Submicron Porous Materials

Paolo Bettotti
Editor

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Preface

Wherever he saw a hole he always wanted to know the depth of it.
To him this was important.

J. Verne, *Journey to the Center of the Earth*

Interfaces mediate our daily way to interact with things and at macroscopic surfaces they are the most common day-to-day experience. Flat surfaces are fundamental in many applications, but the mastering of material's porosity is even more fascinating as it is an effective way to tune both type and strength of materials interactions. This is the main reason why porous materials are very important in science and technology nowadays.

Any material is porous if we consider that its crystallographic unit cells might act as cages for smaller molecular species. More generally, and with the exception of ceramics and metals annealed at high temperature, nearly all materials show a porous structure with a typical length scale much larger than their unit cell. Porosity induces peculiar characteristics to surfaces and largely modifies their properties compared to those of the bulk states: wetting, tribology, chemical reactivity, and optoeletronic properties are only a few significant examples of characteristics modified by the presence of porosity.

Very often, the interest in controlling material's porosity arises because of the new surface-mediated properties created in dense materials upon their porosification.

As stated above, nearly any kind of material can be rendered porous. Generally, organic-based materials allow large flexibility in their synthesis conditions and a good control over their porous structure. In this broad class of materials, porosity is introduced either by adding porogens or by phase separation. Porogens are molecular species (or colloids) that are inserted during the material preparation and successively removed (often) exploiting their thermal degradation and removed as gas species. Otherwise, the pore can be formed by exploiting phase separation reactions, followed by the removal of one of the species to form the voids. On the other hand, some inorganic materials (mainly silicon, III-V semiconductors, alumina and titania) show peculiar corrosion processes that enable the formation of well-controlled porous structure: under controlled etching conditions these materials spontaneously form self-arranged lattices of pores, sometimes with rather good periodicity. Compared to random 3D porous structures, their highly ordered pores permit a better control on applications that require a well-known pore length or highly homogeneous volumetric porosity (for example in some separation techniques). Moreover, they show a greater resistance to thermally and chemically harsh environments. Hybrid materials sit in between the organic and inorganic families. They are formed starting from organic precursors that polymerize to form an inorganic network.

Porous materials might have an extremely high specific area (up to thousands of $\frac{m^2}{g}$) and this fact is exploited to increase their performance in a number of different applications:

- in sensors, a large specific area increases the density of the binding site and thus decreases the minimum detectable signal;
- in thermoelectrics, porosity is a way to decrease thermal conductivity and increase the potential difference created across the junction;
- in catalysis, a porous support maximizes the interaction between the catalyst and the reagent, thus increasing the overall efficiency of the reaction;
- in energy storage, a large porosity is required to maximize the storage capacity;
- in photovoltaics, porous materials are used to decrease reflectance and increase photon absorption probability and thus cell efficiency.

But the simple value of the specific area is not sufficient to completely qualify the properties of a porous material. In fact, it is of fundamental importance that porosity has to be accessible to the species of interest (e.g., they have to be able to reach the active sites). Thus, a fine control over pore size distribution is needed to optimize the material properties, and the design of hierarchically structured porous materials is an important step to achieve an optimal use of the entire material surface.

IUPAC nomenclature defines nanopores as smaller than 2 nm, mesopores in the range 2–20 nm, and macropores greater than 20 nm. Such classification is quite limited because how a porous material behaves largely depends on the ratio between the pore size and the dimension of the species that interact with it, rather than on the absolute pore size. Thus, in this monograph we use the term submicron to underline the importance of the mesoscale, intended as the length scale where the property is not determined by molecular scale details, yet it is different from the one shown by the bulk state. Mesoscale physics addresses such an intermediate scale where the material's properties cannot be described by effective medium theories, yet they are not determined by the fine details of molecular species involved.

This monograph treats a selected series of topics about fabrication, characterization, and applications of topical porous materials. The first two chapters deal with the use of carbon-based porous materials in catalysis and water treatment of silica- and carbon-based materials. Chapters 3 and 4 cover two types of organic-based porous materials. Chapter 5 introduces porous anodic alumina as an inorganic material with highly ordered pores. Chapters 6 and 7 treat silica and titania based sol-gel materials. Chapter 8 describes the basics of porous silicon fabrication, its use in optical sensing, and drug delivery applications. Chapter 9 shows how thermal transport is affected in porous materials. Chapter 10 describes how to model diffusion in porous materials. Chapter 11 describes a peculiar spectroscopic technique to characterize material porosity.

A final note about the etymology of the word “pore”. It comes from the Greek and means passage, to go beyond. I hope this monograph to be a useful document to go beyond our current mastering of material’s porosity at the submicron scale and to help both nonspecialists and scientists to understand and develop innovative porous materials.

Trento, Italy Paolo Bettotti
2016

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