Porous Organic-Inorganic Hybrid Materials: New synthetic Approaches, Engineering and Applications

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The idea of compounding inorganic matter such as metal oxides (MO) into porous organic polymer matrices is not new, as numerous organic−inorganic hybrids and a variety of approaches to create porous structures have been combined in recent decades. Approaches for preparing porous organic-inorganic hybrids include the sol-gel method, electrospinning, chemical vapor deposition (CVD), nanocasting, or template-assisted synthesis, to name a few. However, the choice of a particular synthesis method depends on what specific properties we want to tune/control in a porous hybrid, either the porous structure, the chemical composition, or the spatial distribution of nanoparticles. The ability to design co-continuous organic–inorganic hybrids with a hierarchical porous structure on multiple-length-scales that simultaneously integrates different chemistries is a new trend in materials engineering.

Among the approaches to generate hierarchically porous hybrids, polymerization of high internal phase emulsion (HIPE) templates has lately gained particular attention. The reason for its popularity is that both the chemistry of the polymer backbone and the porous properties, i.e., pore volume, pore size distribution, and degree of three-dimensional (3D) interconnectivity, can be easily tuned and controlled. A number of methods have been developed to incorporate MO nanoparticles (NPs), into a porous polymer matrix, which can be divided into two main strategies. The first is to impregnate the surface of the pores in the preformed polymer with a solution containing the precursor of the desired MO-NPs. A second is to use preformed MO-NPs as a filler in a polymer precursor, in which NPs remains embedded in or attached to the surface of the voids after polymerization. However, both strategies are associated with difficulties, such as aggregation-related defects, homogeneity, lack of control over the location of the NPs (surface vs. bulk phase), batch-to-batch reproducibility, and in some cases, even clogging of the interconnecting pores by the larger NP agglomerates. Therefore, the preparation of functional organic−inorganic hybrids still remains a challenging task, as efficient hybridization is required to achieve synergy of the components at the hybrid interface, otherwise, it is merely a physical mixing.

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In this contribution, in the first part, we focus on silica aerogel-, MOF and zeolites-filled porous hybrids in which mesoporous aerogel, or microporous MOF/zeolites homogeneously fill a macroporous polymer matrix. In a first example, a hydrosol-in-oil HIPE was used, in which monomers were polymerized in the external phase and tetramethyl orthosilicate was hydrolytically condensed in the internal phase, resulting in a highly porous hybrid structure filled with silica aerogel [1]. In a second example, particle-stabilized water-in-oil HIPEs were used as structural templates, a process known as Pickering stabilization, in which various metal oxides (MO) such as MgO, ZnO, or Co_3O_4 or zeolites were fixed in the polymer after polymerization. Subsequently, the MOs were in-situ transformed into the corresponding MOF isostructures by the process called secondary-recrystallization occurring at the metal oxide-polymer interface [2,3,4]. Such co-continuous inorganic-organic hybrid materials form a hierarchically porous system that was advantageously used for thermal insulation or CO_2 capture. In the second part, porous polymer matrices and high-precision of atomic-layer-deposition technique (ALD) were combined, and we succeeded in homogeneously coating the entire surface of the pores in porous polymer beads with TiO_2-, ZnO- and Al_2O_3-based nanocoatings [5]. Parameters such as nanocoating thickness, growth-per-cycle (GPC), and metal-oxide (MO) composition were systematically controlled by varying the number of deposition cycles and dosing time under specific process conditions. Finally, the ALD-derived TiO_2-based porous hybrids were used for the photocatalytic oxidation of an aqueous bisphenol A (BPA) solution.

Keywords: Organic−inorganic hybrids, High internal phase emulsion templating, CO_2 capture, Heterogeneous photocatalysis.

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