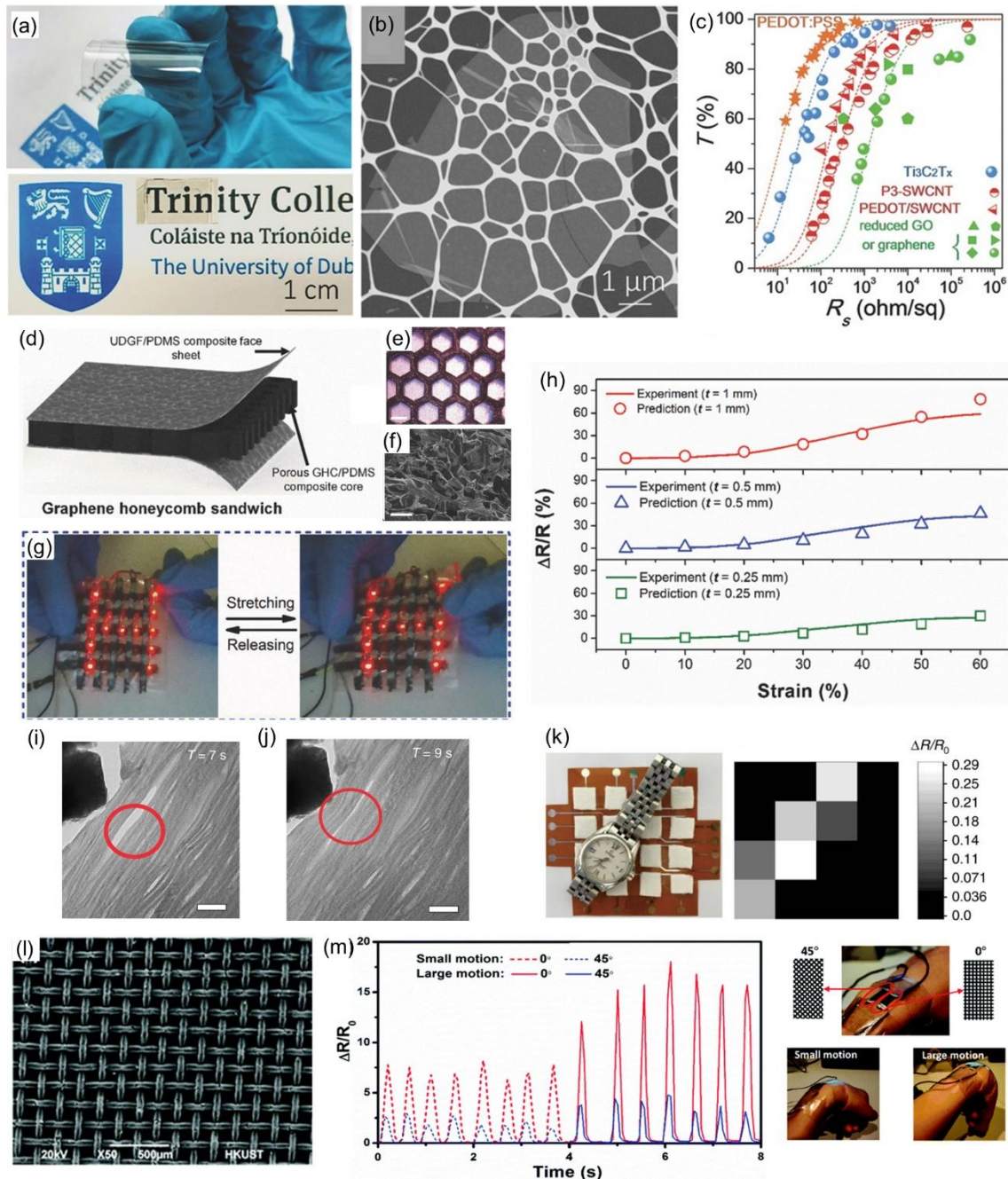


Figure 25. Graphene and $\text{Ti}_3\text{C}_2\text{T}_x$ composites for (a-c) transparent conductive films,[111] (d-h) elastic conductors,[259] and (i-m) pressure [391] and strain [31] sensors. (a) Photographs of $\text{Ti}_3\text{C}_2\text{T}_x$ film on a PET substrate; (b) TEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ sheet; (c) comparison of transmittance and sheet resistance of $\text{Ti}_3\text{C}_2\text{T}_x$ film with CNT and graphene films; (d) schematic of graphene honeycomb sandwich; (e) optical and (f) SEM images of graphene honeycomb/PDMS composites (scale bars: (e) 1 mm; (f) 50 μm); (g) stretchable LED made from a graphene honeycomb sandwich; (h) resistance changes with applied strain in graphene honeycomb/PDMS composites with different wall thicknesses, t ; (i-j) *in-situ* TEM indentation tests showing the decreasing gap between $\text{Ti}_3\text{C}_2\text{T}_x$ sheets under pressure; (k) $\text{Ti}_3\text{C}_2\text{T}_x$ film sensor arrays with spatial resolutions for detecting the position of a watch; (l) SEM images of GWF/PDMS composites; and (m) resistance changes in two GWF/PDMS sensors with different tube orientations attached onto the wrist under small and large motions. (a-c) Reproduced with permission from ref. [111]. Copyright 2017 Wiley-VCH. (d-h) Reproduced with permission from ref. [259]. Copyright 2018 Wiley-VCH. (i-k) Reproduced from ref. [391] under a Creative Commons CC BY 4.0 license. (l-m) Reproduced with permission from ref. [31]. Copyright 2017 The Royal Society of Chemistry.

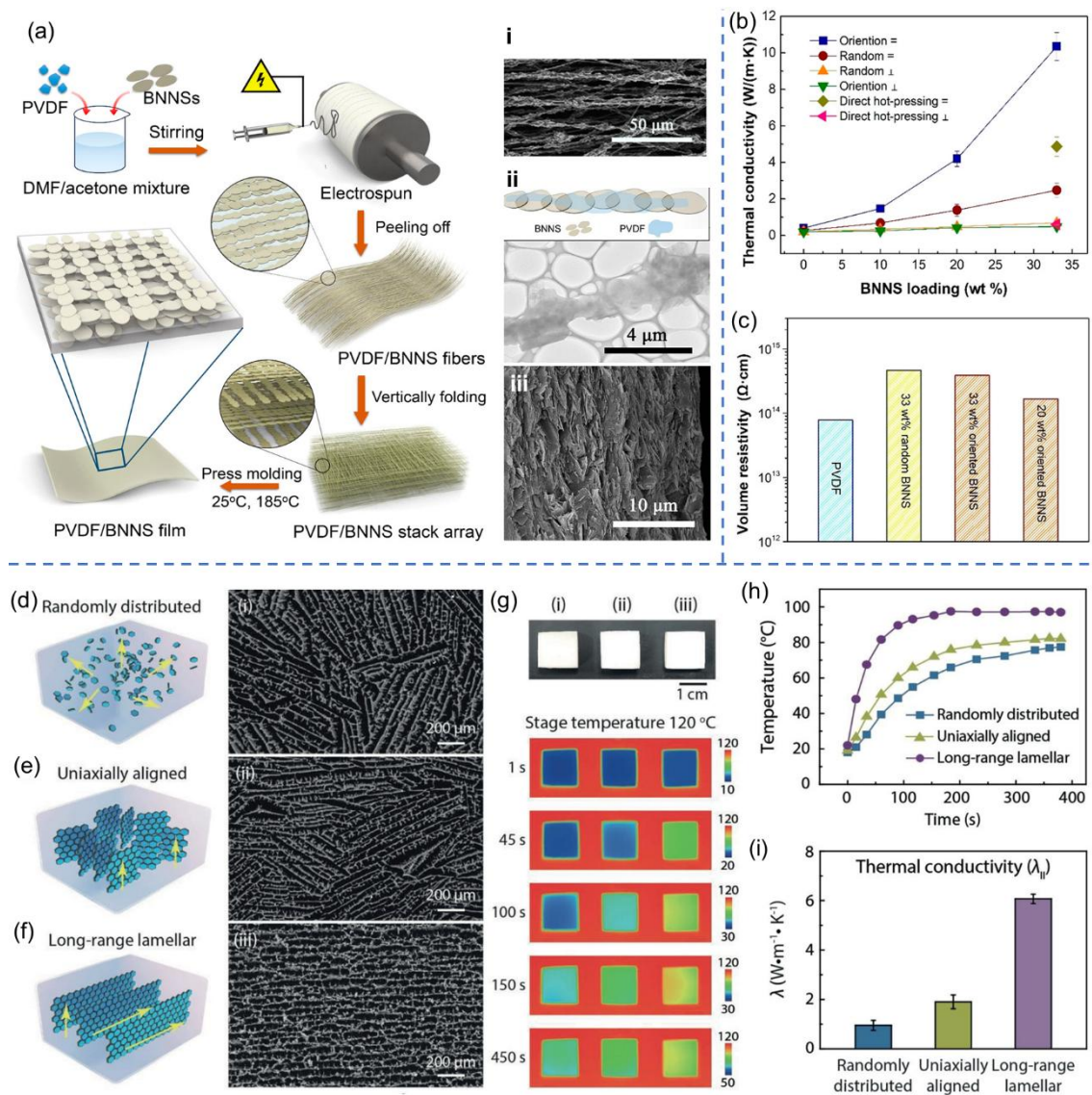


Figure 26. Anisotropic BNNS/polymer composites for thermally conductive and electrically insulating TIMs. (a-c) In-plane aligned BNNS/PVDF composites prepared by electrospinning: (a) schematic of the fabrication of BNNS/PVDF composites; (b) thermal conductivities of randomly oriented and hot-pressed composites along the in-plane and thickness directions; (c) volume resistivities of composites. Reproduced with permission from ref. [153]. Copyright 2019 American Chemical Society. (d-i) Vertically aligned BNNS/epoxy composites by BFC: schematics and SEM images of (d) randomly oriented, (e) unidirectionally aligned and (f) bidirectionally aligned BNNS; (g) thermal images and (f) surface temperature changes of three different composites shown in (d-f) when they are put on hot stages; and (i) thermal

conductivities of three different composites. Reproduced with permission from ref. [223].
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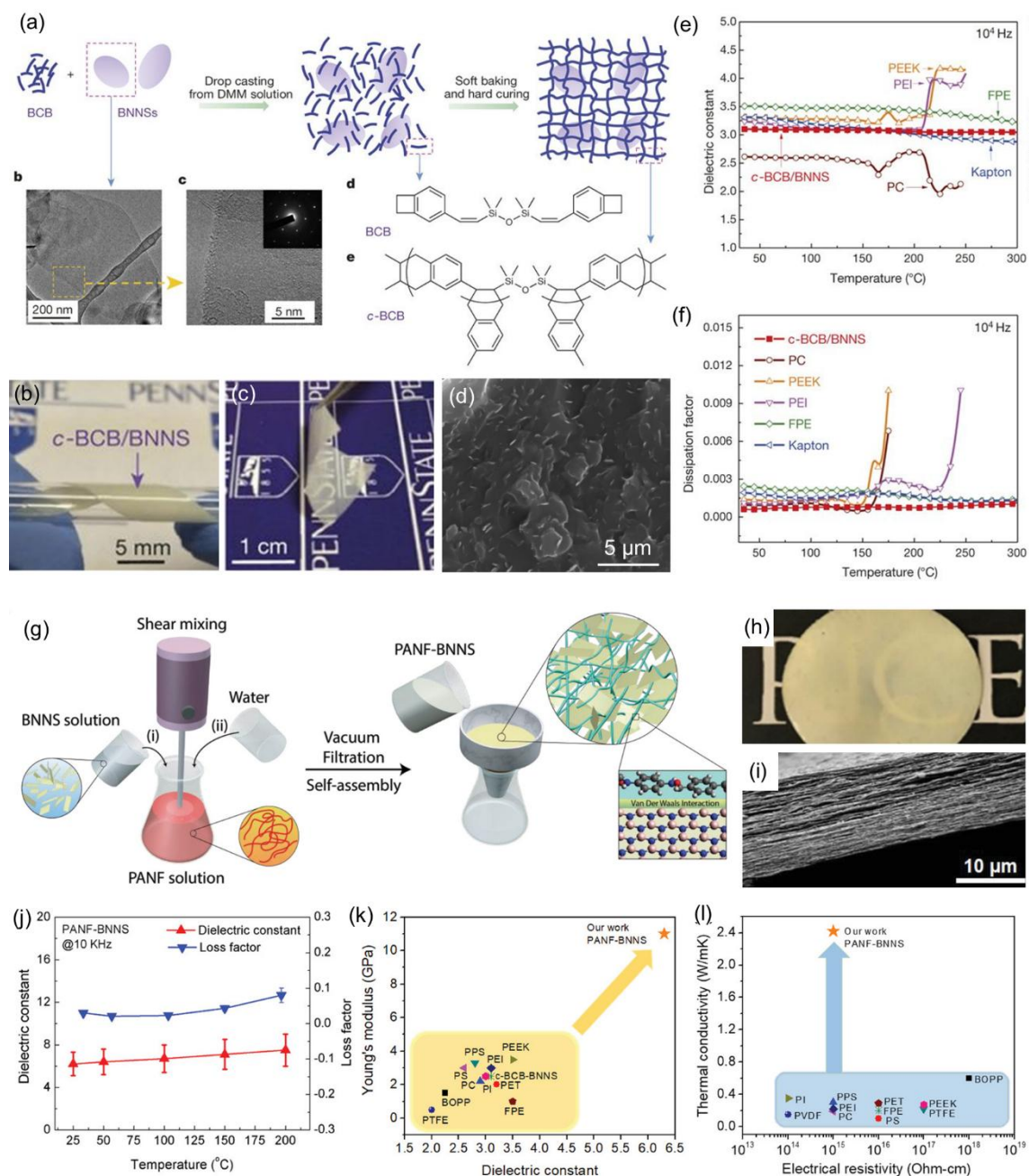


Figure 27. (a-f) Randomly dispersed [7] and (g-l) highly aligned [33] BNNS/polymer composites for high-temperature dielectrics. (a) Fabrication of BNNS/*c*-BCB composites by drop casting with TEM images of BNNS and molecular structures of BCB and *c*-BCB; photographs and SEM images showing the (b) flexibility, (c) semi-transparency and (d)

excellent dispersion of the composite; (e) dielectric constants and (f) losses of BNNS/*c*-BCB composites at different temperatures in comparison with engineering polymers; (g) fabrication of aligned BNNS/PANF composite films by VAF; (h) photograph and (i) cross-sectional SEM image of composite films; (j) dielectric constants and losses of composite films showing high temperature stability up to 200 °C; and (k-l) comparison of multifunctional properties of BNNS/PANF composites with other polymers. (a-f) Reproduced with permission from ref. [7]. Copyright 2015 Springer Nature. (g-l) Reproduced with permission from ref. [33]. Copyright 2019 Wiley-VCH.

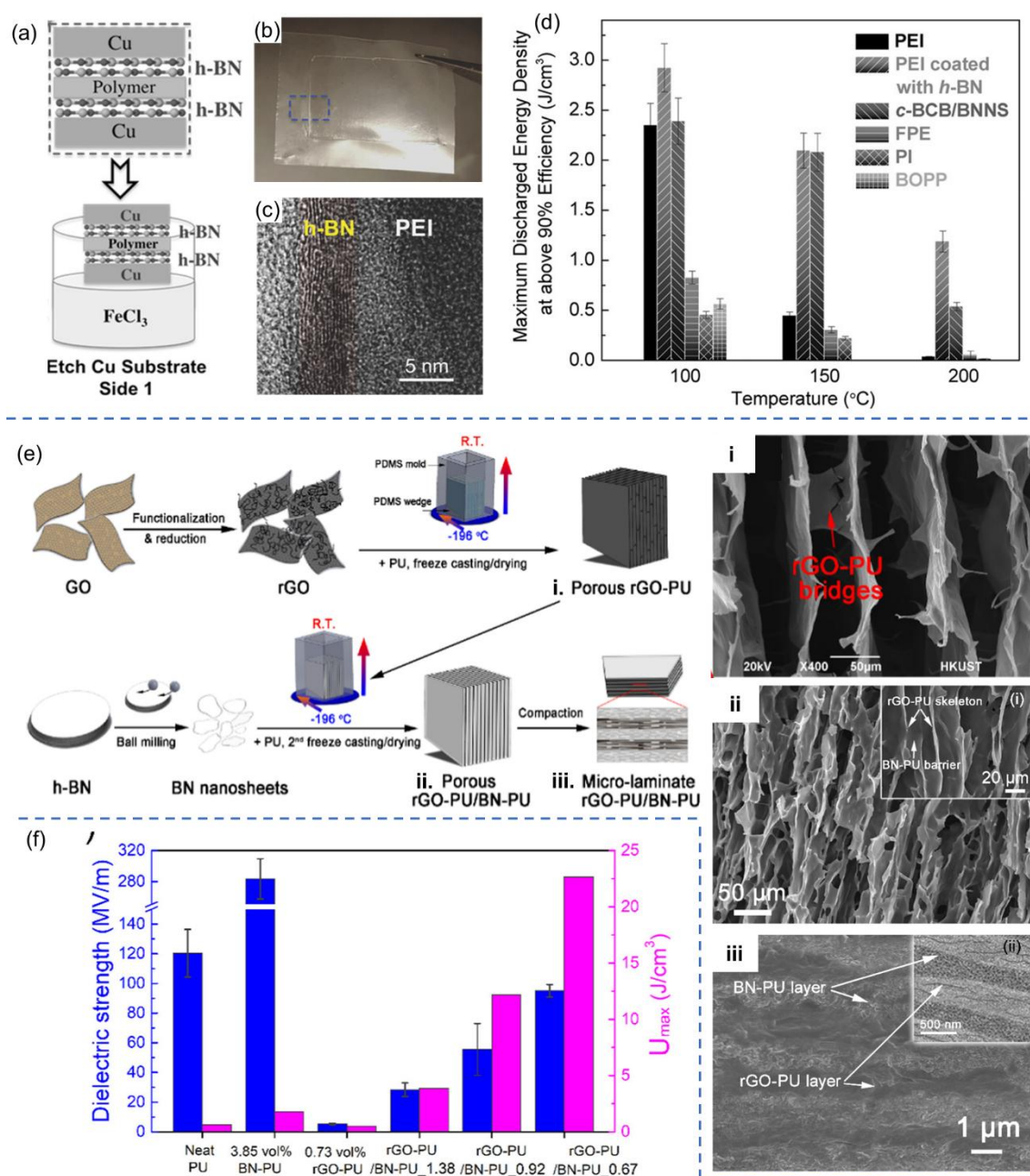


Figure 28. Rational design of (a-d) sandwich [229] and (e-f) microlaminate structures [219] for high-temperature and high energy density storage performance. (a) Fabrication, (b) morphology and (c) TEM image of *h*-BN/PEI/*h*-BN sandwich films; (d) energy densities of sandwich films at different temperatures compared with other dielectric polymers; (e) fabrication of rGO-PU/BN-PU microlaminates: SEM images of (i) rGO-PU aerogel, (ii) rGO-PU/BN-PU aerogel and (iii) their laminate composite after compaction; and (f) dielectric strengths and maximum energy densities of microlaminate composites with different filler

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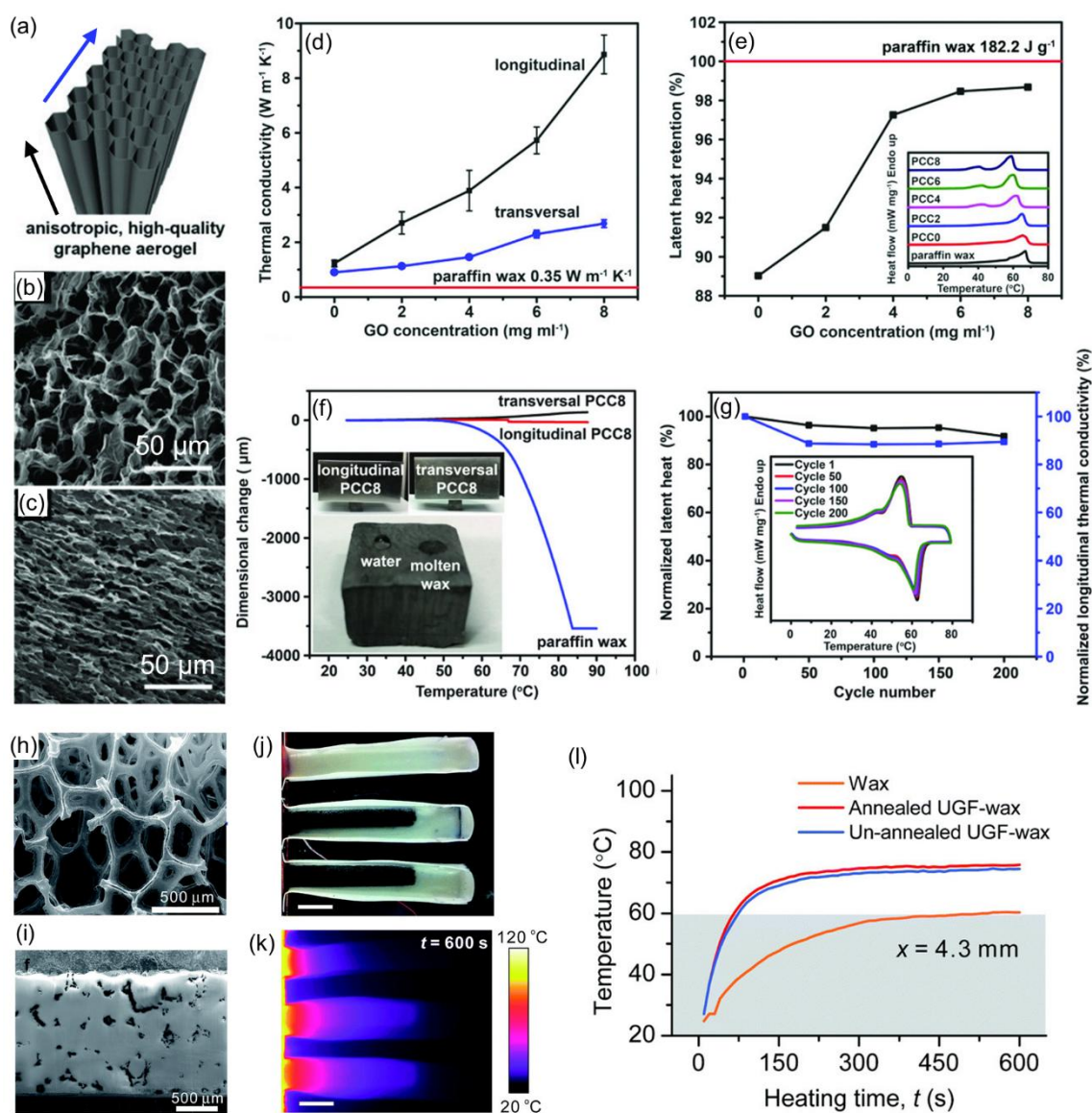


Figure 29. 3D (a-g) GA [454] and (h-l) GF [240] for thermal energy storage. (a) Schematic and (b) top- and (c) side-view SEM images of anisotropic GAs made by UFC; (d) thermal conductivities of GA/paraffin wax phase change composites (PCCs) along two different directions; (e) latent heat retention of PCCs as a function of GO concentration; (f) thermal stabilities of PCCs as indicated by the small dimensional change with increasing temperature; (g) cyclic stabilities of latent heat and thermal conductivity up to 200 melt-solidification

cycles; SEM images of (h) GF and (i) GF/wax composite; (j) photographs and (k) infrared images of wax (top), un-annealed GF/wax (middle) and annealed GF/wax composites (bottom) after heating at one end (scale bars: 10 mm); and (l) temperature changes in the three materials as a function of heating time. (a-g) Reproduced with permission from ref. [454]. Copyright 2018 Wiley-VCH. (h-l) Reproduced with permission from ref. [240]. Copyright 2013 The Royal Society of Chemistry.

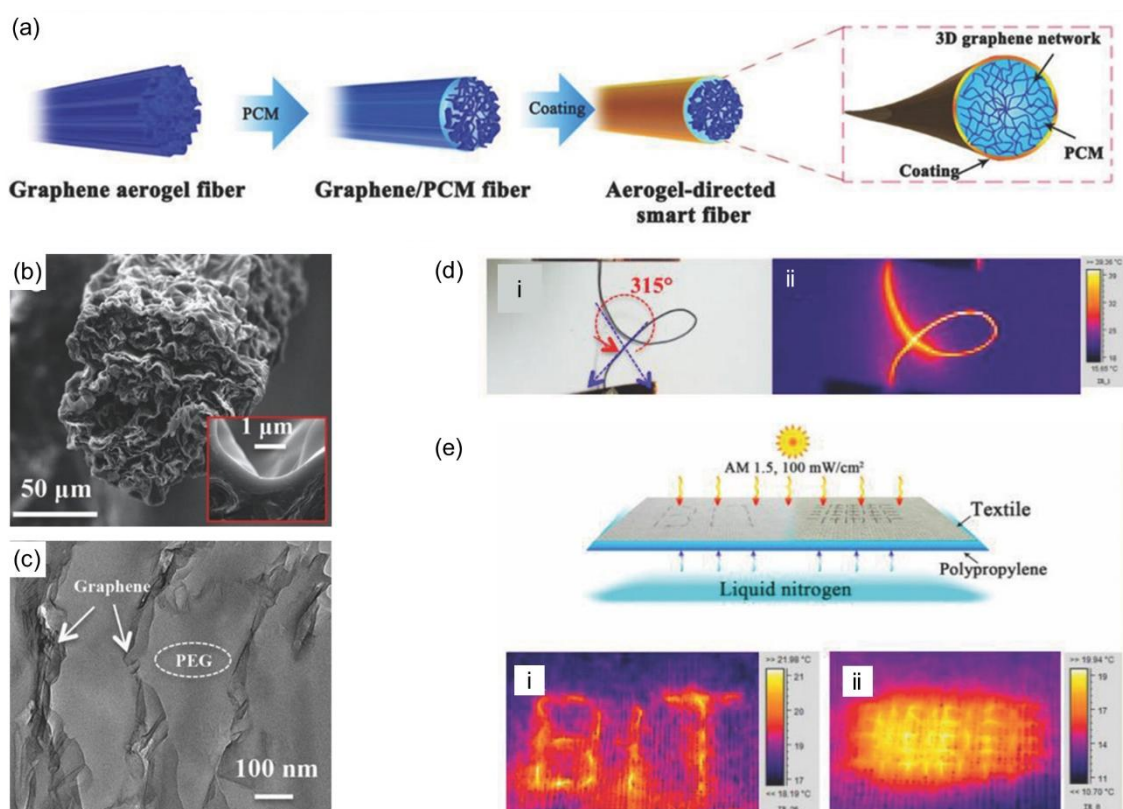


Figure 30. 1D graphene fibers for electrothermal and photothermal energy conversion and storage.[156] (a) Schematic of the fabrication of GA and GA/PCM fibers; (b) cross-sectional SEM image of GA/PCM fiber; (c) TEM image of PEG infiltrated GA fiber; (d) photograph (i) and infrared image (ii) showing the electrothermal effect of twisted GA/PCM fibers at an applied voltage of 30 V; and (e) schematic and infrared images showing the photothermal effect of GA/PCM fibers woven into cotton fabrics under solar illumination of 1 Sun. Reproduced with permission from ref. [156]. Copyright 2018 Wiley-VCH.

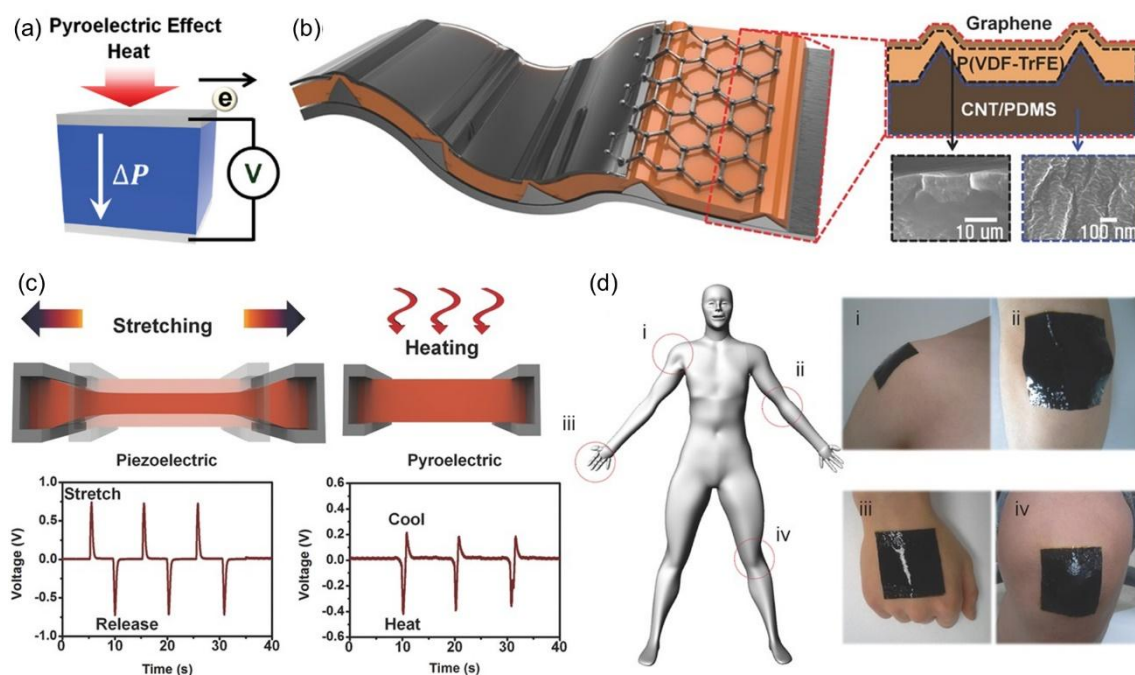


Figure 31. Electrical energy harvesting from thermal energies using pyroelectric generators.

(a) Schematic of the principle of pyroelectric effect. Reproduced with permission from ref. [35]. Copyright 2019 Wiley-VCH; (b) tri-layer sandwich composite consisting of graphene, P(VDF-TrFE) and CNT/PDMS as pyroelectric and piezoelectric hybrid generator; (c) alternating voltages generated from the piezoelectric and pyroelectric effects; and (d) photographs of the composite attached onto different body parts. (b-d) Reproduced with permission from ref. [433]. Copyright 2013 Wiley-VCH.

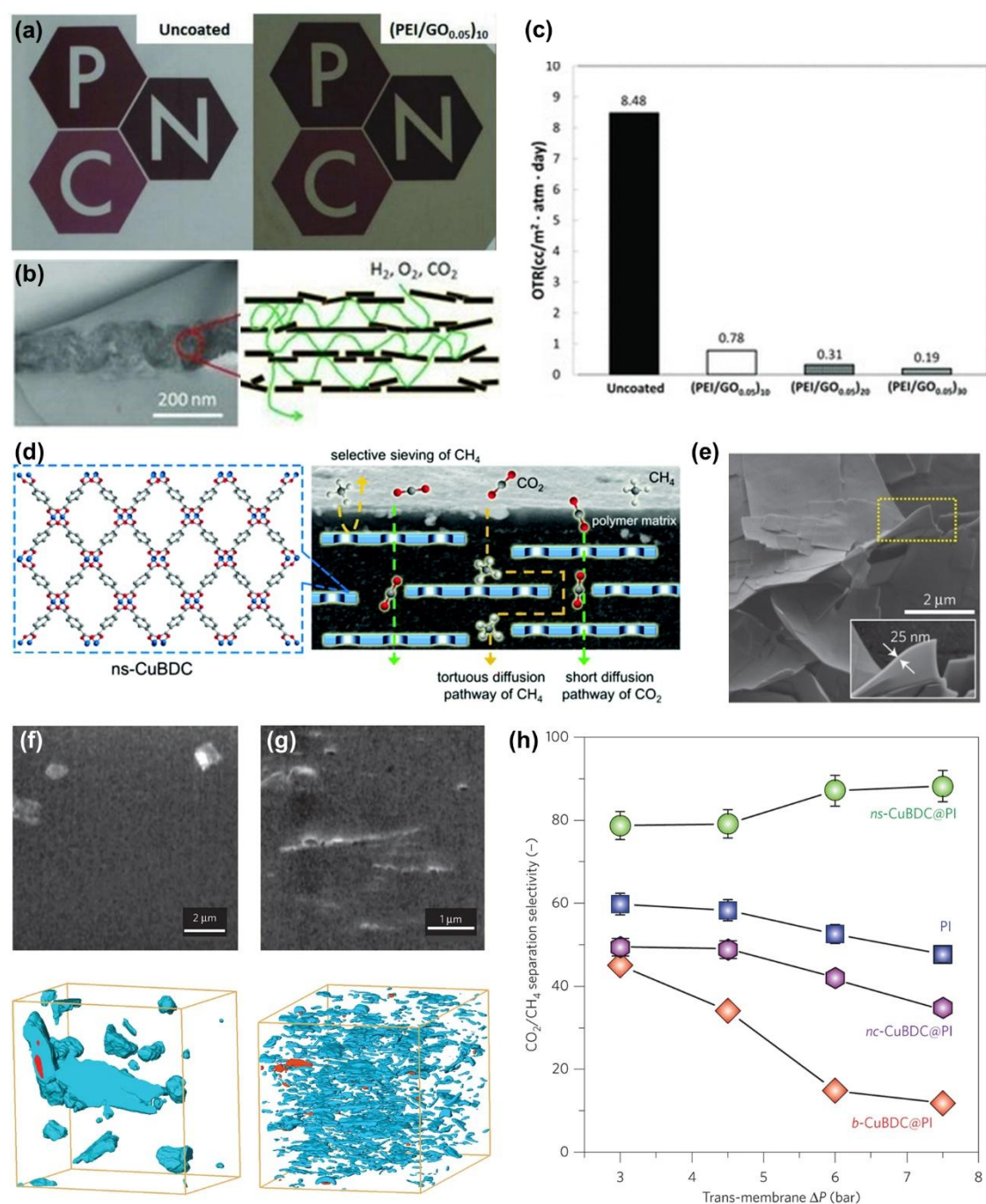


Figure 32. Molecular sieving membranes made from 2D nanofiller/polymer composites for (a-c) barrier and (d-h) gas separation. (a) Photographs of bare PET and GO/PEI-coated PET films; (b) TEM image of the cross-section of GO/PEI and corresponding schematic showing aligned GO sheets; (c) OTR of PET films with different GO/PEI composite coatings; (d) schematic of 2D ns-CuBDC and the mechanism for gas separation; (e) SEM images of ns-CuBDC; SEM images and corresponding tomograms of PI composites containing (f) b-

CuBDC and (g) ns-CuBDC; (h) CO₂/CH₄ selectivity of PI composites containing different types of CuBDC under various trans-membrane pressure differences. (a-c) reproduced with permission from ref. [358]. Copyright 2012 Wiley-VCH. (d) reproduced with permission from ref. [444]. Copyright 2017 The Royal Society of Chemistry. (e-h) reproduced with permission from ref. [375]. Copyright 2014 Springer Nature.

Table 1. Synthesis techniques of 2D nanofillers.

Method	2D nanofiller	Exfoliation/transfer techniques	Qualities of 2D nanofillers	Advantages
Solvent-based exfoliation from bulk crystals				
Exfoliation assisted by mechanical force	Graphene,[37,38] WS ₂ ,[39] MoS ₂ ,[39,40] BNNS,[39]] MOFs [41]	Ultrasonication [38,39]; high-shear mixing [37,40]	Lateral size: a few micrometers (ultrasonication) and 300 – 800 nm (high-shear mixing) for graphene;[37,38] 300 – 900 nm for BNNS Thickness: Mono- to few-layer Crystallinity: small number of defects (Raman $I_D/I_G < 0.4$) Functional groups: no functional groups	1. Simple 2. Good crystallinity
Functionalization-assisted exfoliation	GO,[42,43]] BNNS,[44–49] MoS ₂ [50]	Ultrasonication [42–44]; ball milling [45,46,48]; hydrothermal [47]	Lateral size: 100 nm - 3 µm for BNNS [45] Thickness: monolayer for GO; few- to multi-layer for BNNS Crystallinity: large number of defects (Raman I_D/I_G : 0.8 - 1) Functional groups: oxygenated and amino groups on basal planes and edges	1. Ability to functionalize 2. Scalable
Intercalation-assisted exfoliation	Graphene,[51,52] GNP,[53,54] GO,[55] BNNS,[51,52,56,57] MoS ₂ [52,58], MOFs,[59]	Intercalation by acid [51,53–55], alkali metal ions [56,58], gas molecules [57], ionic liquid molecules [52], organic compound [59]; thermal shock [55,57]; mechanical	Lateral size: 1 - 50 µm for BNNS [51] Thickness: mono- to few-layer for BNNS; monolayer for GO; multilayer for GNPs Aspect ratio: 10 ⁴ - 10 ⁵ for BNNS Crystallinity: few defects (Raman $I_D/I_G \sim 0.1$) Functional groups: minimum functional groups after exfoliation, additional functionalization required	1. Large aspect ratio 2. Well-defined lattice

		stirring [55]		
	$Ti_3C_2T_x$ [12], Ti_2CT_x [4], $Mo_2TiC_2T_x$ [4]	Etching layers in MAX followed by intercalation and exfoliation	Lateral size: 100 nm - 2 μ m Thickness: monolayer Crystallinity: Concentration of defects depending on etching and intercalation methods Functional groups: -OH, -F, -O	Abundant functional groups
			Template-based CVD from precursor gases	
CVD	Graphene [60,61], BNNS [62–64], MoS_2 [10,11], WS_2 [10,11], $MoSe_2$ [10,11]	Etching the templates before or after polymer coating or infiltration	Lateral size: Up to centimeters for films and continuous 3D structures Thickness: Controllable monolayer to multilayer Crystallinity: few defects (Raman $I_D/I_G < 0.3$); large single crystal obtainable Functional groups: No functional groups, additional functionalization required	1. Large lateral size 2. Few defects 3. Functional groups

Table 2. Intrinsic properties of 2D materials.

2D materials	Monolayer thickness (nm)	Mechanical properties	Electrical conductivity (S cm ⁻¹)	Thermal conductivity (Wm ⁻¹ K ⁻¹)
Single crystalline graphene	0.334	Modulus: 1.0 TPa;[86] Strength: 125 GPa.[86]	2×10^4 (ref. [96])	5300 (ref. [94])
CVD-grown graphene	0.334	Modulus: 210-510 GPa;[97,98]	4×10^3 (ref. [60])	2500 (ref. [99])
GO	~1.0	Modulus: 200-250 GPa;[100]	10^{-6} - 10^{-3} (refs. [70,101])	10^{-20} (ref. [102])
rGO	~1.0	Modulus: 250 GPa;[103]	10^3 (refs. [70,101])	500 - 1200 (refs. [104–106])
BNNS	0.330	Modulus: 0.86 TPa;[87] Strength: 70 GPa.[87]	10^{-14} (Insulator, Band gap: ~5.5 eV)[64]	360 (ref. [95])
MoS ₂	0.65	Modulus: 270-330 GPa;[88,89] Strength: 16-30 GPa.[89]	Semiconductor (Band gap: 1.8 eV)[107]	34.5 (ref. [108])
WS ₂	0.65	Modulus: 270 GPa.[90]	Semiconductor (Band gap: 2.0 eV)[109]	32 (ref. [110])
Ti ₂ CT _x :[91] Ti ₃ C ₂ T _x :[27, 91–93,111,112] MoTiC ₂ T _x :[27] MoTi ₂ C ₃ T _x :[27]	1.5	[^] Modulus: 500-600 GPa.[91]	4000 - 9880 (refs. [27,92,93,111])	55.8 (ref. [112])

Notes: [^] These values are obtained from theoretical calculations.

[#] These values are for thin film samples.