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Template synthesis of structured titania using inverse opal gels

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Abstract

Inverse opal gels with varied content of acid groups were used as templates to synthesize structured crystalline titania materials. TiO_2 with opal, inverse opal, and gradient structure were obtained by altering composition of the gels and precursor concentration. The mechanism of the template synthesis by using opal gels was proposed.

Keywords: Template synthesis; Polymer gels; Opal

1. Introduction

Macroscopically ordered materials including macroporous and colloidal crystal ones have gained increasing interest because of their use in a broad area such as selective transportation, in cell cultures, catalysts substrates, acoustic and thermal insulators, biomineralization, chemical sensors and especially as photonic band-gap materials [1–3]. Template-synthesis is a general method to achieve those materials. Ordered macroporous, e.g. inverse opal materials are prepared using colloidal crystals, e.g. opal materials as templates [3–7]. Reversibly, the opal materials can also be further fabricated by using the inverse opal templates [8,9]. Most templates are rigid and only act as molds, the resultant materials are just cast or negatively duplicated of the templates. We have previously report a sulfonated polystyrene soft opal hydrogels as templates to synthesize titania ordered materials with tunable morphologies [10]. Our former results show that hydrogel templates have sponge-like and tunable structures, which render an adjustable microenvironment such as electrostatic interaction, polarity and hydrophilicity. These advantages facilitate to further controlling the association of the templates with precursor, infiltration of the precursors, compaction and consolidation, thus morphology of the structured products thereby.

In this communication, we report using the inverse opal polymer gels to template synthesize structured titania by sol–gel process. It is crucial to tune the morphology of the titania materials by changing the composition of the inverse opal gel templates. TiO_2 is chosen as the studied example owing to its diverse potential applications. Hydrogel template can be used to prepare many kinds of structured materials such as magnetite, cadmium sulfide, TiO_2 and many hybrids. So this method can be extended to other systems leading to interesting structures thus properties.

2. Experimental section

2.1. Materials

N,*N*-Dimethylacrylamide (DMA, Aldrich) as monomer, *N*,*N*′-methylenebisacrylamide (MBA, Sigma) as crosslinking agent, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, Acros organics) as comonomer, potassium persulfate (KPS, Beijing Chemical Regent Co.) as initiator, tetrabutyl titanate (TBT, Aldrich) as precursor and ethanol (Beijing Chemical Regent Co.) were all used as received.

2.2. Preparation of inverse opal gels

The inverse opal gels were template-replicated from the dry silica colloidal crystals. Silica templates were obtained by ambient drying the silica dispersion according to the previous work [11]. Size of the silica colloids can be controlled with 200–900 nm in our study, thus the pore size of the inverse opal hydrogel is controllable accordingly. In this study,

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Table 1
Composition of the inverse opal gels

Gels	H_2O (g)	DMA (g) (wt%)	AMPS (g) (wt%)	MBA (g) (wt%)	KPS (mg)
PG1	2.00	1.200 (95.24%)	–	0.060 (4.76%)	1.70
PG2	2.60	1.604 (93.24%)	0.017 (2.00%)	0.081 (4.76%)	2.20
PG3	2.70	1.604 (90.02%)	0.089 (4.99%)	0.089 (4.99%)	2.40
PG4	2.80	1.612 (85.43%)	0.186 (9.86%)	0.089 (4.71%)	2.70
PG5	3.00	1.626 (80.22%)	0.305 (15.05%)	0.096 (4.73%)	2.70
PG6	3.00	1.652 (64.68%)	0.802 (31.40%)	0.100 (3.92%)	3.40

the dispersion with 290 nm in diameter was chosen as an example. The obtained silica templates with thickness about 1 mm and size about 10 mm^2 were completely infiltrated with the mixture of monomers/initiator/water for about 2 h under room temperature. The silica templates soaked with monomer solution became transparent. A radical polymerization was then performed at 55 °C for 2 h under nitrogen to form silica/gel composites. The final inverse opal polymer gels were obtained after removal of the silica templates by 40 wt% aqueous hydrofluoric acid and washing with a large amount of

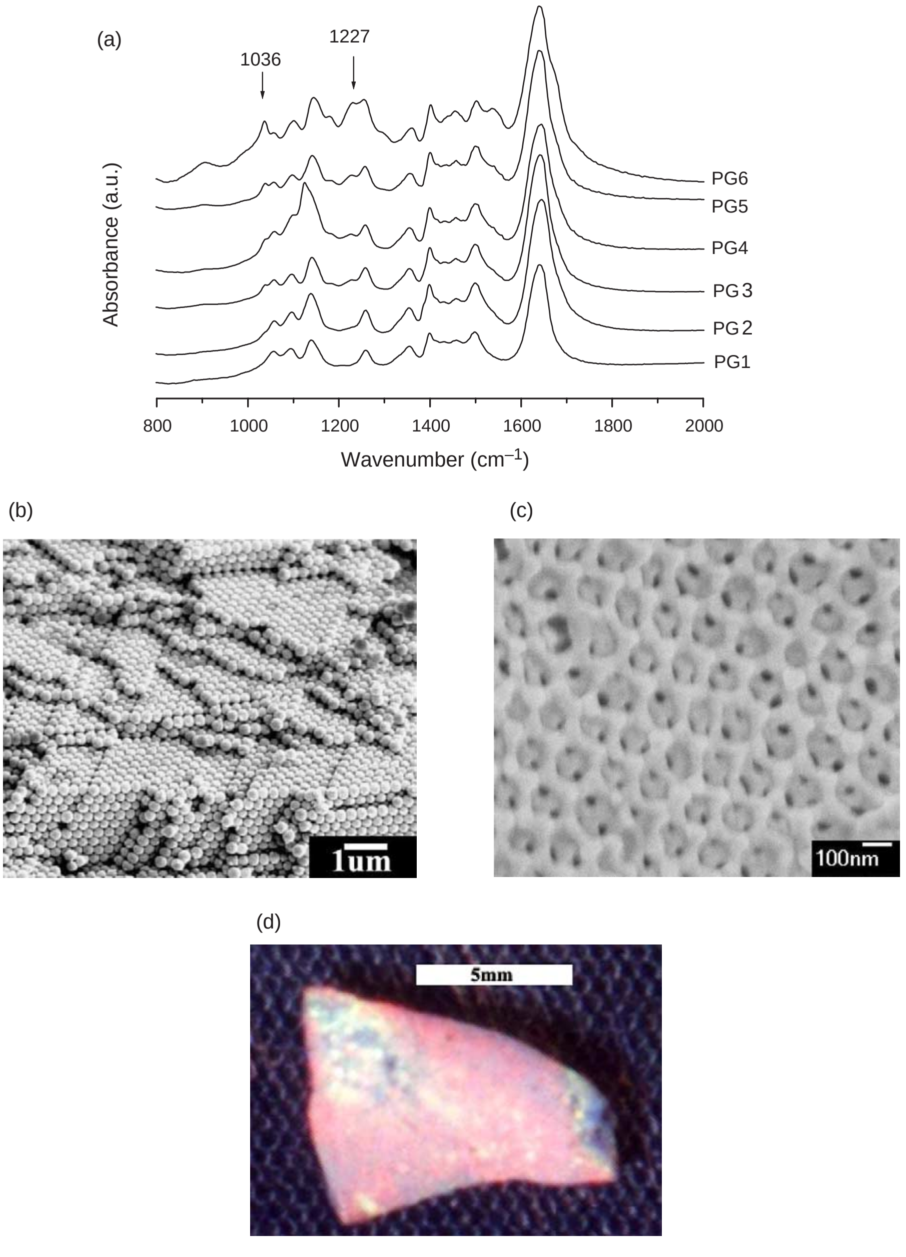

Fig. 1. (a) FT-IR spectra of the PG series gels. Scanning electron microscopy images and optical picture of the ordered samples; (b) the dry silica template; (c) the freeze–dried macroporous gel PG1; and (d) optical picture of PG1 gel soaked in water.

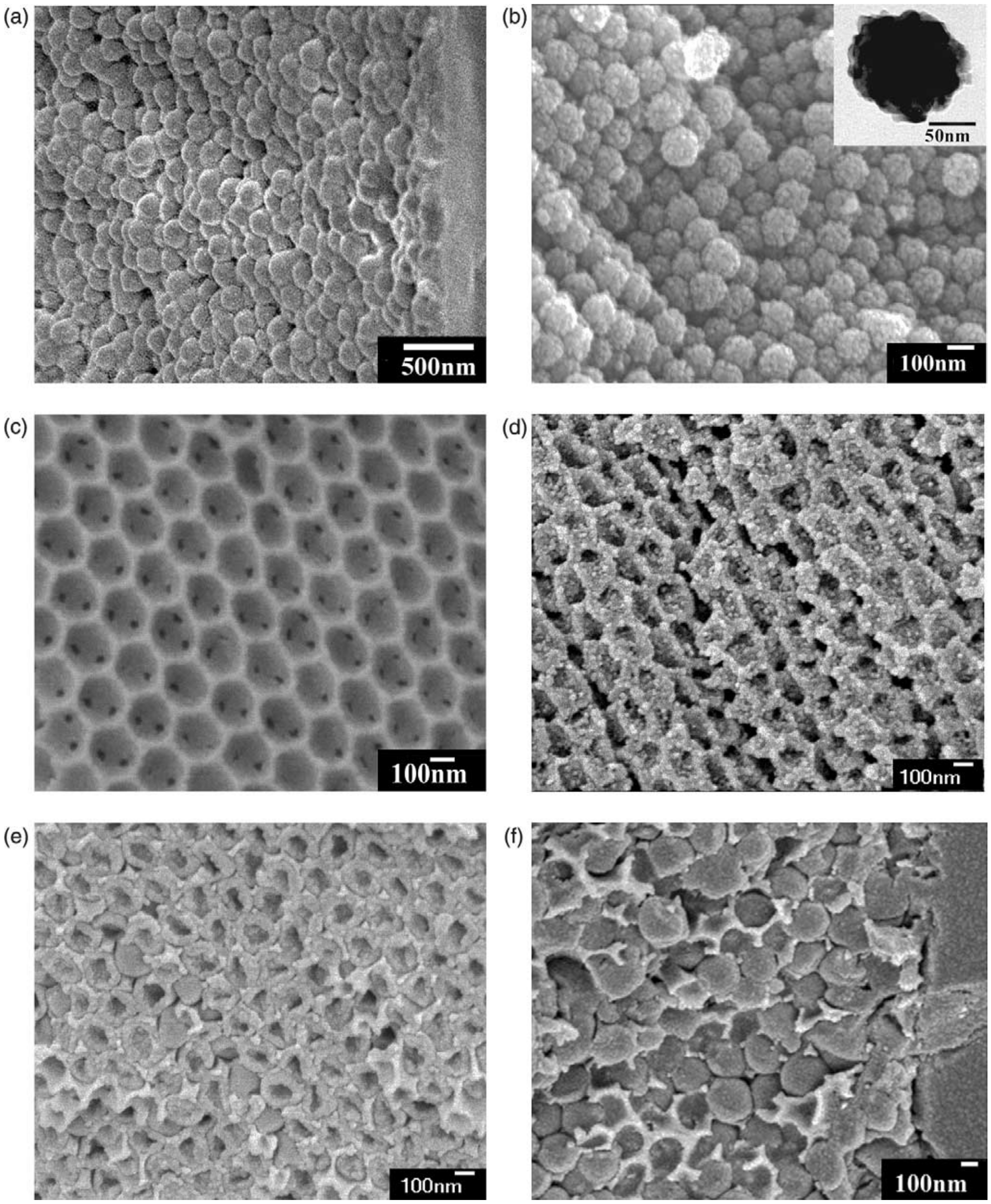

Fig. 2. Scanning electron microscopy images of the ordered samples: (a) and (b) PG1/titania composite before and after calcination at 450 °C; (c)–(f) titania materials after removal of PG6 template by calcination at 450 °C, whose morphology is evolved outwardly.

water. The compositions and abbreviations of the polymer gels used are listed in Table 1, in which the amount of KPS is about 0.13 wt% of total amount of monomer.

2.3. Template synthesis of titania ordered materials

Water in the gels was substituted by ethanol in order to avoid the rapid hydrolysis of tetrabutyl titanate (TBT) in the presence of water. The ethanol-swollen gels were then immersed in pure TBT or TBT/ethanol (1:1 v/v) solution for 24 h to allow the precursor absorption. The precursor-soaked gels were then transferred into an ethanol/H_2O mixture (1:1 v/v) for 5 h to allow the sol–gel process forming gel/titania composites. After being aged and dried at 60 °C for 2 h, the gel/TiO_2 composites were calcined at 450 °C for 3 h to remove the polymers and drive titania crystallization.

2.4. Characterization

Au was vacuum sputtered onto the sample fractures, and a scanning electron microscope (SEM; JSM-6700F) was used to observe the morphologies. For observing morphology of the individual particles by TEM (Hitachi H-600), the titania samples were ground and dispersed in ethanol under ultrasonication to form dispersions, and very dilute dispersions were then dropped onto a carbon-covered copper grid. Wide-angle X-ray powder scattering (Rigaku D/max-2500) was used to characterize the titania crystallinity.

3. Results and discussion

A series of inverse opal gels with varied composition (listed in Table 1) were chosen to investigate the template effect dependence on chemical composition of templates. Template PG1 is a polar gel without acid group, while PG2 to PG6 contain sulfonic acid group with increasing content. This has been confirmed by the increasing intensity of the characteristic peaks of sulfonic groups (1036, 1227 cm^{-1}) from PG1 to PG6 in FT-IR spectra (Fig. 1(a)). The silica opal template is stacked by monodisperse silica spheres about 290 nm in diameter (Fig. 1(b)). The freeze–dried PG1 gel (Fig. 1(c)) possesses uniform pores interconnected through the window channels, which are colorful after being soaked in water (Fig. 1(d)). The other series PG2 to PG6 gels have the same ordered structure and colorful appearance.

The colorful appearance and the original shape of the gels were well preserved after water was exchanged by ethanol from the gels. After TBT-saturated gels were exposed to a water/ethanol mixture, the sol–gel process occurred forming rigid titania/gel composites with somehow shrinkage. After the composite were calcined, the polymer gels were removed accompanying with titania crystallization. The morphology of titania materials is greatly influenced by the composition of the gel templates. The titania/PG1 composite has opal structure (Fig. 2(a)). After removal of PG1 by calcination, the opal structure remained. The coarse spheres are composed of titania crystalline nanoparticles about 10–30 nm in diameter (Fig. 2(b)). The ordered array could be broken into individual colloidal spheres, which are solid (inset TEM). The sol–gel process forming titania only occurs in the pores of PG1 template not in the gel skeleton, which is similar to the rigid templates [8]. When a sufficient amount of acid group is introduced for example PG6 gel containing about 30 wt% AMPS, an unique morphology is formed (Fig. 2(c)–(f)). In Fig. 2(c), the interior region is typical inverse opal structured, which possesses uniform pores interconnected via the window channels. This indicates that the sol–gel process forming titania occurs in the gel skeleton not in the pores. The wall surface became coarse, indicating that the amorphous titania has transformed into anatase phase verified by WAXS spectra. In Fig. 2(d), some titania nanoparticles are dispersed in the pores. Towards the exterior region, more TiO_2 nanoparticles are formed in the pores and started to form spheres (Fig. 2(e)) from hollow to solid ones (Fig. 2(f)).

When AMPS content is small for example less than 2 wt%, monodisperse spheres arrays were achieved (Fig. 3(a)), which are similar to those shown in Fig. 2(b). When AMPS content increases to 5 wt%, spheres and frameworks coexisted (Fig. 3(b)), indicating that the sol–gel process occurs in two sites: the gel skeleton and the pores. With AMPS content further increase from 10 to 15 wt%, formation of porous framework dominated with the spheres retrogressively formed (Fig. 3(c) and (d)). When AMPS content reaches 30 wt%, only titania framework was prepared as shown in Fig. 2(c).

A dilute TBT ethanol solution (1:1 v/v) instead of pure TBT was used to study the effect of precursor concentration on the structure of the inorganic materials. Opal structure composed of uniform titania spheres were formed from PG1 template, which is similar to that as shown in Fig. 2(b). The ordered array could also be broken into individual colloidal spheres. TEM image reveals that the spheres are solid. When PG6 template

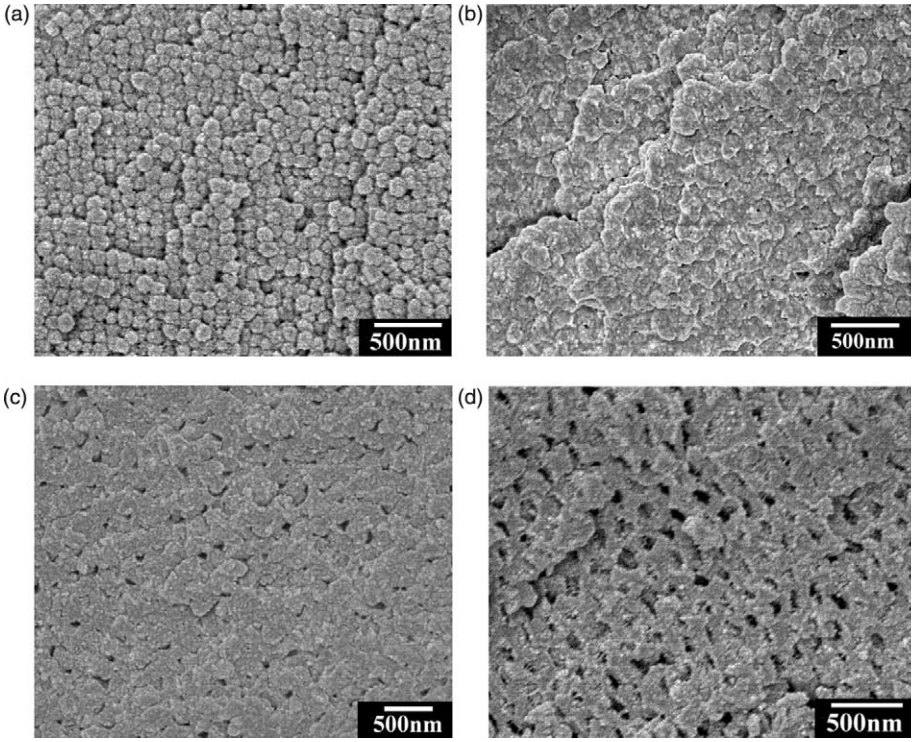

Fig. 3. Morphological evolution of the interior region of the titania materials prepared by using PG2–PG5 templates containing varied AMPS content: (a) PG2 (2.0 wt%); (b) PG3 (5.0 wt%); (c) PG4 (10.0 wt%); (d) PG5 (15.0 wt%).

was used, almost the whole sample is ordered macroporous framework (Fig. 4(b)). Even in the exterior surface (Fig. 4(c)), the inverse opal structure is well retained.

The amorphous titania is transformed into anatase, anatase/rutile or rutile when calcined at 450, 600 or 900 °C, respectively, which revealed by WAXS spectra. However, the ordered structure was lost when the composites were calcined at 900 °C The result is similar those when opals gels were used as templates [10].

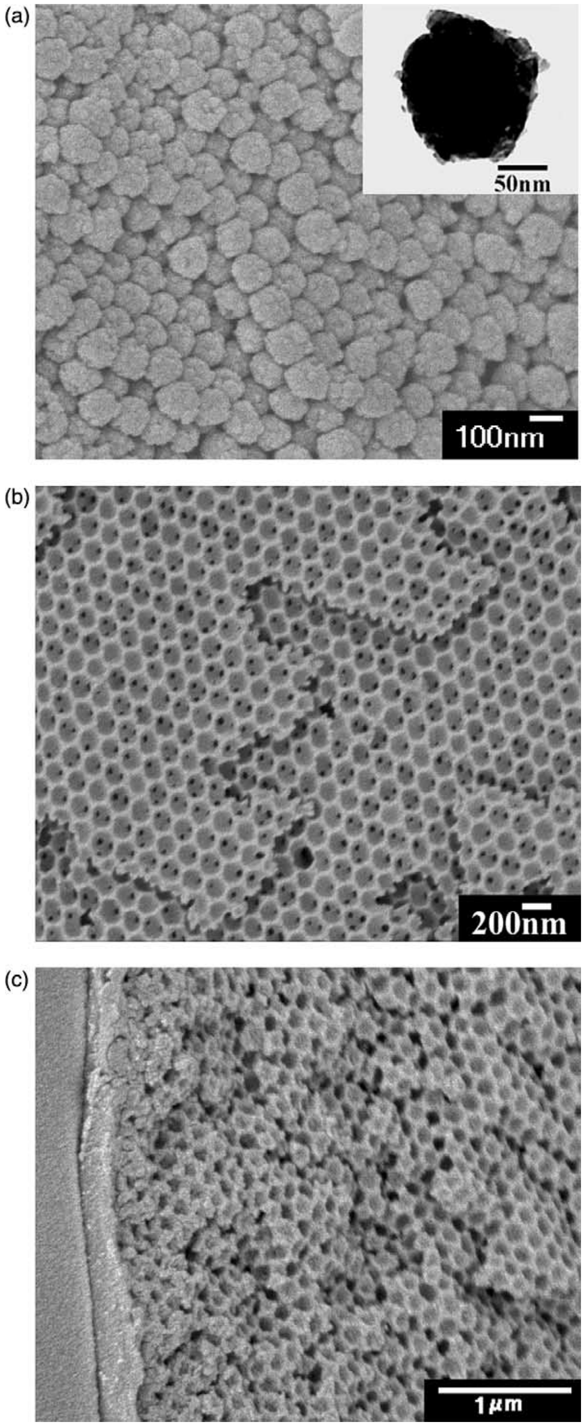

Fig. 4. Scanning electron microscopy images of ordered titania materials using TBT/ethanol (1:1 v/v) solution after being calcined at 450 °C. (a) Using PG1 gel template; (b) and (c) interior and exterior regions of the sample using PG6 gel template.

The template effect of the polar inverse opal gels without acid groups for example PG1 is the same as a rigid one to prepare spherical structures. In contrast, a framework/sphere gradient structure is template prepared using the gels with acid groups for example PG2–PG6. It is understood that the sol–gel process of titania is accelerated under acid condition [12]. During the sol–gel process, water should diffuse inwardly through both the pores and the gel skeleton. In the case of PG6 gel template, sol–gel occurs preferentially in the gel skeleton mainly by the acid group catalyzed, whilst the sol–gel process in the pores is relatively slower. In the outer region of the template, water concentration is higher and the sol–gel process in the pores occurs fast to deplete the precursor. Therefore, while titania formed both in skeleton and pores, the window channels were blocked to constrain water diffusion inward. In the interior region, sol–gel process in the gel skeleton is dominated due to low concentration of water therein, and the precursor in the pores diffuses into the gel skeleton forming a composite framework. In the case of PG1 gel template, the sol–gel process in the pores dominates since no sufficient acid group in the gel skeleton can catalyze the sol–gel process therein. The sol–gel process mainly occurs to form spheres in the pores. In the case of low precursor concentration, the sol–gel process is declined to allow water inward diffusion through the whole sample, almost all the precursor in the pores diffuses into the gel skeleton forming a composite framework of an inverse opal material. In the case of gel templates without acid groups, the sol–gel process in the pores dominates forming the opal structure independent on the precursor concentration. This mechanism is general. We have used a weak acid—carboxylic group instead of sulfonic group to achieve the similar structures [14].

4. Concluding remarks

We have proposed to template synthesize structured titania materials with tunable morphology from the inverse opal gels with varied chemical composition. It is a key to control the acid group content within the gel skeleton and precursor concentration to achieve inverse opal, opal titania materials. It is possible to synthesize composite wall when some functional nanoparticles have previously formed within the template gel skeleton [13].

Acknowledgements

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References

[1] Göltner CG. Angew Chem Int Ed 1999;38:3155–6.
[2] Ruhl T, Spahn P, Hellmann GP. Polymer 2003;44:7625–34.

[3] Xia Y, Gates B, Yin Y, Lu Y. Adv Mater 2000;12:693–7.

[4] Wijnhoven JEGJ, Vos WL. Science 1998;281:802–4.

[5] Vlasov YA, Yao N, Norris DJ. Adv Mater 1999;11:165–9.

[6] Velev OD, Jede TA, Lobo RF, Lenhoff AM. Nature 1997;389:447–8.

[7] Wang D, Caruso F. Adv Mater 2001;13:350–6.

[8] Jiang P, Bertone F, Colvin VL. Science 2001;291:453–7.

[9] Yi D, Kim D. Nano Lett 2003;3:207–11.

[10] Rong J, Ma J, Yang Z. Macromol Rapid Commun 2004;25:1786–91.

[11] Stöber W, Fink A, Bohn E. J Colloid Interface Sci 1968;26:62–6.

[12] Hench LL, West JK. Chem Rev 1990;90:33–72.

[13] Caruso RA, Antonietti M, Giersig M, Hentze HP, Jia J. Chem Mater 2001;13:1114–23.

[14] Rong J, Yang Z. Chin Sci Bull 2002;47:1385–9.