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Editorial

Hierarchical nanostructured materials

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Hierarchical materials encompass a wide range of natural and man-made materials having prominent architectural features in various levels at successively changing length scales. The feature in each level is locally diverse that reflects the contribution of structural hierarchy of a system [1-3]. The organization of a hierarchical material system in homogeneous or heterogeneous way is also known in the domain size from macroscopic to atomic/molecular levels [2]. There are many examples in macroscopic level of hierarchical material system. As for example, a French civil engineer and architect, Alexandre Gustave Eiffel designed the tower in Paris, France in the year 1889, well known as Eiffel tower, named after his name on the basis of idea of macroscopic hierarchical framework. In this design [2], the material hierarchy reflects on its relative density, ρ/ρ_0 (where ρ is the bulk density and ρ_0 is the density of the material) and this ratio can also be used to characterize multi-phased porous materials of different dimensions. The hierarchical system can also be found in the natural system such as leaf, muscles and lungs. It is important to note that the hierarchical structures in polymers, composites, biological, inorganic crystalline and fibrous materials are also known today [1-3]. However, understanding the effects of structural hierarchy, one can synthesize new materials with advanced properties that can also be tailored for different applications. In this respect, the hierarchical nanostructures (HNSs) can be considered as advanced materials for their remarkable properties. These nanostructures in the diameter size upto 100 nm draw special attention for promising applications in various areas such as energy storage and conversion, adsorption, catalysis, sensing and so on. The HNSs can be formed from nano-building blocks [4-6] and according to dimension of the nano-building blocks, the HNSs can be classified into the different assembled blocks from 0-D nanoparticles, 1-D nanowires, nanorods and nanotubes to 2-D nanosheets [5,6]. These HNSs having well-aligned porous structures can provide high specific surface area. On the other hand, colloidal nanocrystals in solution phase can also able to self-organize in three dimensional (3D) nanostructures (e.g. microspheres, nanoflowers) by nanocrystal aggregation into chain formation by self-assembly. Moreover, different hierarchical nanostructures can be formed through combinational growth of 0-D, 1-D, 2-D and 3-D structures. Hollow nanostructures of 1-D or 3-D morphologies having less agglomerated configuration are also very attractive with respect to their high surface area. Now-a-days, metal oxide semiconductor (MOS) based nanocomposites have sparked a greater attention to develop desirable properties at different nanoscale building blocks to improve mechanical, optical, electronic, optoelectronic or magnetic properties. Moreover, the properties can further be enhanced through construction of MOS based binary, ternary and quaternary nanocomposites. This is because a particular property of a composite material can be generated from the interfacial interaction that happened between the components of a nanocomposite and the resultant property of the composite is not the sum of the individual contribution of the components [7].

The hierarchical nanostructured materials can be synthesized by templating method using hard particles. In general, the most useful hard templates are monodispersed silica particles and polymer latex colloids. These are useful due to their narrow size distribution [8]. It is noted that other colloidal systems like carbon spheres and nanoparticles of metals and metal oxides are also useful as hard templates for synthesis of hollow nanostructures. However, in a typical synthesis process, the removal of a template can be performed through selective etching by appropriate solvents or calcination at high temperature. On the other hand, soft-templating approaches are also useful for synthesis of well-defined nanoporosity in hard ceramics. In this regard, a soluble molecule can act as structure directing agent (SDA) for suitable pore structure formation. There are interplay of non-covalent, attractive and repulsive forces like van-der-Waals and Coulombic interactions that can exist between the SDA molecules, causes their self-assembly. It is interesting to note that these self-assembled structures can act as

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templates for the construction of desired structure of a material. In general, the SDAs are amphiphilic molecules having cationic, anionic or non-ionic surfactants especially block co-polymers and other supramolecular micelles, polymer aggregates/vesicles or gas bubbles. This soft-templating approach can be a potential one for the synthesis of ordered porous hierarchical materials. It is worthy to note that by combing of the soft and hard templating processes, hierarchical macro/meso porous nanostructures can also be synthesized [8]. However, template-free processes are most desirable for controlling the size of hierarchical structures [9]. In this regard, one-step self-templated methods by Ostwald ripening [10] can successfully be applied to synthesize hierarchical hollow structures for a wide range of materials. In this case, beside Ostwald ripening, self-assembly and self-aggregate mechanisms are generally observed in the hierarchical nanostructured materials. On the other hand, hydrothermal or solvothermal processes can be adopted for templating or template-free processes that require relatively high pressure and post annealing at higher temperatures for improving the crystallinity of materials. However, in several cases the hydrothermal process has many limitations for understanding the mechanistic principles in a rational synthesis strategy [11]. In this respect, the low temperature solution process is found to be advantageous over the others for the synthesis of several hierarchically nanostructured materials.

Now-a-days, much attention has been paid for the synthesis of hierarchical nanostructures of mixed metal oxide semiconductors such as CuO-TiO_2, Fe_2O_3-SnO_2, Fe_3O_4@TiO_2, SnO_2-Fe_2O_3, SnO_2-ZnO, ZnO-CuO, ZnO-NiO, ZnO-TiO_2 etc. [12-18]. These hierarchical heterostructures are formed via assembling of two different metal oxide semiconductors with low-dimensions. It is worthy to note that the materials can provide an ultrahigh specific surface area. On the other hand, MOS-carbon (carbon nanotube, graphene, and conducting polymer such as polyaniline (PANI), polypyrrole) hierarchical nanocomposites are potential functional materials [19-28]. Among which MOS-graphene/polyaniline nanocomposites are very important for both basic and applied research due to their extraordinary electrical, optical and mechanical properties. For example, the graphene/PANI-based MOS nanocomposites can possess unique mechanical, electronic and electrochemical properties [19-28] as well as these can be used as electrodes for energy storage applications. In the materials, the conductive phases are required to enhance electron transport and electrical contact in the active materials. Moreover, hierarchical nanocomposites can exhibit fast and efficient change transport through porous frameworks with high surface area for applications in energy storage, separations, sensing and catalysis. In this respect, different hierarchical structures of MOS-graphene and MOS-PANI composites had been synthesized by several researchers [19-28] among which graphene/PANI based hierarchical MOS composites, such as reduced graphene oxide-ZnO, NiO-reduced graphene oxide, TiO_2-graphene, iron oxide-graphene, CuO-graphene, SnO_2-graphene, MoO_2-graphene, Fe_2O_3@PANI, TiO_2-PANI, PANI-MnO_2 are very important for applications in diverse areas [19-28]. Beside, the binary hierarchical composites, hierarchical structures of MOS-based ternary or quaternary composites exhibit new or enhanced physicochemical properties and these are highly promising for chemical catalysts, energy storage and conversion, sensors, optoelectronic devices and so on [30-36]. In this respect, researchers synthesized hierarchical MOS-based ternary composites such as graphene-nanotube-iron, porphyrin-ZnO-reduced graphene oxide, Co_3O4@PPy@MnO_2, TiO_2–SnO_2–graphene, Co_3O_4@Pt@MnO_2, etc. for different applications [29-33]. Moreover, hierarchical MOS-graphene-PANI ternary nanocomposites [34-36] can be promising for further improvement on the morphological and microstructural aspects for enhancing electrical, optical and mechanical properties. An interesting work of quaternary composite had already done by Wang et al. [37] for synthesizing the hierarchical graphene@Fe_3O_4 nanocluster@carbon@MnO_2 nano sheet array nanocomposites which showed significantly enhanced microwave absorption property. Adopting cost effective and facile template/surfactant free low temperature (95^{o}C) solution process, our research group also synthesized hierarchical ZnO based graphene/polyaniline nanocomposites having advanced functional properties for various applications [38-40]. Among the hierarchical structures, solid, core-shell structured hollow and hollow microspheres of ZnO-graphene nanocomposites have been synthesized by varying graphene oxide (GO) to zinc acetate dihydrate weight ratio of the precursors and the reaction time. It is noted that in an optimized content of graphene, the material showed an improved textural property (like surface area, porosity) with enhanced visible light harvesting capability. The sample also showed lower photocorrosion behaviour that resulted long term photostability towards efficient photocatalytic degradation of organic pollutants (such as organic dyes) as well as photoelectrochemical water splitting. This can possible due to the existence of chemical interaction of graphene with pristine ZnO nanoparticles in the hierarchical nanostructured materials [39]. In addition, to advance the properties of ZnO-graphene nanocomposites, we synthesized the three dimensional nanoflowers [40] from ZnO, graphene and polyaniline (*in situ* polymerization of aniline monomer) ternary nanocomposite system. The material showed enhanced electrochemical activity for energy storage application. This simple fabrication strategy can open an avenue for development of other inorganic-organic hybrid hierarchical nanostructured materials for advanced applications.

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