Fabrication of Ordered Macroporous TiO₂/SiO₂ Composite from Preformed Water-Soluble TiO₂ Nanocrystals and Silicon Alkoxide

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An aqueous suspension containing preformed water-soluble TiO₂ nanocrystals and tetraethylorthosilicate was used to fill interstices of closed-packed poly(methyl methacrylate) spheres by a centrifugation sedimentation method and finally create three-dimensional ordered macroporous TiO₂/SiO₂ composite. SEM images show that the macroporous composite obtained exhibits a long-range hexagonal ordered array of spherical macropores with a pore size of about 214 ± 5 nm. XRD and HRTEM results reveal that the TiO₂ particles with a grain size of about 9 nm and a crystalline anatase phase structure are embedded in the macroporous silica walls.

Key Words: Macroporous TiO₂/SiO₂ framework, Water-soluble TiO₂ nanocrystals, PMMA spheres template, Synthesis.

INTRODUCTION

Increasing interest in the field of photocatalysis has motivated the design of new materials involving nanostructured crystalline TiO₂ because of its high photocatalytic activity for the total destruction of organic compounds in polluted air and wastewater[1]. For many practical applications, it is very important to improve the efficiency of the TiO₂ particles photocatalysts because the ultrafine TiO₂ powders will agglomerate into larger particles, resulting in a reduction of catalytic activity and the separation and recovery of TiO₂ from wastewater are expensive due to the formation of milky dispersions after mixing the powder catalyst in water[2,3]. The conventional synthesis strategy is the combination of the photoactive TiO₂ particles with a support to improve the dispersibility, mechanical strength and surface area of TiO₂ powders[4,5]. As a catalyst support, especially for the catalytic process of the large molecular reaction, porous silica with large, interconnected void spaces is a desirable support. Over past few years, the synthesis of three-dimensional ordered macroporous materials (3DOM) with a variety of inorganic oxides frameworks has received much attention in physics, chemistry and material science by the replication of the ordered array structure of polymer or silica spheres[6]. The substances that are used to fill the interstitial spaces between the spheres to make three-dimensional order macroporous metal oxides are usually high reactive precursors such as certain metal alkoxides. For example, titanium and silicon alkoxides were used to make three-dimensional order macroporous TiO₂/SiO₂ with an amorphous walls structure[7]. However, the synthesis procedures were dependent critically on the control of the high active Ti(IV) precursors toward hydrolysis, condensation and heat treatment to avoid the formation of large stress cracks and a smaller particle size due to the intense crystallization of titania. In this paper, we report a facile approach that employed an aqueous suspension containing preformed water-soluble TiO₂ nanocrystals and tetraethylorthosilicate to fill interstices of closed-packed poly(methyl methacrylate) (PMMA) spheres by a centrifugation sedimentation method. After densification and subsequent calcination, 3DOM TiO₂/SiO₂ frameworks with TiO₂ nanocrystals embedded in the macroporous silica walls were obtained. The method utilizing the preformed water-soluble TiO₂ nanocrystals is expected to be an effective way to, on one hand, form a homogeneous colloidal aqueous suspension, which can be infiltrated into the interstices of PMMA spheres and on the other hand, incorporate TiO₂ nanocrystals in the macroporous silica walls.

EXPERIMENTAL

Monodisperse poly(methyl methacrylate) (PMMA) spheres were synthesized by a surfactant-free emulsion polymerization technique according to literature[8,9]. The PMMA spheres were packed into ordered colloidal crystal by centrifugation method and dried at room temperature. Water-soluble TiO₂ nanocrystals were synthesized by a simple non-aqueous route reaction between titanium tetrachloride and benzyl alcohol in presence of dopamine as ligand using a modified version of literature method[10], but the reaction was performed in open air condition instead of the glovebox.

The molar compositions of the starting precursor suspensions were 1.0 TEOS : $xTiO_2$: 0.2HCl : 112 H_2O (x varies with the molar ratios of TiO_2/TEOS, TiO_2/TEOS = 0.05, 0.1, 0.15, 0.2, respectively). In a typical synthesis (TiO_2/TEOS ratio = 0.1), 0.04 g of the aforementioned dried dopamine-coated TiO_2 powder was dissolved in 10 mL of H_2O under magnetic stirring, resulting in a red, completely transparent solution. To this solution, 5 mL of HCl (2 M/L) and 1.12 mL of tetraethylorthosilicate (TEOS) were added, followed by stirring for 10 min at room temperature. The PMMA spheres chunks (0.4 g) were placed in the bottom of centrifugal tube and the precursor suspension was placed on top of the PMMA spheres chunks. The mixture was sedimented by centrifugation (2500 rpm, 6 h), then the excess solution was removed and the precipitate was dried at 70 ℃. The macroporous TiO_2/SiO_2 composite was obtained by calcination in air keeping at 310 ℃ for 3 h and then at 550 ℃ for 4 h (heating rate: 2 ℃ per min).

Scanning electron micrographs (SEM) were obtained using a XL30 ESEM-TMP scanning electron microscope or an AMRAY-1910 field emission microscope. Ti content in the product was determined by EDS analysis. Transmission electron micrographs (TEM) were recorded with a Hitachi H-9000HAR microscope, operating at 300 kV. Powder X-ray diffraction (XRD) studies were performed on a Rigaku D/max 2200 diffractometer with CuK_α radiation (λ = 0.15406 nm) and step-scanned over the 2θ range of 20º-80º, operating at 40 kV and 30 mA.

RESULTS AND DISCUSSION

The detailed schematic illustration of the preparation procedure of the present incorporation of TiO_2 nanocrystals in the silica with macroporous structure is shown in **Scheme-I**. The first step in this synthesis approach was to fabricate a closed-packed PMMA spheres template, which was prepared by a surfactant-free emulsion polymerization technique according to literature[8,9] and subsequently centrifugation method. The key consideration in this method was to make a stable colloidal suspension of TiO_2 nanocrystals and TEOS in water, which can be used to fill the interstices of the closed-packed PMMA spheres. Hence, we employed a dopamine-coated TiO_2 nanocrystals (6-8 nm) as TiO_2 source which were described to be resoluble in water and highly crystalline[10]. The water-soluble property of the TiO_2 particles is attributable to surface-modification with dopamine ligands having positively charged terminal ammonium groups, resulting in particle-particle repulsion and leading to a stable aqueous colloidal solution[11]. When TEOS was added to the aqueous colloidal TiO_2 solution, a homogeneous colloidal suspension can be obtained. Moreover, we utilized the centrifugation sedimentation method to promote the aqueous colloidal suspension into interstices of the spheres and avoid the dispersing of colloidal PMMA latex crystals or swelling of the PMMA spheres. As the condensation reaction of silica species occured in interstices of the spheres, TiO_2 nanocrystals were fixed and finally incorporated into silica walls of the macroporous structure.
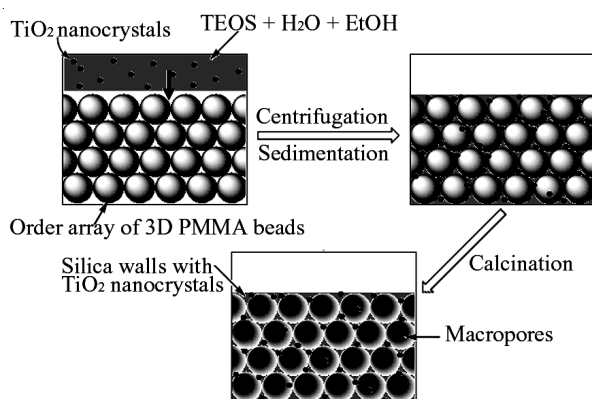
Scheme-I: Schematic illustration of the preparation procedure of macroporous TiO_2/SiO_2 composite fabricated by using preformed water-soluble TiO_2 nanocrystals and TEOS as inorganic sources and PMMA spheres as template

Fig. 1 shows a field emission scanning electron microscopy (SEM) image of the PMMA spheres template. The image shows that the PMMA spheres form 3D ordered array with close-packed stacking. The SEM image at higher magnification (the inset in Fig. 1) shows that each sphere connects to 12 neighbouring ones in 3D direction. On the basis of the SEM images, the average diameter of the spheres was estimated to be about 320 ± 5 nm.
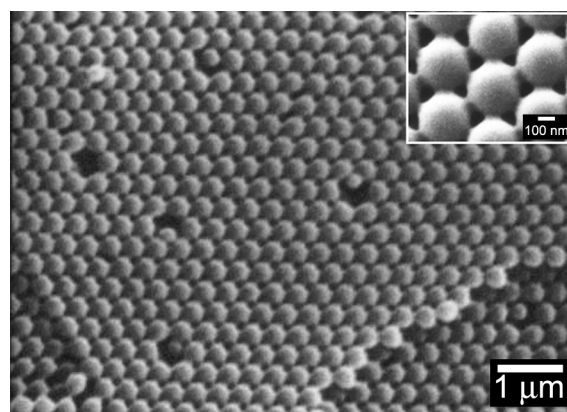

Fig. 1. SEM image of PMMA spheres template. The inset is a higher magnified image

Macroporous TiO_2/SiO_2 frameworks were replicated from the PMMA spheres template and the interstitial voids of which were filled with the aqueous precursor suspensions. SEM images of the macroporous TiO_2/SiO_2 (TiO_2/TEOS ratio = 0.1) are shown in Fig. 2 at different magnifications from low to high. At low magnification (Fig. 2a), the replica exhibits considerable ordered array of the pores in 3D over a range of tens of micrometers. A hexagonal array of the spherical pores can be clearly observed at high magnification (Fig. 2b) and the pores of the top layer have an appearance similar to that of a honeycomb. At higher magnification (Fig. 2c), the smaller "windows" channels (originally connected between PMMA spheres) connecting the adjacent spherical pores in the next several layers are clearly visible from the pores of the top layer, confirming the three-dimensional ordering of the structure. The size of macropores is about 214 ± 5 nm, which is 33 % smaller than that of the original PMMA spheres. Thickness of

the walls between adjacent pores is about 50 nm in average. The inset in Fig. 2c shows a typical HRTEM image of a single nanodomain of the pore wall. An individual TiO_2 particle with grain size of about 9.0 nm and clearly resolved lattice fringes can be observed in the single domain of the pore wall, indicating the high crystallinity of the TiO_2 particles and the existence of TiO_2 nanocrystals in the silica pore walls. The crystalline structure of the TiO_2 particles in pore wall can be further confirmed by XRD (Fig. 3). The XRD pattern shows that the characteristic diffraction peaks of the sample (TiO_2/TEOS ratio = 0.1) can be assigned to the anatase phase (JCPDS card, No. 21-1272), exhibiting a good crystallinity. The average crystallite size estimated by peak-broadening analysis using the Scherrer equation is about 9.75 nm.
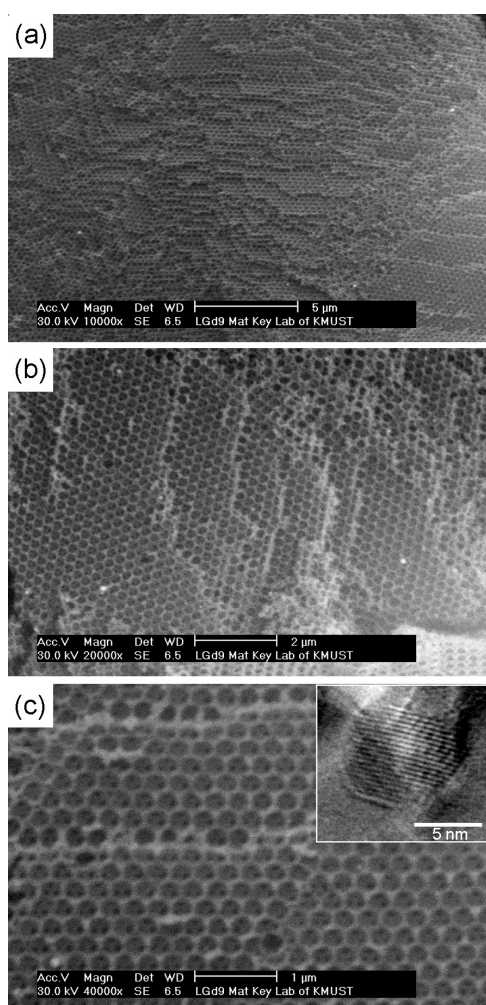

Fig. 3.   XRD pattern of macroporous TiO_2/SiO_2 composite (TiO_2/TEOS ratio = 0.1)

Fig. 2.   SEM images of macroporous TiO_2/SiO_2 composite (TiO_2/TEOS ratio = 0.1) at different magnifications. (a)-(c): The gradual transformation of magnification from low to high. The inset in (c) is a typical HRTEM image of a single nanodomain of the pore wall

Titanium loading content in the calcined samples determined by EDS analysis was 3.35, 7.03, 9.56 and 13.92 wt. % Ti for the TiO_2/TEOS ratios of 0.05, 0.1, 0.15 and 0.2, respectively. It was found that the long-range ordered macroporous structures were obtained only in a limited TiO_2/TEOS ratio range. When the initial mola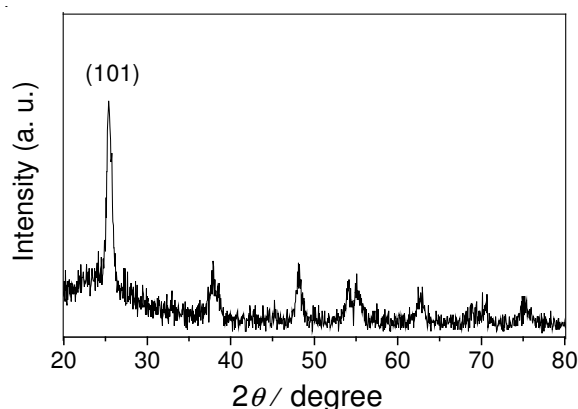r TiO_2/TEOS ratio was less than 0.2, the ordered structures can be maintained, but if the TiO_2/TEOS ratio was further increased over 0.2, the well-ordered skeletons were not produced because the interstices of the closed-packed PMMA spheres would become plugged during filling.

Conclusion

An aqueous colloidal suspension containing preformed water-soluble TiO_2 nanocrystals and TEOS (TiO_2/TEOS molar ratio < 0.2) can be used to fill interstices of the closed-packed PMMA spheres by a centrifugation sedimentation method, finally results in a three-dimensional ordered macroporous TiO_2/SiO_2 framework with TiO_2 nanocrystals embedded in the macroporous silica walls. The method that employs the preformed water-soluble TiO_2 nanocrystals as Ti source is expected to be an effective way to obtain the new macroporous networks containing other crystalline metal oxides nanoparticles.

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