

Synthesis of hierarchically ordered dye-functionalised mesoporous silica with macroporous architecture by dual templating

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Mesostructured silica functionalised with the dye moiety, (2,4-dinitrophenylamine), has been prepared with bimodal pore size distribution. Co-condensation of tetraethoxysilane and 3-(2,4-dinitrophenylamino)propyltriethoxysilane was used to covalently couple the organic chromophore into the wall structure of a silica mesophase formed by surfactant templating. This process was spatially patterned at the macroscale by confining the evaporation-induced precipitation within the regular voids of a colloidal crystal comprising 140 nm-sized polystyrene spheres. Post-synthetic removal of the latex and surfactant templates produced a hierarchically ordered organo-functionalised silica phase.

Introduction

There is currently an extensive effort to develop methods for the production of porous inorganic materials based on silica and other oxides because of their potential for wide practical applications. One goal in structural control has been to increase the size of pores to permit penetration of larger guest molecules into the porous host structures. These materials would also benefit from uniform pores with dimensions on the macroscale (greater than 50 nm) that provide optimal flow and improved efficiencies for applications in catalysis, photonics, chromatography and large-molecule separation processes, and as adsorbents, light-weight structural materials, and thermal, acoustic and electrical insulators.^{1,2}

A key step in the synthesis of porous materials continues to be the use of organic templates to spatially pattern the deposition of inorganic solids over length scales ranging from angstroms to micrometers. In the case of microporous crystalline compounds, the organic additives are molecular and lead to zeolitic structures. In contrast, syntheses of ordered mesoporous oxides employ supramolecular surfactant micellar or block copolymer templates for the inorganic framework, resulting in mesoporous M41S phases.³ Recently, micro-moulding methods using emulsion droplets, latex spheres or bacterial threads have been used to prepare ordered inorganic structures with pore sizes in the micrometre range.^{1,4-9}

These techniques have been expanded to the elaboration of materials with combinations of small and large pores.⁸⁻¹³ Materials with bimodal porosity are of considerable interest for applications in catalysis and separation because they offer multiple benefits arising from each pore size regime. For example, while micro- and meso-pores may provide size- or shape-selectivity for guest molecules, the presence of additional macropores can offer easier transport and access to the active sites that should improve reaction efficiencies and minimise channel blocking.

Chemical functionalisation of the inorganic framework of

porous materials, for example through the covalent coupling of an organic moiety, is a promising approach to specific pore surface properties such as hydrophobicity, polarity, and catalytic, optical and electronic activity.¹⁴ Organo-functionalisation of ordered mesoporous silica-based solids can be achieved either by post-synthetic methods¹⁵⁻¹⁷ or *via* direct routes¹⁸⁻²³ involving co-condensation of tetraalkoxysilanes and organotrialkoxysilanes in the presence of surfactants. The one-pot synthesis method allows a higher organic content and a more homogeneous organic distribution in the material.²⁴ Numerous studies have pointed out the role and importance of the nature of the bonds comprising the hybrid inorganic-organic interface.²⁵ Hybrid materials with covalently bonded organic moieties (class II hybrids)²⁵ can be readily designed by sol-gel chemistry and thus a wide range of materials with tailor-made structure and properties can be reproducibly prepared.²⁶⁻²⁹

Here we report for the first time the synthesis of an organically-modified silica with bimodal pore structure consisting of ordered macropores surrounded by mesostructured walls of dye-functionalised silica. Dual templating methods are employed to control the hierarchical pore system. The macropores are formed by using crystalline arrays of mono-disperse polystyrene (PS) spheres as macrotemplates for the *in situ* evaporation-induced deposition of organically functionalised mesostructured silica. At the mesoscale level, the porosity of the wall is controlled by supramolecular templating using a reaction mixture containing tetraethylorthosilicate (TEOS), 3-(2,4-dinitrophenylaminopropyl)triethoxysilane (DNPTES) and cetyltrimethylammonium bromide (CTAB).

Experimental

Synthesis

Colloidal latex sphere suspension. A controlled free-radical miniemulsion polymerisation of styrene using degenerative

transfer was performed to produce a colloidal suspension of 140 nm-diameter spheres containing short polystyrene chains ($M_n = 4550 \text{ g mol}^{-1}$) with a narrow molar mass distribution.³⁰ The colloidal suspension was stabilised by the addition of sodium dodecylsulfate (SDS).

Formation of crystalline arrays of monodisperse polystyrene (PS) spheres. The latex colloidal suspension was left in an open Petri dish at room temperature to form monodisperse latex sphere crystalline arrays by slow sedimentation and water evaporation.

Precursor solution of organically functionalised mesostructured silica. In a typical preparation, TEOS, DNPTES, ethanol, water and HCl (molar ratios = 0.9 : 0.1 : 3.8 : 1 : 5×10^{-5}) were first refluxed at 60 °C for 90 min. Water and HCl were then added to give a HCl concentration of 7.34 mM (molar ratio = 4 : 3.95×10^{-5}). After stirring at 50 °C for 15 min, the sol was cooled down at 25 °C and diluted with an ethanolic solution of CTAB. The final molar composition was 0.9TEOS : 0.1DNPTES : 22EtOH : 5H₂O : 0.0004HCl : 0.16CTAB. The resulting homogeneous precursor solution was aged for 4 days at room temperature in a closed polyethylene flask prior to the permeation of the latex colloidal crystals.

In order to extract the latex beads, the composite latex/DNPTES-modified silica material was immersed in toluene for 12 hours and then washed twice more in toluene. The resulting latex-extracted solid was dried at room temperature.

Extraction of the CTAB surfactant was performed by stirring a suspension of the latex-extracted solid product (0.99 g dm^{-3}) in a 1.0 mol dm^{-3} HCl in EtOH at 70 °C for 24 h. The extracted material was filtered, and washed several times with EtOH and dried at 50 °C for 12 hours.

Characterization

The scanning electron microscope (SEM) images were observed on solid products (after Au coating) by using a Philips XL 30 SEM working at 5 kV. Samples for transmission electron microscope (TEM) observation were prepared by suspending a ground product in water and air-drying the dispersion onto a carbon-coated copper electron microscope grid. TEM analyses were performed on a JEOL-1200Ex transmission electron microscope working at 120 kV. X-Ray diffraction powder patterns were recorded in the 2θ range from 1 to 10° by using the transmission mode on a STOE STADI-P diffractometer (Cu-K _{α} 1 radiation, $\lambda = 1.5406 \text{ \AA}$). Diffuse reflectance infrared fourier transform (DRIFT) analyses were performed by using a Bruker IFS-66 spectrometer. UV-VIS absorption properties of the final product were analysed by diffuse reflectance on a Uvikon Kontron spectrometer.

Results and discussion

SEM images (see Fig. 1) show that monodisperse latex beads are well ordered into hexagonally close-packed arrays after slow sedimentation and water evaporation from the colloidal suspension.

An evaporation-induced self-assembly process reported by Brinker *et al.*^{31,32} was used to produce mesostructured DNPTES-modified silica walls around the latex beads in the close packed colloidal crystal. The interstices between latex spheres were permeated by the precursor solution of the reaction mixture which was made by adding the CTAB surfactant to an organically-modified silica sol. In a recent study,³³ we have used this reaction system to prepare transparent yellow thin films and monoliths of organic dye-functionalised silica with MCM-41 architecture and showed that it is well adapted to the formation of a continuous mesostructured inorganic-organic hybrid siloxane network on

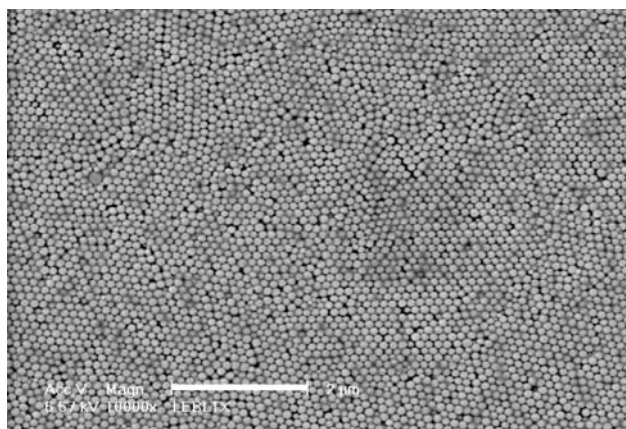


Fig. 1 SEM images of a close-packed array of latex beads used for macrotemplating of organically functionalised mesostructured silica; surface view of the top layer (bar scale = 2 μm).

the macroscale. The process provides a homogeneous yellow solution of soluble organo-silicate and silicate species in ethanol/water with an initial surfactant concentration below the critical micelle concentration (cmc) but which becomes progressively enriched in water, HCl, and surfactant by ethanol evaporation. As the surfactant concentration increases above the cmc level, a lyotropic liquid crystalline mesophase is formed in association with an organically-functionalised siloxane framework.

After complete evaporation of ethanol, the resulting dried composite solid was stored for 2 days at 50 °C to improve the condensation of the siloxane network. After removal of the latex spheres, the resulting dye-functionalised silica replica of the colloidal crystal template showed long range order and a high degree of monodispersity in macropore size (Fig. 2). The mean center-to-center separation between cavities was 115 nm (SEM measurements) which was *ca.* 17% smaller than the diameter of the original latex spheres, suggesting significant shrinkage during latex sphere extraction. Because of the low molecular weight of the polystyrene, dissolution of the macrotemplate was achieved without disruption of the regular structure. Transmission electron micrographs confirmed the reverse opal structure of the inorganic framework after latex removal as well as the silica wall mesostructure (Fig. 3). Significantly, some of the lattice images of the wall domains showed short range periodic hexagonal order (Fig. 3(b)). No changes in macrostructure were observed by SEM for samples of the latex-free dye-functionalised silica after the CTAB extraction procedure.¹⁸

Small angle X-ray diffraction (XRD) patterns recorded on the material after latex removal showed one peak at 39 \AA

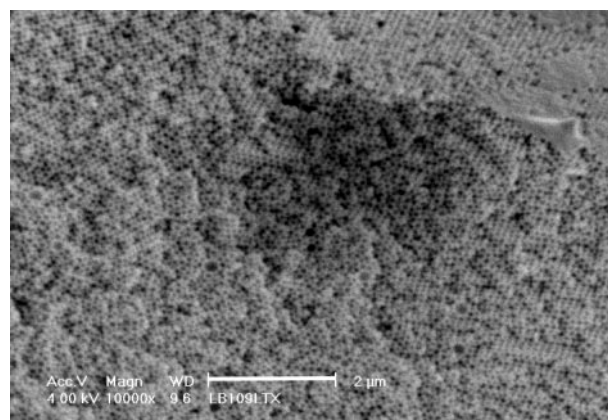


Fig. 2 SEM image of macroporous dye-functionalised silica after extraction of the latex bead colloidal template (bar scale = 2 μm).

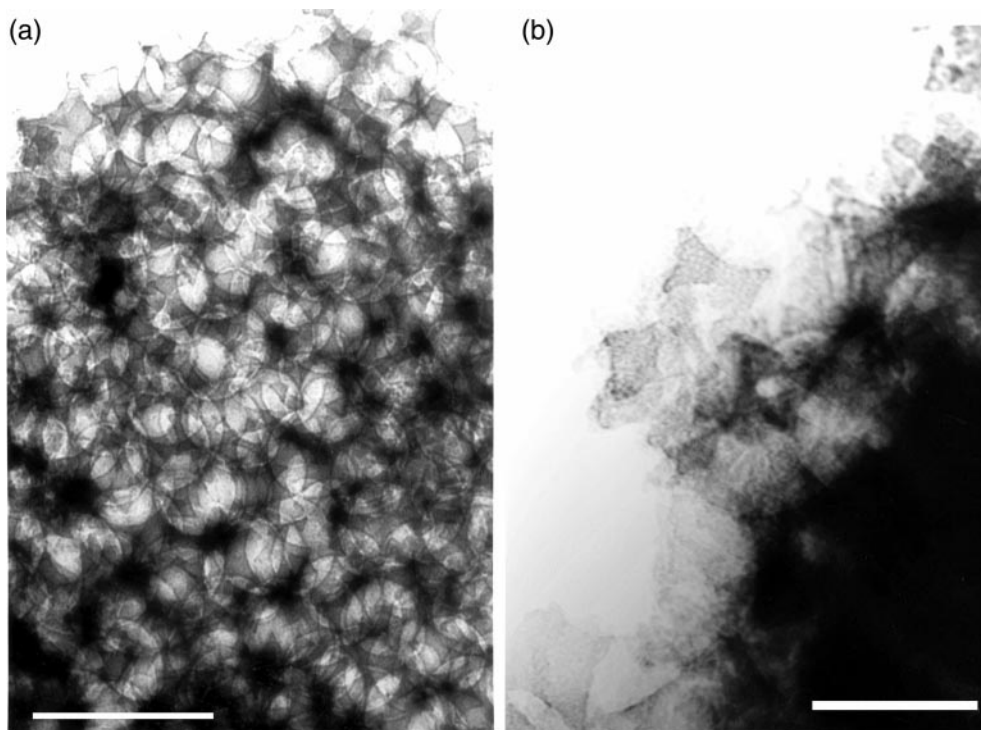


Fig. 3 TEM images of dye-functionalised silica after extraction of latex beads showing: (a) inverse silica replica of the latex opal (bar scale = 200 nm), (b) ordered mesostructured dye-functionalised silica wall (bar scale = 50 nm)

indicative of a single phase with mesoscopic order. A broad but distinct XRD reflection at 39 Å was still observed after removal of the surfactant template, indicating that the mesoscopic order was retained during the extraction process. The single XRD reflection is consistent with a pore structure based on a three-dimensional disordered network of worm-like porous channels arrays. This arrangement is characteristic of the recently prepared MSU materials^{34,35} although mesostructured hybrid monoliths made in the bulk by a similar method are usually ordered.³³

Reflectance FTIR spectra of the hierarchically ordered materials showed characteristic Si–O–Si framework vibrations at 1080 cm⁻¹ (large band), 1200 cm⁻¹ (shoulder), 900 and 800 cm⁻¹, and a Si–C band at 1150 cm⁻¹ (shoulder), as well as vibrations corresponding to the chromophore (1338, 1621, and 3368 cm⁻¹), indicating that the dinitrophenylaminopropyl chromophore was covalently linked into the mesostructured silica network as an intact unmodified moiety. Removal of the CTAB surfactant was confirmed by a large decrease in the intensity of –CH₂ vibration bands at 2850–3000 cm⁻¹ and the absence of the –NMe₃ band at 1468 cm⁻¹. Furthermore, two absorption bands at around 350 nm and 440 nm were observed in the UV-VIS diffuse reflectance spectrum, indicating that the –NO₂ chromophore groups³⁶ remained intact and covalently linked to the silica network of the hierarchical structure.

Conclusion

We have shown that the simultaneous use of two complementary templating strategies involving nanolatex colloidal crystals and surfactant supramolecular assembly can be used to synthesize a hierarchically ordered organo-functionalised silica with bimodal pore size distribution. The current work has demonstrated this approach using a dye functionality with nonlinear optical properties, but it is clear that the method can be easily extended to many other organosilane moieties tailored to specific applications such as selective chromatographic supports for combinatorial chemistry, ferrocene-based devices in electrochemical sensors, dye-based pH sensors, and

rhodium/ruthenium-based organometallic complexes for catalysis.

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