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Review

A critical review of nanohybrids: synthesis, applications and environmental implications

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Environmental context. Recent developments in nanotechnology have focussed towards innovation and usage of multifunctional and superior hybrid nanomaterials. Possible exposure of these novel nanohybrids can lead to unpredicted environmental fate, transport, transformation and toxicity scenarios. Environmentally relevant emerging properties and potential environmental implications of these newer materials need to be systematically studied to prevent harmful effects towards the aquatic environment and ecology.

Abstract. Nanomaterial synthesis and modification for applications have progressed to a great extent in the last decades. Manipulation of the physicochemical properties of a material at the nanoscale has been extensively performed to produce materials for novel applications. Controlling the size, shape, surface functionality, etc. has been key to successful implementation of nanomaterials in multidimensional usage for electronics, optics, biomedicine, drug delivery and green fuel technology. Recently, a focus has been on the conjugation of two or more nanomaterials to achieve increased multifunctionality as well as creating opportunities for next generation materials with enhanced performance. With incremental production and potential usage of such nanohybrids come the concerns about their ecological and environmental effects, which will be dictated by their not-yet-understood physicochemical properties. While environmental implication studies concerning the single materials are yet to give an integrated mechanistic understanding and predictability of their environmental fate and transport, the importance of studying the novel nanohybrids with their multidimensional and complex behaviour in environmental and biological exposure systems are immense. This article critically reviews the literature of nanohybrids and identifies potential environmental uncertainties of these emerging 'horizon materials'.

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Introduction

Materials development at the nanoscale has progressed from single particle synthesis to multi-component assemblies or hierarchical structures, where two or more pre-synthesised nanomaterials (NMs) are conjugated to extract multifunctionality.[1] These ensembles are termed as nanohybrids (NHs).[2,3] The underlying focus of NH synthesis is property modulation, which results in alteration to inherent physicochemical properties, i.e. size, shape, composition and surface chemistry. Such changes also give rise to novel emerging properties[4] that are not observed during classical NM health and safety (EHS) evaluation. This new direction in NH synthesis and use thus presents unique challenges and necessitates systematic evaluation of nano EHS.

Demand for multifunctionality has resulted in physical and chemical modification to NMs, in general. Size and shape modulation alongside physical or chemical functionalisation are used to achieve hierarchical[5] and heterostructures.[6] Such functionalisation has altered inherent surface attributes and extracted novel electronic configuration, intrinsic hydrophobicity, dissolution properties, etc., from nanoscale materials. The successes of such manipulations have further encouraged achieving a higher degree of functionality by combining multiple NMs, each possessing unique and novel advantages. For example, nanoscale iron oxide, nanogold and graphene nanosheets individually possess paramagnetism, plasmon resonance and superior charge carrying capability respectively. However, careful combination of two or more of these materials enhanced their functional performance as observed in the development of the first sets of bimetallic NHs. Iron oxide when conjugated with gold to form core–shell particles, provided inherent magnetism of the iron oxide shell, while preserving the surface plasmon resonance of the gold core.[7] Such multifunctional bimetallics were used as magnetic resonance imaging (MRI) agents with added nanoheating capabilities, useful for laser irradiated drug delivery systems.[8] Similarly, gold, when intercalated within layered clay, was used for protein or organic molecule immobilisation, applicable for biocatalysis and sensors.[9,10] Paramagnetic iron oxides, in contrast, when combined with novel graphene oxides, resulted in unique drug delivery systems with superior drug release and targetability.[11] Again, graphene nanosheets have also been combined with porphyrins, titanium dioxide (TiO_2), carbon nanotubes, quantum dots, etc., and have generated NHs for enhanced optical emitting[12] and limiting[13] devices, supercapacitors,[14] lithium-ion batteries[15,16] or transparent conductors.[17] It is evident that benefits of conjugation and ensembles of multiple materials are well realised and thus will likely widen the NH material domain, affecting a much larger application space and in large amounts. For example, it is projected that by the year 2050, at least 1.0×10^7 kg of platinum carrying titania-modified multiwalled carbon nanotube (MWNT) NHs will be deployed in fuel cells for vehicles alone, assuming 20 % platinum in the NH by mass.[18,19]

The development of novel materials comes with an intrinsic uncertainty regarding their potential environmental and biologic consequences. Material release can occur from nano-laden products and devices as well as during their manufacture and use.[20] Upon release, NMs undergo transport and transformation in either occupational or environmental settings.[21] Such processes are highly influenced by the material attributes and the form of release; e.g. NM release from personal care products and medicinal applications will possess distinctive physicochemical properties compared with their release from solid-state optoelectronic systems. As the material complexity increases with conjugation and assemblages of materials with uniquely different properties, their environmental processes will also be altered and likely present higher uncertainty when predicted using their parent material classes. To date, environmental fate, transport and transformation literature of NMs have systematically generated a critical information mass – by measuring physicochemical properties and their influence on environmental behaviour manifestation – that has begun to effectively determine material safety and risk.[22,23] However, the uncertainty of environmental behaviour for hierarchical and conjugated materials continues to prevail. The uncertainty emanates from the knowledge-gap of 'conjugated materials' in an environmental setting – because an ensemble of multiple materials will most likely behave differently compared with their parent components. For example, carbonaceous NMs (CNMs), such as fullerenes[24] and carbon nanotubes (CNTs),[25] show a high aggregation propensity due to their inherent hydrophobicity and strong van der Waals interaction forces; whereas, metallic nanomaterials (MNMs) (such as silver or zinc oxide), possess unique dissolution and complexation properties.[26,27] When combined, behavioural manifestation of metal–carbonaceous conjugates can either present dominant hydrophobicity or dissolution–complexation reactions; which will be influenced by the nature of conjugation. Thus risk evaluation of these hierarchical NHs will require systematic environmental studies.

This account presents an EHS-relevant definition of hybrid NMs, classifies the NHs, reviews the NH literature, and discusses the need for environmental studies. Probable environmental exposures of NHs and relevant altered fate, transport and toxicity as a result of transformed physicochemical and emergent properties are discussed. Challenges regarding the prediction of environmental behaviour of NHs from their individual component characteristics are also delineated. Overall, this account will serve as an environmentally relevant summary of the ever-expanding class of NHs, and hopefully will accentuate the importance of evaluating these nano-ensembles for enhanced risk assessment.

Defining nanohybrids

Definitional ambiguities are evident in NH literature[28] similar to the debate that exists for singular nanoscale materials (National Nanotechnology Initiative, see http://www.nano.gov/nanotech-101/what/definition, accessed 30 November 2014).[20,29]

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We attempt to clarify the nuances in the NH literature and also to make way for defining NHs from a EHS perspective. A strong tendency of claiming simple surface modification – with inorganic, organic and soft molecules – as hybridisation has been observed in the material science literature. For example, attaching a monomer or polymeric molecule onto a metallic nanoscale material has been claimed to form a NH[30,31]; similarly, large polymeric structures with conjugated inorganic–organic atoms–molecules are claimed to be NHs as well.[32] Although such minor surface modifications can enhance the material performance, it is likely that the parent physicochemical properties will be preserved and therefore they should not be considered as novel NHs for environmental evaluation purposes. Our rendition of an environmentally unique NH definition can be formulated as follows: *when more than one NM of unique chemical origin or differing dimensionality are conjugated by molecular or macromolecular links or physicochemical forces or when one nanomaterial overcoats another possessing a unique chemical identity or when complex soft molecules are engineered to chemically bind to NM surfaces*, *all to enhance the existing functionality or achieve multifunctional usage*, *can be defined as NHs.* This definition concurs with the literature definition of NHs[2–4]; however, it confines the material class to those NHs that will likely result in unpredicted and unique environmental fate, transport and toxicity.

Classification, synthesis and applications of nanohybrids

The growth of NH literature in the recent decade has been noticeable. To assess the importance of this emerging material class, a comprehensive literature search using the Web of Science database was performed (Fig. 1). A list of 758 peer-reviewed journal articles and 123 additional publications on speciality carbonaceous NHs (peapods, nano-onions, nanobuds, nano-horns, etc.) during the years 1998–2012 were identified. After careful screening on the basis of the NH definition, 752 articles dealing with NHs of environmental importance were selected and classified (Table S1, Supplementary material). The remaining 129 articles were not considered as they were deemed beyond the definitional scope. Overall, the literature search shows an exponential increase in publication number over the last decade (Fig. 1). This substantial published body of literature thus makes a strong case to carefully evaluate their physicochemical properties, relevant to environmental safety. The environmentally relevant classification of NHs is established based on the primary constituents. Four major classes of NHs are identified, namely: carbon–carbon, carbon–metal, metal–metal, and organic molecule-coated NHs (Fig. 2a).

The simple classification above should not deceive the readers of the inherent complexity of each of these NH classes; e.g. carbon–carbon NHs include rather simple CNMs such as single-walled and multiwalled carbon nanotubes (SWNTs and MWNTs), fullerenes and graphene sheets as the primary components, which are then conjugated with other carbonaceous entities[33,34] to form hierarchical structures. Similarly, carbon–metal NHs are formed by a conjugation of carbonaceous materials with metallic NMs.[35,36] Metal–metal NHs, however, are assemblies of individual metallic NMs[37] or are formed as core–shell structures of different metals[38] and metal oxides.[39] When metallic NMs combine with long chain polymers,[40] drug molecules,[41] cell-synthesised proteins,[42] DNA,[43] long chain organic molecules,[44] etc. they form organic molecule-coated NHs.

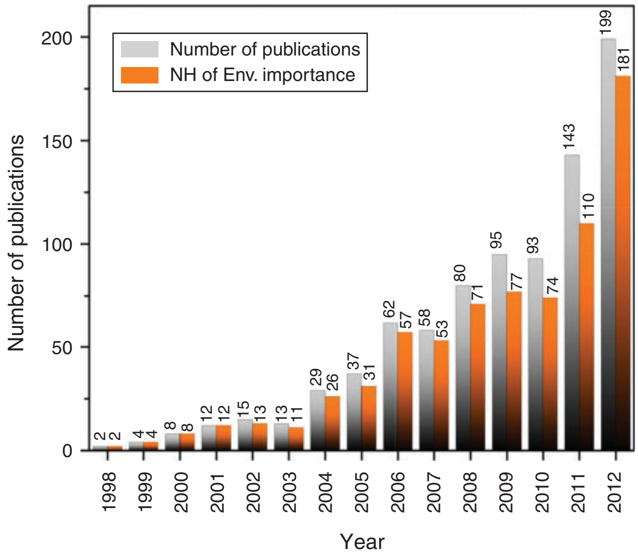

Fig. 1. Total number of publications per year from 1998 to 2012 using the Web of Science search engine searching for 'nanohybrid' or 'nano-hybrid', and total number of nanohybrids of environmental importance. Literature was selected when it originated from scientific articles and referred specifically to the following combination of keywords, special character (*), and search field (Title): 'Title = (nano-hybrid*) OR Title = (nanohybrid*)'. Title was selected as the search criteria to try and limit the results to those articles dealing particularly with nanohybrid research. Meeting abstracts, reviews and proceeding papers, were not included. More search combinations 'Title = (nano-horn* OR nanohorn*) AND Title = (hybrid*)', 'Title = (peapod* OR pea-pod*) AND Title = (hybrid*)', 'Title = (nanobud* OR nano-bud*) AND Title = (hybrid*)', and 'Title = (nanoonion* OR nano-onion*) AND Title = (hybrid*)' were used to identify some popular carbonaceous nanohybrids having speciality names because of their interesting morphologies.

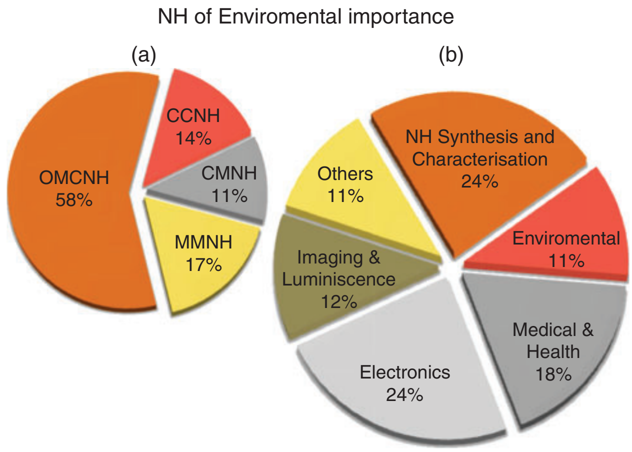

Fig. 2. Distribution of research article publications based on (a) environmental classification of nanohybrids and (b) relevant application premise.

The retrieved literature also provided information in relation to the application potential of the NHs (Fig. 2b and Table S2, Supplementary material). NH applications are categorised as follows: (1) electronic: solar and fuel cells, Li–ion batteries, semiconductors–superconductors–conductive materials, imaging and sensing applications; (2) environmental: contaminant sorption, membrane technology, catalytic–photocatalytic–electrocatalytic applications, and antimicrobial–antibacterial processes and devices and (3) medical: cancer treatment and

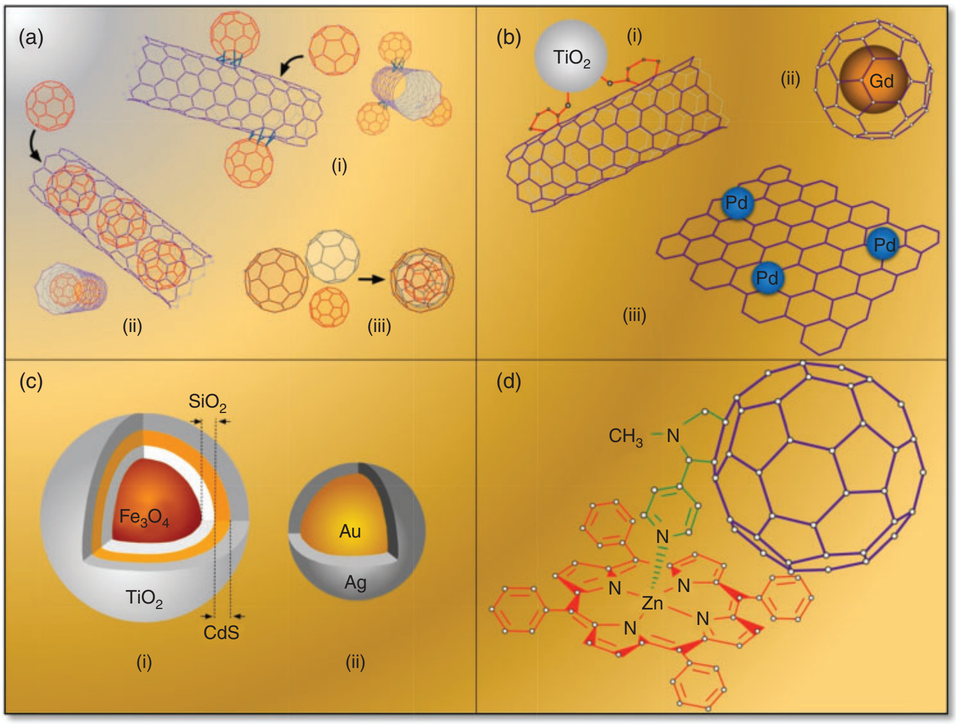

Fig. 3. Schematic representations of nanohybrids (NHs). (a) Carbon–carbon: (i) nanobud (fullerenes covalently bound to the outer sidewalls of single-wall carbon nanotube), (ii) peapod (fullerenes encapsulated inside a single-wall carbon nanotube), and (iii) nano-onion (multi-shelled fullerenes); (b) Carbon–metallic: (i) titanium dioxide nanoparticle conjugated with single-wall carbon nanotube, (ii) gadolinium encapsulated within a fullerene, and (iii) graphene decorated with palladium; (c) Metal–metal: (i) multimetallic core–shell structure of TiO_2–CdS–Fe_3O_4@SiO_2 and (ii) bimetallic Au–Ag core–shell; (d) Organic molecule-coated: zinc tetraphenylporphyrin coordinated with pyridyl fulleropyrrolidine (C_{60}Py-ZnTPP) dyad.

detection, biomaterial–biohybrids, delivery carriers and drug compound controlled release, UV protection, etc. Detailed and more specific usage of NHs along with their synthesis processes (Tables S3–5, Supplementary material) will be discussed in the following section in context of their environmental release and interaction.

Carbon–carbon nanohybrids (CCNHs)

Carbon-based NHs include combinations of three major carbon nanostructures – zero dimensional fullerenes (Fig. 3a), 1-D CNTs (SWNTs and MWNTs) and 2-D graphene and carbon nanohorns (CNHs). Open-ended hollow structures of CNTs or CNHs and cage-like fullerenes offer unique advantages to produce endohedral NHs as well as allow for generation of their exohedral forms.[45] Fullerenes or graphene (pristine or functionalised) when encapsulated within the CNTs or CNHs by thermal annealing,[34] by in situ growth from vapour-based deposition reactions[46] or by dispersion-assisted cavity filling processes, are called 'nano-peapods'.[47] Similar synthesis processes as well as the water-assisted electric arc process can create an exotic multi-layered hybrid fullerene structure named a 'carbon nano-onion'.[48–50] In contrast, the exohedral conjugation of CNTs, graphene and fullerenes employ long-range electrostatic or short-ranged specific interactions[51]; where conjugating molecules or polymers and covalent functionalities[52] drive the ensemble process. Such functionalisations include: oxidation of CNTs and graphene to attach polar carboxyl or hydroxyl surface groups (–COOH or –OH)[51,53] and attachment of chemically active molecules[54] or polymeric assemblies.[55] For example, fullerenes functionalised with porphyrin-derivatives are refluxed with acid-treated CNT–COOH suspensions to generate fullerene–CNT NHs by reaction between the carboxyl functionality on the CNT and amine-groups on the porphyrin molecules.[56] Producing seamless exohedral bonding between CNT and graphene[52] or CNT and fullerene[33] (nanobuds) through covalent modification is typically achieved by catalytic reaction processes involving vapour phase reactant molecules. Moreover, drop-cast,[57] spin-cast[58] and dipping[55] methods of these graphitic NMs can produce layered assemblies of NH-based thin films by electrostatic and non-covalent interactions.

The usefulness of hybridisation among CNMs has been obtained from multifunctional and improved properties emanating from individual species. Whereas graphene has a high reactive surface area, mechanical and thermal stability and high electrical conductivity, CNTs present unique electrical, mechanical, optical and charge carrying properties. Fullerenes, in contrast, provide high electron density and photoactivity. Thus, fullerenes when conjugated with graphene or CNTs can lead to improved organic photovoltaics[59] and optoelectronic devices, optical limiting and switching,[60] field effect transistors[61] by enhancement of the photoinduced electricity production, charge transfer and electron–hole shuttling,[61] singlet excited state quenching,[54] non-linear optical properties,[60] bandgap tenability,[45] etc. Hybridised graphene can act as a major candidate for transparent conducting films for optoelectronic and photovoltaic devices, which possess high surface area, conductivity, transmittance and low physical thickness as they conjugate with CNTs or fullerenes.[62,63] Such modifications also render their applications in various avenues; such as in electrochemical and biomolecular sensing,[64] structural health monitoring,[65] etc.

Carbon–metal nanohybrids (CMNHs)

Carbon-metal nanohybrid (CMNH) synthesis processes involve a combination of CNMs (CNTs, graphenes and fullerenes) with different metallic or metal oxide NMs[66] (Fig. 3b). CMNHs include assemblies with a variety of metallic NMs (MNMs) ranging from noble metals like Ag, Au, Pt, Pd, Ru, Rh, etc. to lanthanide series metals (La, Sc, Gd, etc.), metal oxide NMs (ZnO, TiO_2, SiO_2, Fe_3O_4, CuO, etc.), semiconducting quantum dots (CdSe, CdTe, etc.) and ligand-based metallic compounds (ferrocene). CMNHs can be synthesised following four key pathways – (i) filling the inner cavities of CNTs and fullerenes with MNMs using vapour deposition,[67] arc discharge,[68] thermal annealing[69] and wet chemical approach[70]; (ii) attaching MNMs onto CNT surfaces functionalised with pyrene, porphyrin derivatives[71] and similar linking molecules[72]; (iii) decorating CNM surfaces with MNMs by sol–gel,[73] hydrothermal[74] and aerosol-based processes[75] and (iv) in-situ growth of MNMs on CNM surfaces by electrochemical,[76] eletroless deposition[77] and redox reactions.[78]

Combinations of graphitic and metallic nanostructures result in the emergence of unique and synergistic electrical, optical, mechanical, catalytic, sensing ability and magnetic properties, which can be utilised for applications in various fields; e.g. chemical reactivity and catalysis,[79,80] organic photovoltaics and solar cells,[81] optoelectronics,[82] supercapacitors[83] and batteries,[84] proton exchange fuel cells,[85] gas and chemical sensing,[86] biomedical imaging,[87] environmental pollution monitoring and mitigation,[88,89] etc. The thermal and mechanical stability of CNTs and graphene with high active surface area are particularly promising in the development of Li–ion storage units with high efficiency, capacity and durability.[74] Similarly, antibacterial activities of TiO_2, ZnO or Ag are enhanced when conjugated with CNMs and thus facilitate their use in water treatment and other purification or detoxification applications.[89] Better sensors for gas, protein or chemicals (H_2O_2,[86] trinitrotoluene,[86] etc.) are being prepared using CMNHs utilising their enhanced sorption and electrical sensitivity. In contrast, endohedral metallofullerenes by themselves[90] or when encapsulated inside CNTs or CNHs[91] have great potential to be used as MRI contrast agents with extremely high water relaxivities – a holy grail in MRI contrast agent research. Such a wide range of applications of CMNHs has encouraged major research efforts in material development and their application necessitating extensive environmental implications studies.

Metal–metal nanohybrids (MMNHs)

Metal NMs, i.e. metals and metal oxides, when conjugated to form multi-metallic ensembles are classified as metal–metal nanohybrids (MMNHs, Fig. 3c). Metals can be grouped based on their functionalities; e.g. plasmonic (Au, Ag, Pt),[92] magnetic (Fe_3O_4, Fe_2O_3)[93] and semiconducting oxides (TiO_2),[94] quantum dots (CdSe, ZnS, CdTe, ZnO, PbS),[95] etc. Synthesis processes to prepare conjugated metallic NMs depend on the desired hybrid properties, structures and applications. Wet chemical processes involving reduction or thermal decomposition of metal salts are the most used synthesis techniques.[96] Wide variations of wet chemical processes include: polyol methods,[97] photochemical deposition,[98] electroless plating,[99] solvothermal,[100] hydrothermal,[101] sol–gel,[39] ion-implantation,[102] epitaxial growth,[103] etc. Vapour–gas phase processes, such as flame aerosol[104] and plasma-assisted deposition[105] are also commonly used. Core–shell based nanostructures can be formed by co-reduction[106] or sequential reduction,[97] where a metal NM previously formed can act as a 'seed' for subsequent growth of another NM with different chemical origin. Optical lithography is also combined with common methods to obtain patterned growth.[107] Template-based growth processes can be used to obtain hollow spherical,[108] porous[109] or tubular[110] structures. Matrix bound methods, however, utilise inorganic silica, the oil–water interface, and polymer or block-co-polymer matrices, where co-precipitation,[111] ion implantation,[102] emulsification[112] and reverse micellisation[113] processes grow NHs. Core–shell metallic layers sometimes include inorganic[114] or organic[115] linkers or spacers between them. Biogenic or green synthesis approaches for MMNHs have also been developed using natural extracts as solvents or reducing agents.[116] This is a synopsis of MMNH synthesis processes. Careful review of the existing literature will further elaborate on such techniques.

Property synergies in MMNHs allow their application in the diverse fields of photovoltaics and solar cells,[100] biomedical engineering and nanotherapeutics,[117] catalysis,[118] chemical sensing[119] and degradation[118] and bactericidal applications.[120] For example: co-axial Ag–TiO_2 core–shell nanowire arrays with high specific surface area and rapid electron transport can improve the electron collection efficiency for application in dye-sensitised solar cells.[100] Bioapplications, such as enhancement of contrast in MRI for disease[121] and pathogen detection,[122] photo-thermal destruction of these cells by near-IR irradiation[121] and separation of cancer cells from cell mixtures[8] have begun to employ plasmonic, semiconducting and magnetic metal NM-based MMNHs.[117] Plasmonic properties of Au and Ag are combined to produce high efficiency localised surface plasmon resonance (SPR) and surface enhanced Raman scattering (SERS) to detect disease-specific biomolecules.[96] Photoluminescent properties of semiconducting quantum dots have been shown to be enhanced when combined with magnetic (e.g. $Fe_3O_4 \cdot CdS$[123]) or plasmonic particles (e.g. Au–CdSe–ZnS[124]) and can be used for bioimaging or fluorescence microscopy. Conjugating TiO_2, Ag or ZnO with other metal NMs has also been shown to enhance photocatalytic activities and bandgap modulation combined with excellent charged separation and charge transfer processes have made them excellent candidates for organic contaminants degradation[109] and bacteria inactivation under UV to visible light irradiation.[120] Such diverse applications, particularly in biomedicine, increase the MMNHs' environmental relevance.

Organic molecule-coated nanohybrids (OMCNHs)

A wide body of literature identifies metallic, carbonaceous or polymeric NMs coated with organic molecules, biomolecules or polymers as NHs (Fig. 3d). Layer-by-layer hierarchical thin films have also been called NHs. Although such identification is debatable, environmental evaluation of NHs in this category should be pursued with reflection on already existing classical coated-NM studies. The literature on OMCNH involves a wide range of synthesis processes that include: physisorption of organic molecules,[125] electrochemical immobilisation of protein, enzyme or DNA molecules,[44] polymer grafting from or grafting to NM surfaces,[126] emulsification[40] and ion-exchange.[127] Such coated NMs are researched in the application areas of nanoelectronics,[125] photovoltaics,[125] chemical and bio-sensing,[128] bio-imaging,[129] controlled drug delivery[130] and cancer therapy.[131] CNMs are surface functionalised with porphyrin,[125] phthalocyanine[125] and other molecules to attain higher efficiency in charge transfer for photovoltaics and dye sensitised solar cells. Similarly, magnetic or plasmonic particles are grafted or coated with organic polymers, such as polyethylene glycol (PEG)[132] and poly(vinyl pyrollidone) (PVP)[133] to enhance their solubility for enhanced bio-imaging, drug delivery or sensing. Metallic NMs are also attached to organic fluorophores for enhanced tagging and contrasting.[129]

Most of these materials appear to be merely coated-NMs for environmental purposes, thus might not require systematic and independent environmental evaluation for accurate risk estimation. Already established environmental fate and toxicological literature have focussed on physisorbed coatings. For example, citrate, PVP, PEG, gum arabic, copolymers, etc. are typically adsorbed onto the NMs to enhance dispersion in a desired solvent and have been studied for environmental implications.[134–137] However, the recent surface modification of NMs are performed with rather complex supramolecules or heterocyclic structures (e.g. porphyrins), which are covalently bound to the NM surfaces.[138–140] As per the NH definition, chemically bound coatings of this nature will lead to altered nano-EHS behaviour. For example, heterocyclic porphyrins not only provide stabilisation to NH dispersions but will also provide excellent electronic charge transfer properties[138] and antimicrobial capabilities.[141] Moreover, conformational differences of organic molecules or polymers present on the NM surface are known to present unique fate, transformation and toxicity behaviour.[142] Systematically evaluating nano-EHS behaviour of these complex chemically coated NHs is thus imperative. Existing environmental literature on NMs with physisorbed coatings will enhance the understanding of OMCNH environmental behaviour.

Environmental interaction of nanohybrids

The novelty in NH ensembles lies in multifunctionality, resulting from a non-linear combination of advantageous properties of each of the component nanostructures.[45,75] Such assemblies not only contribute to enhanced functionality but also present unknown and unique physicochemical properties, which will likely cause unpredictable environmental behaviour from their release and exposure. However, while researchers focus on the merits of such NHs, their potential toxic and environmental implication studies have gained attention only recently and require a significant systematic approach.

Eco-toxicity of singular NMs and their microbial and organismal uptake are known to be influenced by material-specific physicochemical properties such as size,[143] shape,[144] aggregation state,[145] surface functionality and coating,[146] reactive oxygen species (ROS) generation capability,[143,147] photoactivity,[148] crystallinity[149] and dissolution[26,145] of metal NMs and bandgap[150] of metal oxide NMs. When NMs are exposed to the environment they experience aggregation in aqueous media[25] and deposition onto solid surface[151] and porous media,[152] which contribute to their mobility in the aqueous environment. Moreover, transformation of NMs[153] can occur by sorption of geo- and bio-macromolecules, reaction with chemical species (presence of reactive ions, ozone or oxygen) and by solar irradiation in case of photoactive NMs – contributing towards NM fate and toxicological effects. The fate, transport and transformation of NMs in the environment are also highly dependent on the intrinsic NM properties. As these NMs conjugate to form hierarchical ensembles, their physicochemical properties alongside their environmental behaviour and toxicity response will likely be altered. How such alterations will occur depends on the mode of conjugation as well as the application type, influencing their release and exposure. Here the altered fate, transport, transformation and toxicity of some common NHs will be discussed to lay out the uncertainties in nano-EHS.

Fate and transport

Singular NMs, either carbonaceous or metallic, have been studied extensively to evaluate their aggregation, deposition and transport behaviour. Such behaviour has been characterised in relation to their physicochemical properties and major mechanisms are elucidated in terms of electrostatic interactions,[24,151] van der Waal's attraction forces, steric hindrances contributed by physical morphology and unique material-specific forces, such as magnetism (in case of iron-based NMs[154]) or chirality.[155] However, conjugation of two or more NMs will likely alter contributions from these forces, resulting in uncertain stability and mobility of the NHs.

Carbon nano-peapods, that are highly attractive for solid state electronics[156] or MRI contrast agents,[91] are prepared by encapsulation of fullerenes (C_{60}, C_{70} or higher order fullerenes) inside CNTs or CNHs. Such conjugation exhibits bandgap tuning[157] and electron density differences.[158] Such alterations occur as a result of SWNT diameter changes upon conjugation as well as of the entrapment of fullerenes that causes overlap of electron clouds.[157,159] Peapod formation often involves SWNT oxidation in the presence of acid mixtures that forms surface defects and also causes shortening of the SWNT length.[159] Such surface property changes will likely influence van der Waals and electrokinetic interactions of nano-peapods (Fig. 4a). For example C_{60}@SWNT peapod bundles can have stronger van der Waals forces compared with C_{70}@SWNT bundles as demonstrated by spectral characterisation.[158] Moreover, other higher order fullerenes also induced size-dependent electronic structure variation in peapods followed by van der Waals' disparity.[160] Furthermore, fullerene encapsulation may also result in increased mechanical strength of SWNTs,[161] resulting in stiffer tubules.[162] Altered van der Waals forces and shorter, stiffer tubes, will likely demonstrate unique environmental behaviour compared with the component fullerenes and SWNTs.

Similarly, emergent properties, such as dimensional modifications, occur as a result of hybridisation. For example, nano-peapods mask the presence of zero-dimensional fullerenes[158] and two-dimensional graphene[163] inside one-dimensional CNTs; whereas their exohedral conjugation results in unique three-dimensional configurations. Covalently bonded fullerenes on the surface of the graphene[60] or CNTs[33] (in case of nano-buds) can have debundling or intercalating effects and can result in enhanced stability. However, such dispersion enhancement can also be compromised by a superimposed or combined inherent hydrophobicity of the CNMs.[45] Exohedrally attached

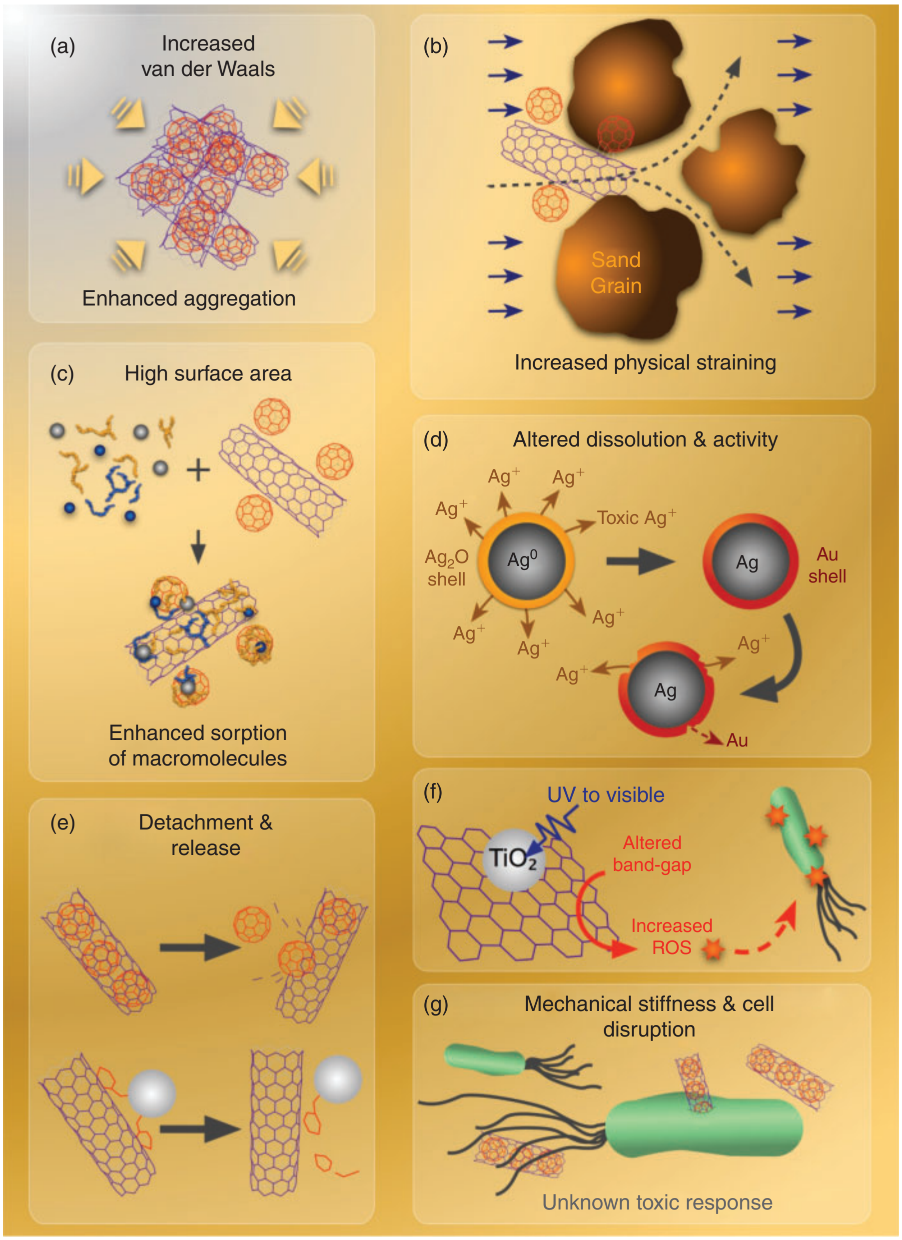

Fig. 4. Plausible environmental interactions of nanohybrids (NHs). (a) Increased van der Waals attraction forces in fullerene–carbon nanotube (CNT) peapods may lead to enhanced aggregation. (b) Exohedrally conjugated fullerenes with CNTs may enhance physical straining during transport through porous media. (c) Ag–Au core–shell NHs may show decreased dissolution and enhanced chemical stability. (d) Exohedral conjugation of CNTs and fullerenes may provide more surface for sorption of geo- and bio-macromolecules. (e) Fullerenes may be released from nano-peapods during transformation and result in different surface chemistry compared with component NMs. (f) Bandgap alteration of TiO_2 by conjugation with graphene can increase reactive oxygen species (ROS) production under visible light, leading to enhanced nanotoxicity. (g) Increased stiffness as a result of hybridisation may induce greater cellular interaction, uptake and membrane disruption.

fullerenes may increase physical straining during their transport through porous media (Fig. 4b). Altered stability and porous media transport will likely lead to uncertain NH fate and transport in the natural environment.

Understanding of NH aggregation and transport necessitates resolving the following key questions. Will altered electrostatic or van der Waals forces dictate aggregation or deposition of exohedrally hybridised nanotube–fullerene conjugates? How will metal NMs change the NH surface interaction? What will be the roles of the linking molecules? How will overcoating influence the aggregation and deposition behaviour of metallic NHs? Such questions require immediate attention to address uncertainties from the emerging properties of NHs.

Transformation

Upon environmental release, NM characteristics can be altered by various transformation processes. For example, fullerenes and CNTs can undergo various transformation processes that include: reaction with atmospheric oxygen or ozone,[164] ultraviolet (UV) or solar light mediated photochemical change,[165] adsorption of macromolecules[166] and natural organic matter (NOM).[165,167,168] Similarly, TiO_2 and ZnO transformation can also occur under UV-exposure and during interaction with geo- and bio-macromolecules.[169] These transformations take place because of the NMs' inherent photoactivity, chemical reactivity and sorption ability; which are functions of their size, shape, surface charge and chemistry.

NOM sorption on carbonaceous and metallic NMs showed enhanced stability in aqueous media.[166,169] After NOM sorption, TiO_2 has exhibited reduced photoactivity and suppressed ROS production.[169] However, unknown alterations of transformation results may be experienced by hybridised NMs. For example, the photoactivity of TiO_2 (under visible light) has been shown to enhance upon conjugation with CNTs or graphene, because of lowering of the bandgap energy.[73,170] Such enhancement is attributed to the synergy in electronic properties between titania and carbon nanostructures; e.g. small-sized TiO_2 particles on CNT surfaces reduce the electron–hole pair recombination rate and thus enhance the photoactivity.[73] Moreover, the high electron transport ability through hollow CNT structures and conductive graphene – e.g. photoactivity transfer from UV region to visible range – is also known to improve photodynamic activity.[171,172] Similarly, a substantial increase in the available surface area during hybridisation can also invoke excellent sorption properties[75]; as demonstrated in the case of flowerlike hierarchical structures of TiO_2 on CNTs.[173] Sorption of geo- and bio-macromolecules on CNTs can also be enhanced by exohedral attachment of fullerenes, which will likely add to available sorption sites (Fig. 4c).[33] Increased adsorption can enable higher coverage of the NH surfaces with geo- and bio-macromolecules and thus can alter the subsequent fate, transport and toxicity.

Dissolution and reaction with inorganic species such as sulfide (S^{2-}) or chloride (Cl^-) ions in the aquatic environment are two important transformation processes for metallic NMs, such as Ag[26,145] (or ZnO[27] and CuO[174]). These transformations are governed by the inherent solubility, reactivity and sorption ability of AgNMs, influenced by physicochemical characteristics such as: size,[175] shape,[26] surface structures,[26] surface chemistry[176] or coatings.[134] However, hybridisation of chemically active AgNMs with a relatively inert gold overcoating can reduce Ag^+ dissolution (Fig. 4d).[177] Electron transfer properties of a Ag-core through to a Au-shell were shown to increase the oxidative and chemical stability of these NHs.[178] On the contrary, an 18 times higher catalytic activity was observed for Ag–Au core–shell structures when compared with monometallic Au particles.[179] Thus, overlapping of chemical or electronic characteristics can have an unprecedented effect on the transformation behaviour of Ag–Au NHs.

In addition to the above discussed probable uncertain alterations of transformation behaviour, some key questions arise that necessitate systematic transformation studies of NHs. What will the relative roles of parent materials be in such transformations? Will there be new transformation processes resulting from the instability of NHs in the environmental matrices – e.g. detachment of TiO_2 from CNT surfaces or release of fullerenes from nano-peapods (Fig. 4e)? How does the release of NMs from NHs alter their previously predicted environmental interactions? Such questions need to be researched to better understand NH environmental transformation.

Toxicity

Substantial literature exists regarding the toxicity of singular NMs, delineating mechanisms and correlating the effects with physicochemical properties. Several carbonaceous (fullerene,[180,181] CNT[182] or graphene oxide[183]) and metallic NMs (Ag,[26] TiO_2,[149,184] ZnO,[184] CuO[184]) are known to illicit toxicological effects on biological species. The key mechanisms associated with such toxic responses include: ROS mediated oxidative stress,[143] direct interaction of metal NMs with cell membranes,[144] lipid peroxidation,[185] ROS independent protein oxidation,[186] dissolution and relevant reactive membrane or enzymatic damage,[26] asbestos-like inflammation by CNTs[187] and physical rupture of cell membranes.[183] Material characteristics such as size and surface area,[188] shape,[144] crystalline structure,[144] surface coatings,[189] aggregation state[145,190] and electronic properties,[150] have been known to influence NM bioaccumulation and toxicity. However, the likelihood of altering the toxicity following NM hybridisation has not been well studied. Among few recent efforts, most are directed towards beneficial antimicrobial applications but only a handful of studies report concerns regarding NHs' harmful implications.[4,191] For example, bimetallic conjugation of non-toxic parent materials Au and Pt with variable compositions has generated antimicrobial responses against *E. coli*, *Salmonella choleraesius*, and *Pseudomonas aeruginosa* by cell membrane damage and incremental increses in the intracellular level of adenosine triphosphate (ATP).[192] Recent studies involving graphene–ZnO[193] and graphene–Cu[194] NHs showed increased toxicity in comparison to their parental components towards a model organism transgenic *Drosophila melanogaster* as demonstrated by enhanced lipid peroxidation and apoptosis. On the contrary, the presence of a silica-based shell structure reduced ZnO toxicity towards *E. coli*.[195] A comprehensive toxicity evaluation of *E. coli* on exposure to iron-based bimetallic NHs has shown differences in toxicity based on the presence and type of a second metal.[191] Component dependent toxicity was observed as bare Fe, Fe–Cu and Fe–Ni showed comparable toxicity whereas Fe–Pd and Fe–Pt presented with significantly lower toxicity. These differences were attributed to diverse interactions of these NHs with the cellular membrane as a result of differences in surface charge, particle size and reactivity, caused by conjugation. This evidence of altered bio-compatibility hints towards the necessity of a systematic and mechanistic exploration of NH toxicity.

A recent study[196] involving colloidally stable graphene–TiO_2 NHs showed enhancement in photocatalytic ROS generation under visible light irradiation, whereas pristine TiO_2 showed photoactivity, only in the UV spectrum (Fig. 4f). This has been possible because of the excellent charge separation abilities of graphene; which could reduce TiO_2's bandgap in the hybridised form. However, the NHs didn't exhibit enhanced toxicity compared with singular TiO_2 to model aquatic organisms, *Daphnia magna* and *Oryzias latipes* (Japanese Medaka fish). The lack of toxicity may be explained by ROS quenching, which resulted from rapid aggregation of the NHs in high ionic strength culture media. Hybridisation of NMs thus has been shown to alter nanotoxicity.

Emergent properties, such as changes in surface roughness and mechanical stiffness, have shown to be responsible for differential cell–NH interactions; as was observed in the case of multicomponent hierarchical NHs prepared by sequential coating of functionalised CNTs with Ag, DNA, and poly(vinyl alcohol) (PVA).[197] Similarly a stiffness increase attributable to fullerene encapsulation inside CNTs may also have physical interaction mediated toxicological consequences (Fig. 4g).

Thus questions may arise when combining graphitic nanostructures with metallic ones. Will emergent mechanical properties dominate the NH toxicity? How will metal dissolution be altered and mediate nanotoxicity? Will alteration of dimensionality, e.g. from 2-D (graphene) to 3-D (fullerene–graphene), influence shape-dependent toxicity? Thus the potential environmental interaction of emerging nanoscale hybrid materials are ostensibly unique, complex and may not be predictable from simple one or two parametric combinations of physicochemical characteristics; addressing the aforementioned questions can be a starting point for NH toxicity evaluation.

Conclusion and perspectives

This article has reviewed the NH literature and has highlighted the emergent properties of this new ensemble material class. The novel properties already emerging from conjugation and overcoating are altering fundamental physicochemical properties. Such differences will alter EHS behaviour of NHs, thereby warranting careful consideration and strategising for systematic evaluation. Their environmental exposure appears to be more eminent when NH-laden real-world applications are marketed in electronics (e.g. silicon oxycarbide–CNTs[198] and CNF–lithium titanate[199] NHs for Li–ion electrodes), in dentistry related products,[200,201] antimicrobial coatings[202] and protective devices[203] (e.g. Ag–TiO_2) and in bio-imaging or graphene-based MRI contrast agents.[204,205] On the one hand, NHs such as Ag–Cu, Fe–Ni or Ag–In are being commercially synthesised as research-grade materials (US Research Nanomaterials, Inc., see http://us-nano.com/contact_us, accessed 27 November 2014), whereas on the other, invention disclosures and patents[206,207] on lithium-ion batteries (graphene–VO_2), supercapacitors (graphene–Mn_3O_4) and solar cells (CNT–fullerenes), are enabling active technology transfer. The key issue is not about the NHs' unique EHS behaviour, but about how and by which attribute such alteration will affect nano-risk determination. The review identifies the following concerns in regard to NH EHS: do the NHs of concern possess unique properties to behave unpredictably in the environment? What will be the form of release for these NHs? Are these NHs going to be environmentally stable; i.e. will they retain their hybrid ensemble entities or detach to individual NM components during environmental exposure? What functionalities or derivatives of these NHs should be studied?

The next generation NHs are headed towards further complicated hierarchical structures, where NMs from more than two chemical origins are being conjugated; e.g. CdS/ZnS–Au,[124] MWNT/Ag–TiO_2[208] or CdS–TiO_2–Fe_3O_4.[209] Thus a possibility of infinite combinations and functionalisation of NMs presents an almost unmanageable matrix to evaluate their environmental risk. Thus robust strategies for handling this large material set are necessary. Strategy formulation can choose material properties, their structural integrity during environmental exposure or target specific groups based on aggravated risk potential realised from the component behaviour. However, such strategies necessitate detailed and systematic studies before formalisation.

Supplementary material

Table S1 includes the annual number of publications regarding NHs from 1998 to 2012. Table S2 includes the total number of publications categorised according to the potential applications. Table S3 includes all the listing of the retrieved articles, classifications according to the material types, their usage, and research areas. Table S4 includes specific NH class examples and their synthesis processes. Table S5 includes specific NH class examples and their corresponding potential application premises.

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