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The co-micelle/emulsion templating route to tailor nano-engineered hierarchically porous macrospheres

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ABSTRACT

Here we present a new class of nano-engineered hierarchically porous materials in which the entire framework is mesoporous. This material is engineered into macrospheres of controllable size with a highly interconnected macropore network to facilitate molecular diffusion access. To achieve this, a new co-micelle/emulsion templating (co-MET) technique was developed. In this technique a block copolymer plays the dual roles of emulsion stabilization and micelle formation within the aqueous phase of that emulsion to produce the hierarchical structures. The emulsion templating provides the macroporous structure while the mesoporous structure is formed by hydrolyzation of silica around block copolymer micelles. Increasing the copolymer concentration improves the mesoporosity up to a certain concentration where the emulsion phase behavior changes and the macroporosity is affected. Unlike other hierarchically porous materials, the walls of the co-MET macrospheres are entirely mesoporous, which provides high surface areas (>500 $m^2\,g^{-1}$) and pore volumes (>1 $cm^3\,g^{-1}$) and narrow mesopore size distributions (~10 nm). This interconnected hierarchical meso/macroporous structure combined with the controlled particle size makes this new class of materials promising for applications requiring high diffusion and throughput rates, alleviating the problems of using typical fine particle mesoporous materials.

1. Introduction

Hierarchical meso/macroporous materials have attracted much attention recently [1–14]. They have the potential to provide high diffusion and throughput rates, in addition to the unique benefits of ordered mesoporous materials such as controllable and uniformly sized (2–50 nm diameter) mesopores and pore size distributions [15], high surface area and porosity, and variety of interconnected mesopore structures, selected through the synthesis pathway and conditions. Significantly, they may solve the problems associated with ordered mesoporous structured (OMS) materials, such as MCM-41 [15], SBA-15 [16], MCF [17], and FDU-12 [18], which are typically formed as fine powders and lack macroporosity. Hierarchical meso/macroporous materials have potential applications in areas as diverse as catalysis, adsorption, biosensors, and bioseparations [19,20].

Consequently, there have been attempts to make enlarged hierarchically meso/macroporous particles to facilitate applications requiring high throughput rates [12]. The methods used to date involve templating OMS materials onto preformed macroporous structures [3,5,21–23], including polymer foams [9,24,25] and polymer beads [26,27]. These templating processes lead to large particles that have a bimodal pore size distribution: the mesoporous structure of the OMS material is preserved but larger macropores also exist, dictated by the structure of the template. However the application of hierarchically porous materials is currently limited by relatively low mesoporosity [28], broad mesopore size distributions [29], low surface areas [26,27,30] and small macroporous interconnection windows [4,7,8].

We have developed a new class of hierarchically macro/mesoporous silica beads via a novel co-micelle/emulsion templating (co-MET) route, as outlined in Fig. 1. In brief, this method involves formation of mesoporous silica, templated around the oil droplets of an oil-in-water emulsion. The emulsion is stabilized by a surfactant that also forms micelles with silica precursors in the aqueous phase of the emulsion. The silica precursors polymerize to form mesoporous silica reminiscent of SBA-15 [16]. The emulsion is used as a template to create macropores in the beads by forming an organic polymer around the oil droplets. Large (~2 mm diameter) droplets of the emulsion are injected through a nozzle and sedimented in a column of oil to provide time for polymerization of the organic polymer and silica precursors. The emulsion droplet size, controlled by the diameter of the nozzle, dictates the final size of the silica beads. Upon removal of the organic components, a hierarchical macro/mesoporous silica structure remains.

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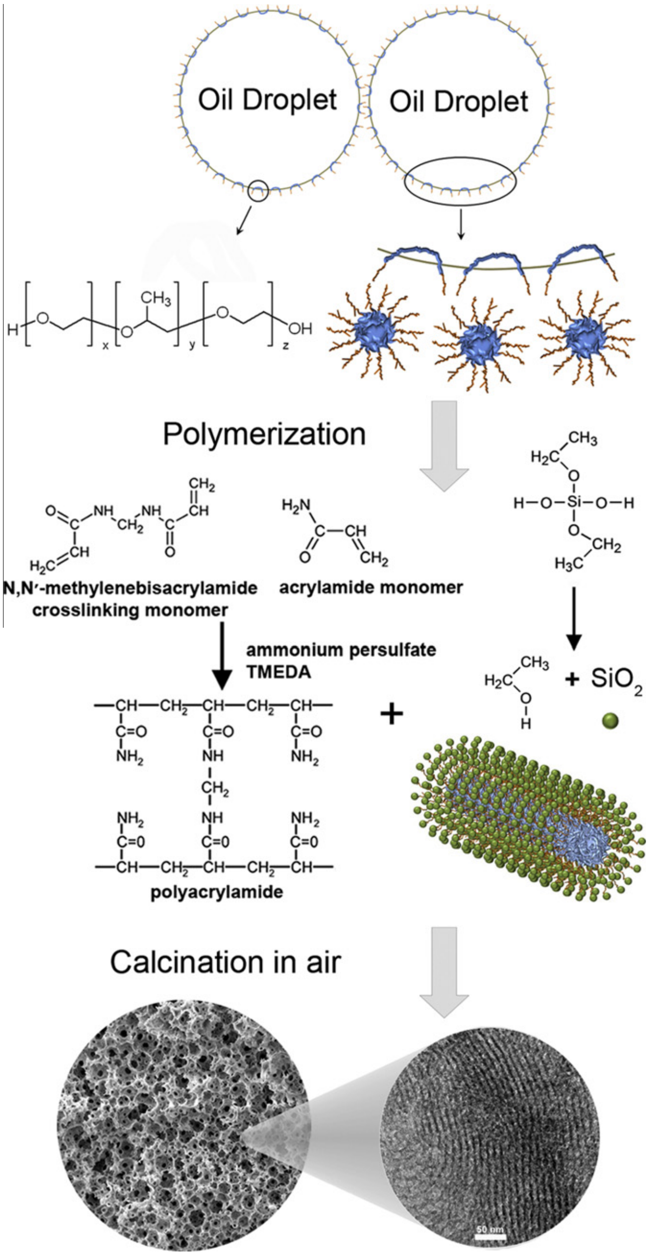

Fig. 1. Schematic representation of the formation of hierarchically meso/macroporous silica using the co-micelle/emulsion templating (co-MET) technique.

The resulting co-MET macrospheres are nano-engineered porous materials that can be tailored on three distinct length scales: the silica walls are entirely mesoporous and formed into interconnected macroporous spheres of controllable size, as detailed below.

2. Experimental section

2.1. Materials

The poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20}$, with molecular weight of 5800 Da), acrylamide (99%), *N*,*N*′-methylene-bisacrylamide (99%), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (99.5%), tetraethylorthosilicate (98%), light mineral oil (0.838 g/mL), heavy mineral oil (0.862 g/mL), and ammonium persulfate (98%), were supplied by Sigma–Aldrich. The 0.9 M hydrochloric acid was made from a 35% w/w solution (Ajax) with purified water. All chemicals were used as received without any further purification. Water was deionized using a Millipore Simplicity unit to achieve a resistivity of 18.2 MΩ cm at 25 °C.

2.2. Co-micelle/emulsion templating

The synthesis procedure of the co-MET silica beads is summarized in Fig. 2. Co-MET silica was synthesized by first dissolving the block co-polymer $EO_{20}PO_{70}EO_{20}$ at the required percentage (2.5, 5, 10, 15 or 20 w/v%) in water and mixing for 24 h at room temperature. Hydrolyzed tetraethylorthosilicate (TEOS) solution was prepared using the method reported by Brennan et al. [31]. TEOS (33.75 mL), water (10.5 mL), and hydrochloric acid (0.15 mL of 0.9 M HCl) were sonicated in an ice bath until formation of a homogeneous solution, then stored in a sealed container at −20 °C for two weeks before use. Monomer solution was prepared as reported by Zhang and Cooper [32]. Acrylamide (2.555 g) and the cross-linker methylene-bisacrylamide (MBAM) (0.518 g) were dissolved in water (6.667 mL).

Monomer solution (3 mL) and $EO_{20}PO_{70}EO_{20}$ solution (4 mL) were mixed with 1.6 mL of 0.9 M hydrochloric acid at room temperature for 15 min using an overhead radial impeller at 500 rpm, followed by the dropwise addition of hydrolyzed TEOS (3 mL) with continued mixing. Light mineral oil (36 mL) containing

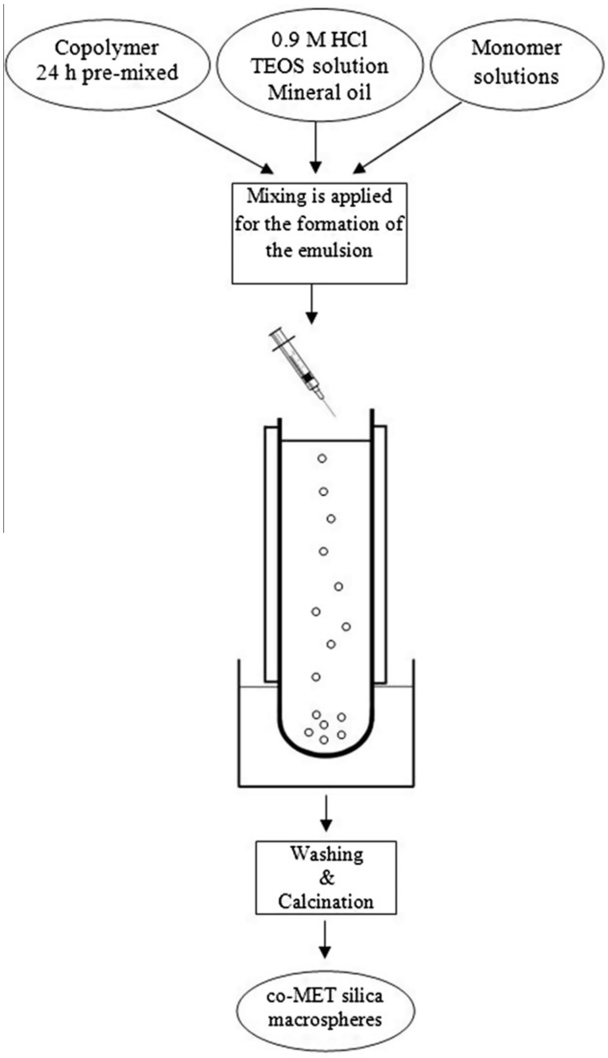

Fig. 2. Synthesis procedure for formation of co-MET silica macrospheres.