

Fabrication of heterogeneous macroporous materials based on a sequential electrostatic deposition process

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Heterogeneous macroporous materials are prepared by the sequential electrostatic deposition of fluorescein isothiocyanate-labeled poly(allylamine hydrochloride) and cadmium telluride nanocrystals onto macroporous titania structures.

Ordered macroporous materials with pore diameters in the nanometer to micrometer range have attracted significant interest because of their unique properties, *e.g.* high specific surface area, high damping capacity, low thermal conductivity and low dielectric permittivity. They have a wide range of applications (both structural and functional), including their use as light-weight structural materials,¹ catalytic supports and surfaces,² thermal and acoustic insulators,³ optical devices⁴ and as candidates for high speed computer device packaging.⁵

Recently, considerable effort has been devoted to the use of colloidal assemblies as templates for the fabrication of interconnected three-dimensional (3D) macroporous materials.⁶ Monodisperse colloidal spheres, either polystyrene, silica or poly(methyl methacrylate),⁶ or emulsion droplets,⁷ can self-assemble into ordered 3D arrays. These ordered structures offer a 3D scaffold for a variety of precursor materials, which can be infiltrated in the voids between the colloidal spheres. After subsequent solidification of the precursors and removal of the templated colloids, 3D macroporous materials are obtained. The pore dimensions of the structures depend on the diameters of the colloidal spheres employed. This method provides a simple and effective route to the fabrication of macroporous materials with controlled pore sizes and well-defined periodic structures. In the last few years, a variety of organic, inorganic, and metal precursor materials have been used to prepare a wide range of 3D ordered macroporous structures.⁶

The development of heterogeneous (*i.e.* multicomponent) 3D ordered macroporous structures is expected to yield promising materials for use in the areas of catalysis and optical devices based on photonic crystals. However, to date there have been few studies on the fabrication of such materials. For example, Yin and Wang have recently doped macroporous titania with cobalt by the precipitation of mixed precursors,⁸ while Stein and co-workers have prepared 3D ordered macroporous organic/inorganic hybrids⁹ and alloys¹⁰ using a similar procedure. Here we report a method for creating 3D heterogeneous structures by using a sequential electrostatic deposition process that involves the post-modification of macroporous titania. This technique is based on the electrostatic attraction between sequentially deposited species, and represents a general approach for the fabrication of multicomponent films on planar supports¹¹ and colloid particles.¹²

Based on electrostatic attractions, poly(allylamine hydrochloride) (M_w 8000–11 000) labeled with fluorescein isothiocyanate (FITC-PAH) and cadmium telluride (CdTe) nanocrystals (3–4 nm in diameter)¹⁴ were consecutively deposited on macroporous titania (TiO_2), which was produced by templating colloidal crystals of polystyrene (PS) spheres with titanium isopropoxide (TIP). The advantages of our approach are that it allows tailoring of the composition (and consequently function) of the heterogeneous macroporous structures through

the electrostatic deposition of charged components that coat the inner surface of the materials.

Colloidal crystals of monodisperse PS spheres of diameter 640 nm were used as the template and TIP as the precursor for the formation of macroporous TiO_2 structures, as described earlier.¹³ The resulting TiO_2 material was treated with basic solution (1 M sodium hydroxide aqueous solution), after which the macroporous TiO_2 was placed into 2 mL of a 0.5 mg mL⁻¹ FITC-PAH solution containing 0.5 M NaCl, and 12 h was allowed for FITC-PAH adsorption. After removal of the FITC-PAH solution, the TiO_2 material was washed five times with 2 mL of water to ensure removal of FITC-PAH not electrostatically bound to the TiO_2 . The adsorption of FITC-PAH changes the surface charge of the macroporous TiO_2 to positive due to charge overcompensation.¹¹ Subsequently, negatively charged CdTe nanocrystals were adsorbed from aqueous solution onto the surface and within the pores of the macroporous TiO_2 modified with FITC-PAH (the electrostatic interactions occur between the NH_3^+ groups of the FITC-PAH and the negatively charged hydroxy and thiol moieties on the surface of the nanocrystals¹⁴). This resulted in the sample turning red, suggesting a relatively high loading of the CdTe nanoparticles.¹⁵

The macroporous materials prepared were examined by scanning electron microscopy (SEM). Fig. 1 shows a SEM micrograph of a cross-section of the macroporous TiO_2 produced when using PS colloidal crystals as templates. The center-to-center average distance between the pores is 432 ± 10 nm, reflecting a linear shrinkage of 33% (compared to the diameter of the PS spheres, 640 nm). The round channels in the pore walls are clearly visible, and confirm that the pores in the structure are interconnected with each other. There are small openings in the middle of each of the triangular intersections of the macroporous TiO_2 (indicated by the arrow). These openings are likely caused by incomplete filling of the voids between the spheres.¹⁶

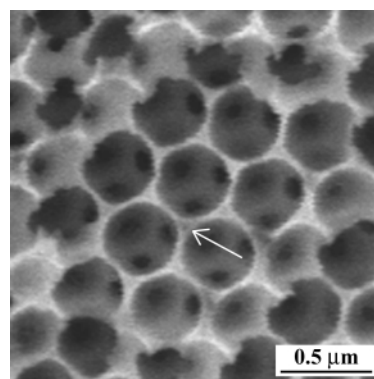


Fig. 1 SEM micrograph of the macroporous TiO_2 structure fabricated by templating pure PS colloidal spheres of diameter 640 nm. The arrow points to the small openings that are present in the middle of each of the triangular intersections of the macroporous TiO_2 material.

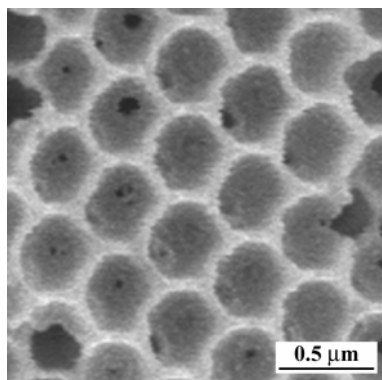


Fig. 2 SEM micrograph of the heterogeneous (TiO_2 -FITC-PAH/CdTe) macroporous structure fabricated by the sequential electrostatic adsorption of FITC-PAH and CdTe nanocrystals onto macroporous TiO_2 .

Fig. 2 displays a SEM micrograph of a cross-section of the macroporous TiO_2 structure modified with FITC-PAH and CdTe nanocrystals. The resulting heterogeneous (TiO_2 -FITC-PAH/CdTe) macroporous material has the same structure as that of the original macroporous TiO_2 (Fig. 1). The center-to-center distance of 427 ± 10 nm is also the same (within experimental error) to that obtained for the unmodified TiO_2 structure. It is clearly observed that the pores are still interconnected with each other (round channels are seen). However, the small openings in the middle of each of the triangular intersections of the pure macroporous TiO_2 material (Fig. 1) are not observed. This suggests that the TiO_2 structure has been coated with the FITC-PAH/CdTe hybrid layer. Energy disperse X-ray (EDX) analysis of the heterogeneous macroporous material indicates the presence of Ti, O, Cd and Te [Fig. 3(a)], demonstrating that the CdTe nanocrystals were adsorbed on the TiO_2 . Fig. 3(b) shows the luminescence spectrum of the heterogeneous macroporous

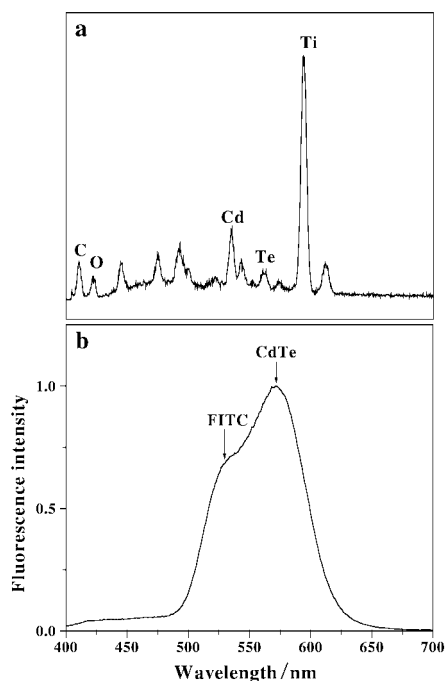


Fig. 3 (a) EDX and (b) luminescence spectra of the heterogeneous macroporous material shown in Fig. 2.

material. The shoulder observed around 530 nm corresponds to the emission of the FITC molecules of the labeled PAH, confirming that FITC-PAH was also deposited. The maximum at 570 nm is attributed to the 'excitonic' emission of the 3–4 nm CdTe nanocrystals. It is important to note that the SEM, EDX and fluorescence experiments were conducted on cross-sections of the heterogeneous macroporous structures. The above results verify that the PAH-FITC and CdTe nanocrystals infiltrated the macroporous TiO_2 structure and coated the inside surface. In addition, all of the cross-sectioned samples showed a red color. Preliminary experiments revealed an intensified color for cross-sections of the heterogeneous material when additional FITC-PAH/CdTe nanocrystal multilayers were deposited. Characterization of the growth of FITC-PAH/CdTe nanocrystal multilayers on macroporous TiO_2 structures is currently in progress.

In this study, we have used FITC-PAH, CdTe nanocrystals and macroporous TiO_2 to demonstrate the feasibility of fabricating heterogeneous macroporous materials by using the sequential electrostatic deposition approach. This strategy provides a simple and versatile means to prepare novel macroporous materials, allowing control over their composition and functional properties. Given the general nature of the method, it is expected that complex and tailored structures can be produced with defined multilayers of polyelectrolytes, small organic molecules, inorganic nanoparticles, clays and proteins. Such studies are being undertaken. The creation of such structures should open up new and interesting possibilities for the applications of heterogeneous macroporous materials.

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