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Effects of additives on the morphologies of thin titania films from self-assembly of a block copolymer

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Abstract

The effects of additives of poly(methyl methacrylate) (PMMA) and $HAuCl_4$ on the morphologies of hybrid titania films formed via co-assembly of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) copolymers, titania sol–gel precursor in a selective solvent were investigated. The results show that addition of PMMA or $HAuCl_4$ has an important influence on the morphologies of hybrid titania films. Addition of PMMA or $HAuCl_4$ can induce the morphology transition of the PS-*b*-PEO/titania sol–gel mixture from spherical micelles to vesicles. Therefore, the morphologies of the hybrid films formed on silicon substrate surfaces by spin-coating can be controlled by the addition of homopolymer (PMMA) or inorganic precursor ($HAuCl_4$) into the PS-*b*-PEO/titania sol–gel mixtures, allowing access to nanoparticles or nanoporous films. After removing the polymer matrix, nanoparticle aggregates or nanobowl-like structures are left behind on the substrate surfaces.

Keywords: Block copolymer; Titania film; Sol–gel

1. Introduction

TiO_2 is one of the most important oxide materials due to its wide range of applications [1–4]. Among these applications, for example, TiO_2 has been used as an excellent photocatalyst for the removal of hazardous organic substances and as an electrode material for dye-sensitized solar cells [5–9]. It is well known that the properties of nanostructured materials are of the size, shape, interface, and structure dependence [10–12]. Control of the morphologies is one of the key issues in developing new applications of the nanostructured materials [13,14]. Many recent efforts have focused on the fabrication of TiO_2 nanostructures, such as nanoparticles [15,16], nanowires [17,18], nanotubes [19–21], nanobowls [22], mesoporous materials [23], etc [9,24–34]. Although various nanostructured TiO_2 materials mentioned above have been prepared, for both fundamental and application issues, it still remains a significant challenge to develop facile and effective methods for tuning the morphology of TiO_2 nanostructures.

The self-assembly characteristics of diblock copolymers permit to control the superstructures, vary the typical length scales and add specific functions. The properties of block copolymers can be tuned by adjusting solvent composition, molecular weight or polymer architecture [35–40]. In selective solvents, block copolymers can self-assemble into various microstructures, such as sphere, cylinder and bilayer membrane, helices, cylindrical networks, nanotubes, the hollow hoop, the bowl-shaped micelles, and the ringlike supramolecular assemblies [41–48]. For example, self-assembled micelle morphologies of amphiphilic block copolymer polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) and PS-*b*-PEO have been intensively investigated [49–51]. These aggregates may also be applied to generate nanostructured materials.

In recent years, superstructures formed by block copolymers have been used as templates for the preparation of various nanostructures of metallic, inorganic, and semiconductor

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[52–64]. Along the line of these schemes, sol–gel chemistry using block copolymer templates has been successfully extended to non-silica frameworks. PEO-based block copolymers (PEO–PPO–PEO or PEO–alkyl copolymers) are the most usual templates [29,30,32,65–70]. Arrays of TiO_2 nanoparticles [63,64], Au/TiO_2 composite nanoparticles [71,72], foamlike bicontinuous nanostructures [73] and other types of titania nanostructures have been prepared by using PEO-based block copolymers as templates [64].

Recently, sol–gel chemistry using asymmetric amphiphilic PS-*b*-PEO block copolymer templates has been used to produce arrays of titania nanoparticles on the film surfaces [71,72]. PS-*b*-PEO is also used as a structure-directing agent to produce organic–inorganic hybrid TiO_2 films [74,75]. By adjusting the weight fractions of 1,4-dioxane (a good solvent for PS and PEO blocks), concentrated HCl and titanium tetra-isopropoxide (TTIP), hybrid films with a variety of interesting morphologies are obtained [74]. By using PMMA-*b*-PEO block copolymer as templates, vesicle morphology of a hybrid titania film was observed [75]. It has been reported that the morphologies of the materials prepared using sol–gel process depend on the type of the template, composition, concentration, pH, solvent, etc. and different nanostructures can be created by adjustment of some of the factors [76,77]. Moreover, as an alternative route, the addition of additives such as homopolymer or inorganic compounds to a block copolymer provides relatively simple means to control the morphologies of the block copolymer films [78–81]. Till now, the influences of various additives on the morphologies of hybrid titania films prepared by using block copolymer templates have been rarely reported and needs systematical investigations.

In this work, we report the morphology control of the hybrid and TiO_2 films in a sol–gel process using a diblock copolymer as template. Titania sol–gel precursor was prepared by mixing TTIP, isopropanol, toluene and concentrated HCl. Asymmetric PS-*b*-PEO block copolymer was dissolved in toluene (a selective solvent for PS) to form micelles solution. Then the block copolymer micelles solution and titania sol–gel precursor were mixed together. The morphological changes of the hybrid titania films indicate that the morphologies of the PS-*b*-PEO/titania sol–gel mixtures can be induced from spherical micelles to vesicles by addition of homopolymer PMMA or inorganic $HAuCl_4$ precursor.

2. Experimental part

2.1. Materials

PS-*b*-PEO diblock copolymer with a polydispersity index of 1.05 was purchased from Polymer Source, Inc. The number average molecular weights of PS and PEO blocks are 19 000 g/mol and 6400 g/mol, respectively. Poly(methyl methacrylate) had a weight molecular weight and polydispersity of 9800 g/mol and 1.08, respectively. Titanium tetra-isopropoxide (TTIP, 97%), and tetrachloroauric(III) acid ($HAuCl_4 \cdot xH_2O$, $M_w = 333.79$) were purchased from Aldrich and used as received. Analytical grade toluene, isopropanol and hydrochloric acid (HCl, 37%) were purchased and used as received.

2.2. Substrates

Silicon (Si) wafers with a native oxide layer (ca. 1 cm × 1 cm) were cleaned in a piranha solution (70/30 v/v of concentrated H_2SO_4/30% H_2O_2. Caution! Piranha solution reacts violently with organic compounds and should not be stored in closed containers.), thoroughly rinsed with Milli-Q water, and then blown dry with nitrogen gas.

2.3. Film preparation

Toluene solutions of PS-*b*-PEO (1.0 wt%), the Au-loaded PS-*b*-PEO (molar ratio of $HAuCl_4$/EO was equal to 0.1) or the PS-*b*-PEO/PMMA (10–50 wt% of PMMA relative to (r.t.) PS-*b*-PEO copolymers, noted as PMMA10–50) mixture were stirred for about 12 h to make clear solutions. The preparation process of the sol–gel precursor solutions was described previously [71,72]. The molar ratio of HCl/TTIP in the sol–gel precursor solution was adjusted from 0.5 to 2.5. The desired amount of sol–gel precursor solution was mixed with the PS-*b*-PEO solution or the Au-loaded PS-*b*-PEO solution or the PS-*b*-PEO/PMMA mixture solution and stirred for 30 min. The amount of titania relative to (r.t.) the block copolymers (φ) was adjusted from 10.0 to 20.0 v/v% (noted as SG 10–20).

The hybrid inorganic–organic titania films were produced simply by spin-coating the mixture solution on a piece of silicon substrate. The obtained films were dried under ambient condition to induce crosslinking of the sol–gel precursor. In order to remove the block copolymer template and avoid the structure rearrangement or collapse, and reduce $HAuCl_4$ into metallic Au, the films were treated with deep UV irradiation in air ($\lambda = 254$ nm) for 4 days [82].

2.4. Characterization

AFM height and phase contrast images were obtained using a Digital Instruments Dimension 3100 scanning force microscope in the tapping mode with Olympus cantilever. Field emission scanning electron microscopy (FESEM) images were obtained with a LEO 1530 “Gemini”. The average diameters of the nanoparticles or the pores were determined by Image J program (NIH). Dynamic light scattering (DLS) were carried out with a Nano ZS (Malvern Instruments, Ltd., UK).

3. Results and discussions

3.1. Effect of PMMA amount

It has been reported that, when a precursor solution of titania is added to the PS-*b*-PEO solution, titania incorporate into the PEO domains selectively [71,72,74,75]. Nanoparticle arrays of titania are obtained after spin coating and removal of the block copolymer matrix [71,72]. In this case, it is found that the addition of homopolymer has a significant influence on the surface morphologies of the hybrid titania films. The mole ratio of HCl/TTIP in the sol–gel precursor solution used in samples (Figs. 1 and 2) was equal to 1.0. Nanoparticle packings on the surfaces of hybrid titania films were observed when φ was 10.0%. The average sizes of hybrid nanoparticles are about 12.9 nm, 13.4 nm, 17.0 nm and 20.0 nm for samples with the PMMA content of 0.0, 15.0, 30.0 and 50.0% (insets in Fig. 1). One can also see from Fig. 1 that if PMMA contents relative to PEO blocks are increased to 30.0 or 50.0%, the hybrid films with a sol–gel precursor amount of $\varphi \sim 10\%$ exhibit well ordered, hexagonal packing with a relatively uniform particle size.

From above results, it can be deduced that spherical micelles forms in the PS-*b*-PEO/PMMA/SG mixture solution [71,72]. It is well known that the morphology of a micelle basically depends on three factors [83]: (1) the stretching of the core-forming chains, (2) the core–corona interfacial energy, and (3) the repulsion among coronal chains. These factors are directly related to the Gibbs free energy of the micelles, if it were the enthalpic or entropic term. A change in one of these three parameters directly affects the free energy of the micelles. In other words, the micelles could become thermodynamically unstable and will modify their morphology in order to reach another stable state [83]. Solubility parameters of PS, PEO, toluene, isopropanol and water are 8.7–9.1, 9.9, 8.9, 11.5, and 23.2 $(\text{cal/cm}^3)^{1/2}$, respectively [84]. The block copolymers form the spherical micelles composed of hydrophilic PEO cores and hydrophobic PS coronas in toluene. If the sol–gel precursor is mixed with the PS-*b*-PEO/PMMA solution, the titania sol–gel precursor will be incorporated into the PEO domains due to their favorable interactions [72,85]. It is well known that PEO and PMMA are miscible in melt and amorphous states. To minimize the interfacial energy, PMMA should be located in the PEO microdomains. During spin-coating process, the amount of PMMA located in the PEO microdomains is increased with the increase of the PMMA content. At the same time, more titania sol–gel precursor will incorporate into the PEO microdomains. Therefore, the sizes of the hybrid nanoparticles increase with the increase of PMMA content if the sol–gel precursor amount is fixed at $\varphi \sim 10\%$. After spin coating, the hybrid films composed of clustered nanoparticles are formed. After removal of organic matrix, aggregates formed by spherical nanoparticles were observed [72].

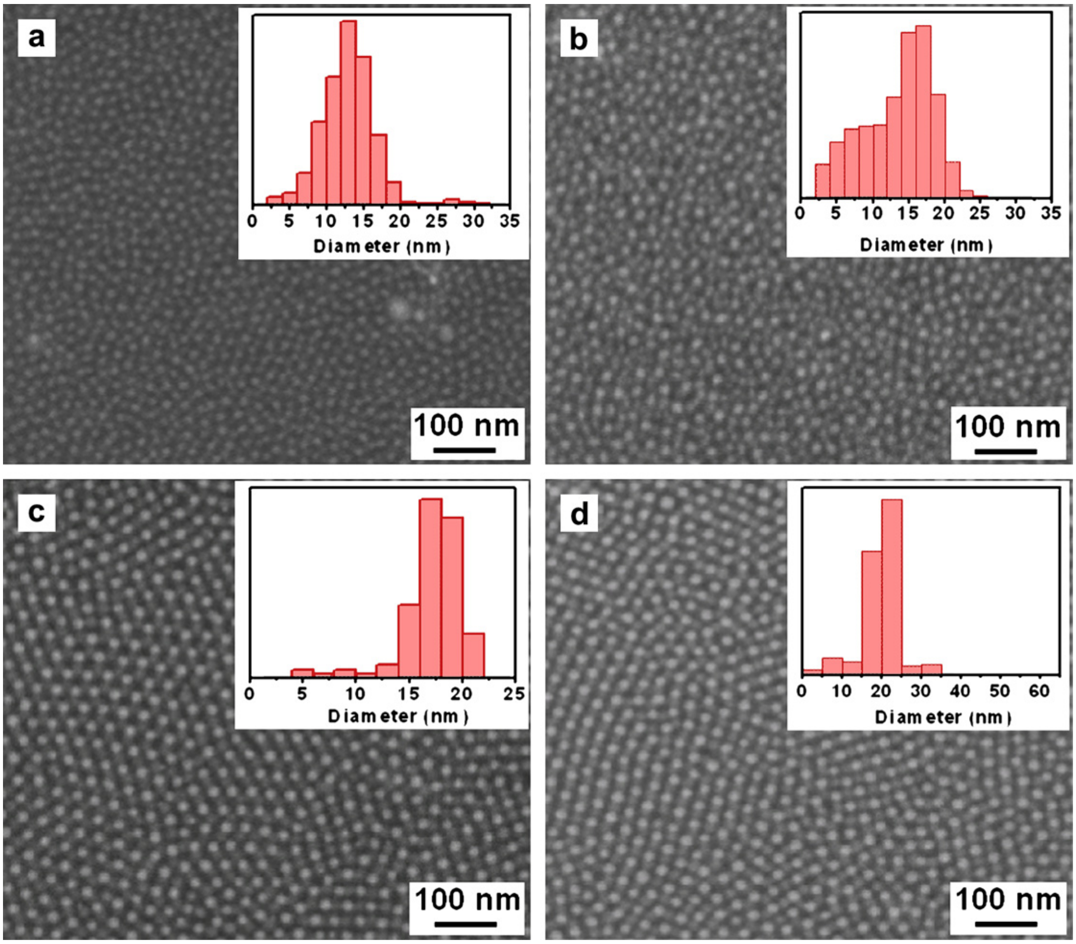

Fig. 1. FESEM images of spin-coated PS-*b*-PEO/PMMA/SG10 films with different amount of PMMA: (a) 0.0%; (b) 15.0%; (c) 30.0%; (d) 50.0%. Insets are diameter distribution of nanoparticles.

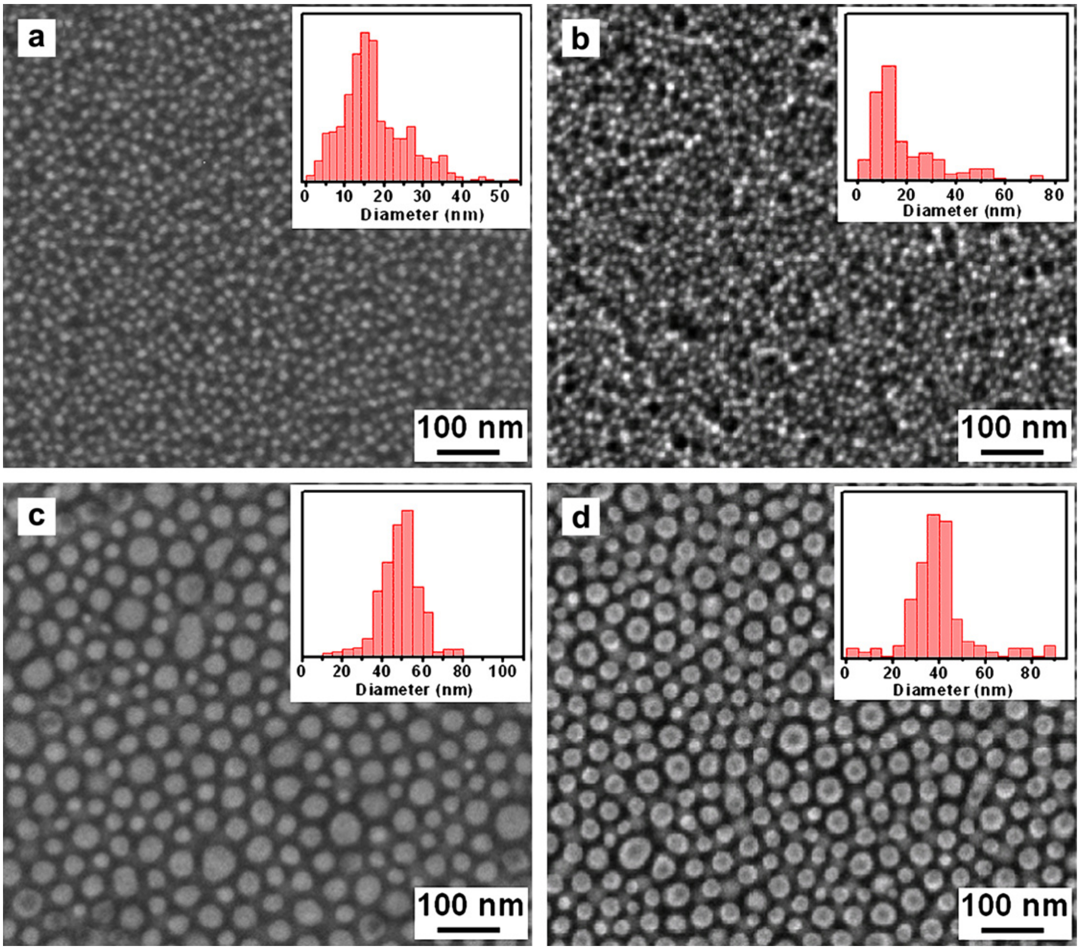

Fig. 2. FESEM images of spin-coated PS-*b*-PEO/PMMA/SG20 films with different amount of PMMA: (a) 0.0%; (b) 15.0%; (c) 30.0%; (d) 50.0%. Insets are diameter distribution of nanoparticles.

If a sol–gel precursor amount of $\varphi \sim 20\%$ was used, nanoparticles on the surfaces of hybrid films were also observed if PMMA content was 15.0% (Fig. 2b). Larger nanoparticles with wider distribution were observed if PMMA content was increased to 30.0%. Nanoparticles with small depressions on the center of the particle surfaces were observed when PMMA content was further increased to 50.0%. From Fig. 2c and d, one may deduce that the spherical micelles structures transform into vesicles if the content of PMMA is larger than 30.0% in solution. That is, the addition of PMMA homopolymer can induce the morphology transition from micelles to vesicle. To further prove this observation, the sample of Fig. 2d was treated with UV light in vacuum for 30 min and washed in acetic acid to remove PMMA component. A distinct phase contrast between the center and the edge of a particle was observed as shown in Fig. 3. The brighter and darker parts correspond to the harder domains containing titania and the soft continuous PS matrix. The result illustrates that vesicle structures are formed in solution. Such separate nanodomains in Fig. 3 also reveal that titania sol–gel precursor is incorporated into the wall of the vesicles and the outer surface is composed of PS blocks. Giant compound vesicle structures have been reported for polybutylene-*block*-poly(ethylene oxide) (PB-*b*-PEO) in aqueous

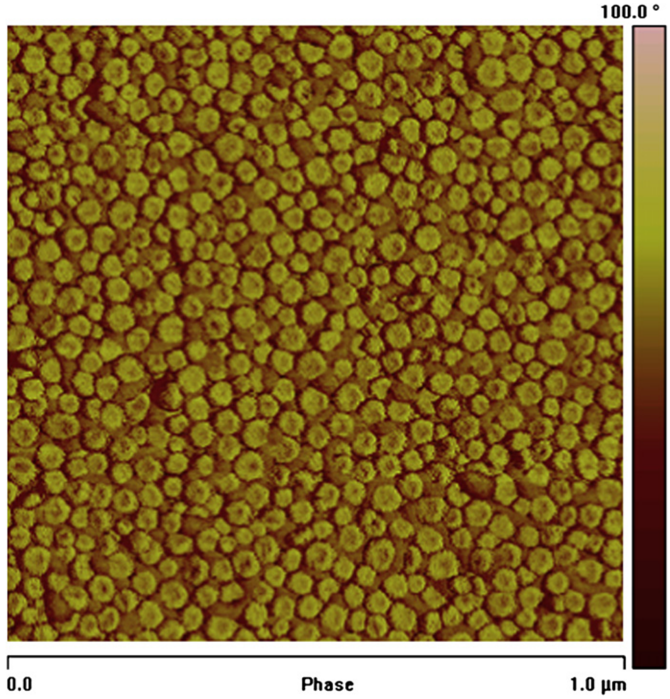

Fig. 3. AFM phase image of PS-*b*-PEO/PMMA50/SG20 film after treated with UV light in vacuum for 30 min and washed in acetic acid to remove PMMA.

solution [86]. PS-*b*-PEO and PS-*b*-PAA block copolymer micelles with spherical and various other morphologies have also been studied in detail [87] and can undergo the morphology transformation in solution [50,51]. It is demonstrated that with increasing PS contents the dominant morphologies become spherical micelles, then rod and lamellae and finally vesicles [50,51,83]. Cheng et al. also observed various vesicle structures in the PS-*b*-PEO/TTIP/HCl/1,4-dioxane system [74]. Comparing Fig. 2c and d with Fig. 1c and d, the increase of the amount of sol–gel precursor, i.e., more amount of isopropanol and HCl solution in the mixture, can lead to the increase of the surface free energy between the PS blocks and surrounding solvents. To minimize the extra interfacial energy, the morphology is transformed from micelles to vesicles.

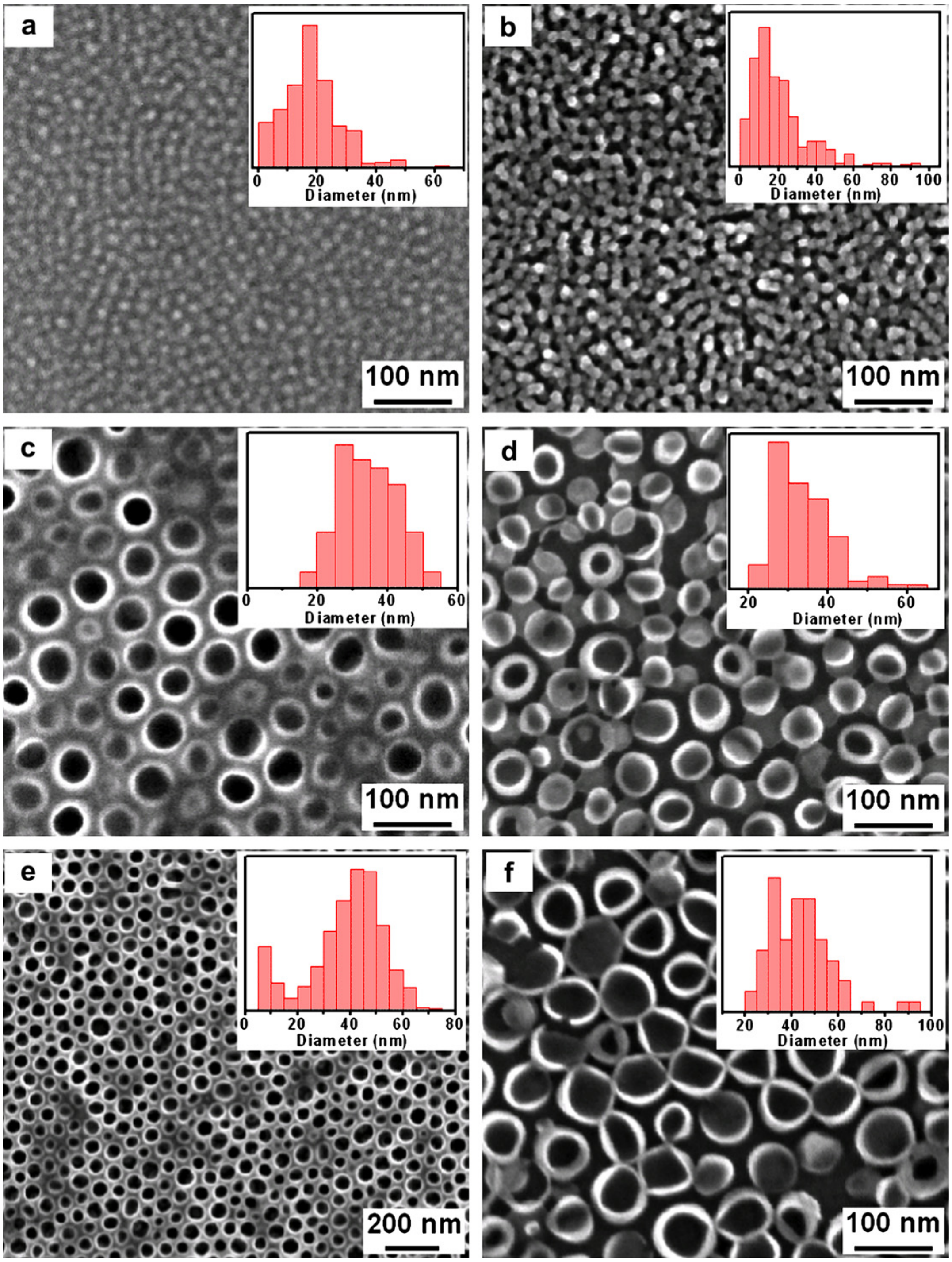

Fig. 4. FESEM images of PS-*b*-PEO/PMMA30/SG10 films with different molar ratio of HCl/TTIP: (a), (b) 0.5; (c), (d) 1.3; (e), (f) 2.1. (a), (c) and (e): spin-coated films. (b), (d) and (f): the films were treated with UV light in air for 4 days to remove polymer matrix. Insets are diameter distribution of nanoparticles or nanopores.

3.2. Morphology under different concentration of HCl solution

In the templating sol–gel process, the content of acid has an important effect on the morphologies of the hybrid materials. Acidic water can promote Ti(IV) hydrolysis to form hydrophilic Ti-oxohydroxo species (which can swell PEO block), can better define the inorganic-template hybrid interface, and enhance microphase separation of block copolymer [1–4,74,75,88]. Because $HAuCl_4$ is also an acid, to distinguish the effects of $HAuCl_4$ and HCl on the morphologies, the influence of HCl content on the morphologies of titania nanostructures is investigated first. The weight fractions of PS-*b*-PEO, PMMA and sol–gel precursor are fixed, while only the molar ratio of HCl/TTIP in the sol–gel precursor solution is changed. It is found that the morphologies of the hybrid titania films depend significantly on the molar ratio of HCl/TTIP in the sol–gel precursor solution (Fig. 4 vs. Fig. 1c). If the molar ratio of HCl/TTIP in the precursor solution is less than 1.0, spherical nanoparticles are formed (Fig. 4a). After removal of polymer matrix, aggregates of nanoparticles are obtained (Fig. 4b). If the molar ratio of HCl/TTIP in the precursor solution is increased to 1.3, porous hybrid films are formed after spin-coating the mixture of the PS-*b*-PEO/PMMA solution and the sol–gel precursor on silicon substrates. Fig. 4c shows the FESEM image of the hybrid PS-*b*-PEO/PMMA30/SG10 film spin-coated on silicon substrates. Circular pores were observed on the film surface. Similar porous morphologies were also observed if molar ratio of HCl/TTIP in the precursor solution was further increased to 2.0 (Fig. 4e). After removal of polymer matrix, bowl-like nanostructures were observed (Fig. 4d and f). However, turbid solution was observed if HCl/TTIP was increased to 2.5, indicating that large-scale structures formed or macrophase separation took place. Cheng et al. observed that the increase of the amount of concentrated HCl can induce the morphology transformation from nanowires to versicles in 1,4-dioxane solution [74]. The driving force is attributed to the increase of the interfacial energy between PS blocks and surrounding solvents with increasing the content of HCl in solution. In our case the morphology transforms from spheres to vesicles. In this case, no nanowires were observed if the content of HCl in the precursor solution was changed. This may be due to the fact that the current solvent (toluene) is different from that in the previous work [74].

3.3. Effect of $HAuCl_4$ on the morphology

To improve the efficiency of the photocatalytic and photoelectrochemical responses, TiO_2-based systems containing transition metal ions (mainly group VIII metals) and noble metals have been investigated extensively [1–4]. To prepare TiO_2/Au composite nanostructures, $HAuCl_4$ is usually used as a precursor. It is found that the addition of small amount of $HAuCl_4$ precursor (the molar ratio of $HAuCl_4$/EO and HCl/TTIP were adjusted to 0.1 and 1.0, respectively.) has an important influence on the morphologies of hybrid PS-*b*-PEO/PMMA/SG films. Figs. 5 and 6 show the morphologies

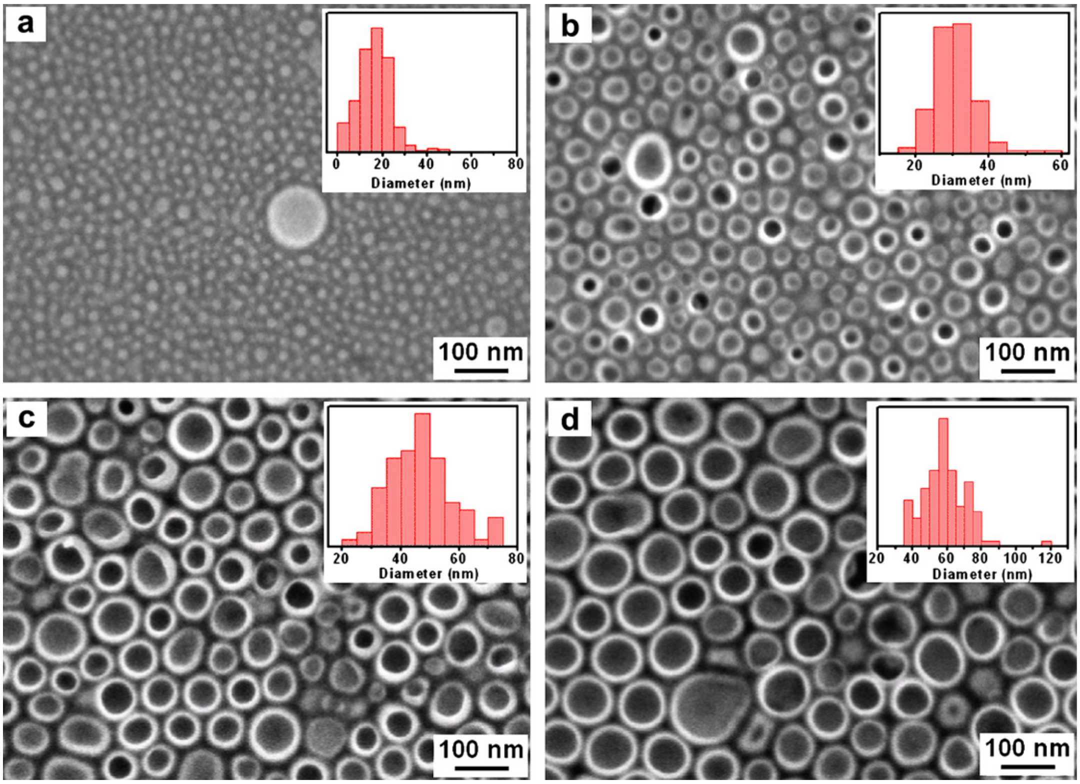

Fig. 5. FESEM images of spin-coated PS-*b*-PEO/PMMA50/$HAuCl_4$(0.1)/SG films with different sol–gel content: (a) 5%, (b) 10%, (c) 15% and (d) 20%. Insets are diameter distribution of nanoparticles or nanopores.

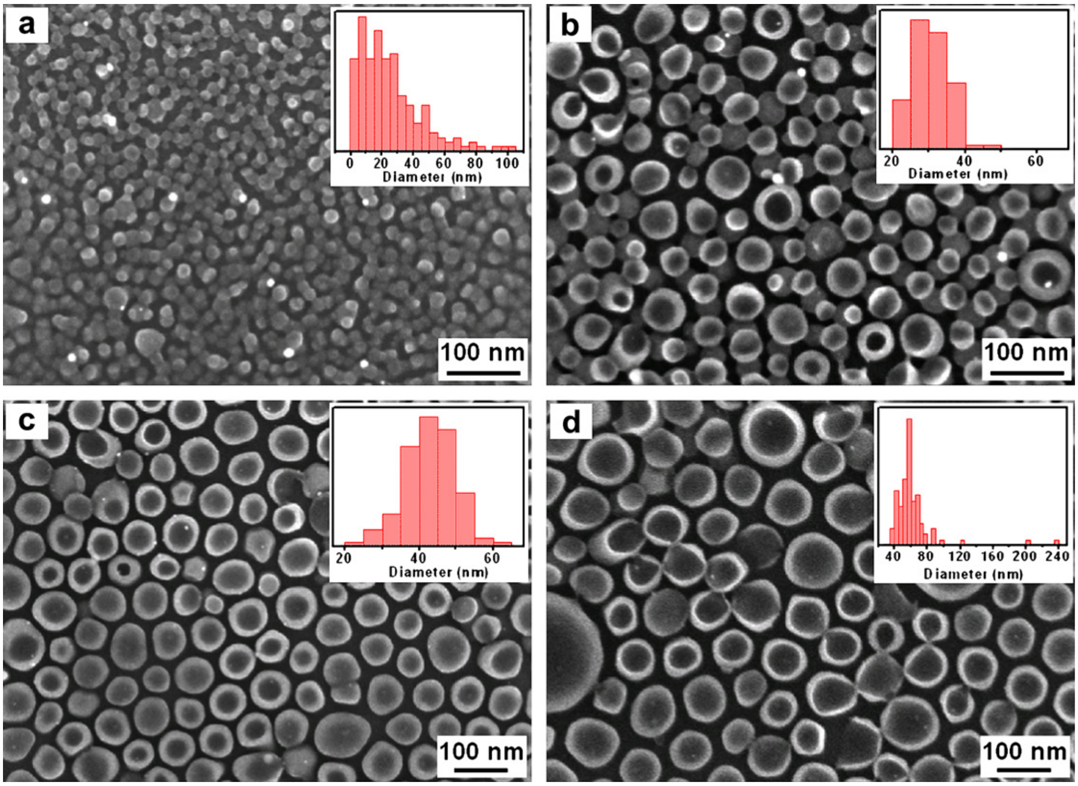

Fig. 6. FESEM images of PS-*b*-PEO/PMMA50/HAuCl$_4$(0.1)/SG films after treatment with UV light in air for 4 days to remove polymer matrix. Sol–gel content: (a) 5%, (b) 10%, (c) 15% and (d) 20%.

of PS-*b*-PEO/PMMA50/HAuCl$_4$(0.1)/SG films before and after removal of polymer matrix. It is found that nanobowls form even in case sol–gel content is 10%. Based on the experimental observations, the correlation of the additives and the resulting morphologies are summarized in Table 1. It can be seen that if φ is less than 10%, spherical structures are formed. For $\varphi \sim 10\%$, the porous films are observed when PMMA content is equal to or larger than 30%. If φ is greater than 15%, porous films are always formed when the amount of PMMA is changed from 15% to 50%. After removal of polymer matrix, titania nanobowls are left on the substrate surfaces, indicating that vesicles are formed in the solutions. It can be concluded from the results that addition of PMMA or HAuCl$_4$ induces the morphology transition from spherical micelles to vesicles at relatively low sol–gel content. Addition of HAuCl$_4$ precursor had a similar effect to the increase of the amount of HCl solution. The effects of additives on the morphologies of hybrid titania films after removal of polymer matrix are summarized in Fig. 7.

The formation of the porous nanostructures may be interpreted as follows. PS-*b*-PEO can form micelles in toluene. The titania sol–gel precursor is composed of TTIP, HCl solution, toluene and isopropanol. If the sol–gel precursor is mixed with the PS-*b*-PEO solution, titania oligomer will be incorporated to the PEO domains due to their favorable interactions. It is believed that HCl plays an important role in the synergetic assembly process. It enhances microphase separation of PS-*b*-PEO and leads to the morphology transition. Addition of small amount of HCl into the PS-*b*-PEO or PS-*b*-PEO/PMMA solutions can make the hydrodynamic sizes increase greatly (Fig. 8), illustrating the formation of vesicles. If PMMA is added in the PS-*b*-PEO/SG system, PMMA is sequestered in the PEO domains and further increase the interfacial curvature. If the HAuCl$_4$ precursor is added to the PS-*b*-PEO/PMMA/SG system, it plays a dual role in the sol–gel process. At first, it forms a complex with the EO units and mainly locates within the PEO microdomains. Second, it serves as an acid catalyst to the hydrolysis of Ti(IV), then hydrophilic Ti-oxohydroxo species are generated and

Table 1
The morphologies of the hybrid PS-*b*-PEO/PMMA/HAuCl4(0.1)/SG films before and after removal of polymer matrix with UV irradiation

PMMA (wt% r.t. PS-*b*-PEO)	Before/after UV	Titania sol–gel volume fraction to PS-*b*-PEO (v%)			
		5	10	15	20
0	Spin-cast	S	S	S	S
	UV	W	W	W	W
15	Spin-cast	S	S	H	H
	UV	W	W	B	B
30	Spin-cast	S	H	H	H
	UV	W	B	B	B
50	Spin-cast	S	H	H	H
	UV	W	B	B	B

S: spherical structure; W: wormlike structure; H: holey structures; B: bowl-like structure.

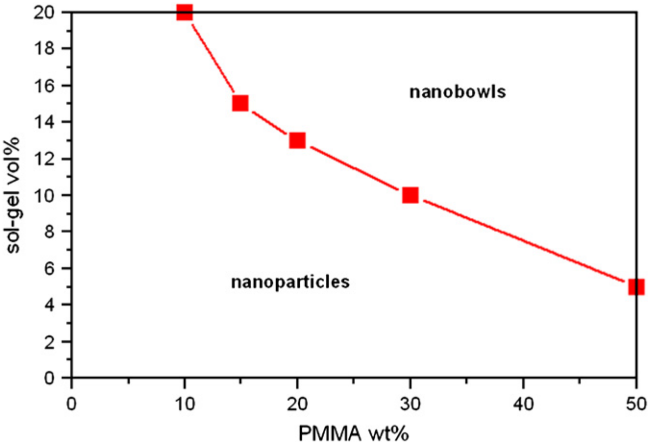

Fig. 7. The compositional regions where nanoparticles and nanobowls are formed in PS-*b*-PEO/PMMA/$HAuCl_4$(0.1)/SG films.

incorporated into PEO domains, which swell the PEO blocks. The mass fraction of the hydrophilic domains including PEO, PMMA, $HAuCl_4$ precursor and titania relative to the mass of the PS-*b*-PEO block copolymer increases with addition of $HAuCl_4$ or PMMA. Discher and Eisenberg proposed one rule for polymersomes in aqueous solution. If the mass fraction of the hydrophilic block to total mass of the copolymer is $\sim 35\% \pm 10\%$, vesicles are observed [47]. The effects of the starting nonselective solvent and added salts during the micellization process on the morphologies ultimately observed are also rationalized using this simple approach [89]. It is believed that cooperative self-assembly of PS-*b*-PEO copolymers, PMMA, $HAuCl_4$ and titania oligomer in the mixed solvents leads to vesicles consisting of a soluble PS corona and a large core containing PEO chains, titania oligomer, isopropanol and water. During spin coating, the coalescence between vesicles is prevented because the hydrophilic domains are encapsulated by PS blocks. Complicated surface currents (the gas flow, the convection, and Marangoni flows) induce the compact arrays of the vesicles composed of the hydrophilic cores and outer PS blocks. After the evaporation of solvent and water from the hybrid polymer layer, the film with porous structures forms [90].

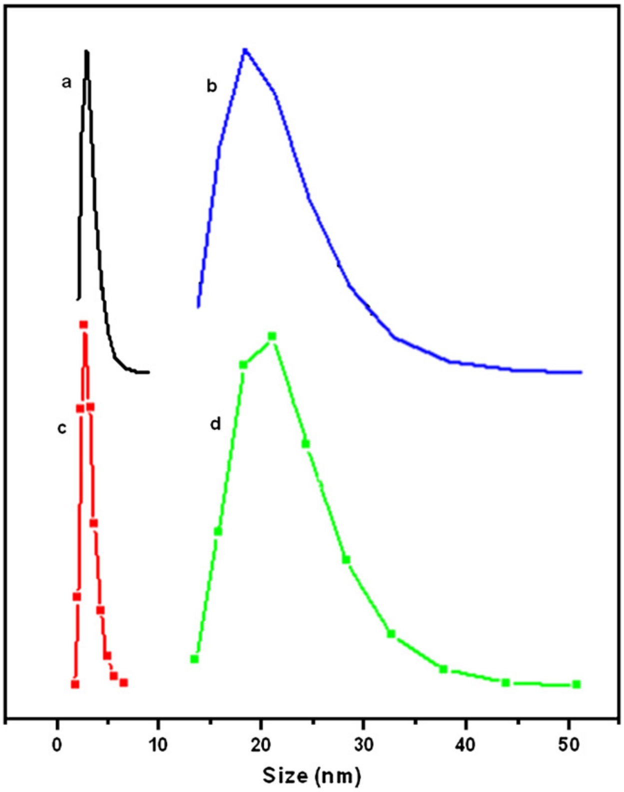

Fig. 8. Aggregate size distributions measured by DLS: (a) 1 wt% PS-*b*-PEO toluene solution, (b) 1 wt% PS-*b*-PEO toluene solution containing 1.18 wt% HCl solution (37%), (c) 1 wt% PS-*b*-PEO/PMMA30 toluene solution, (d) 1 wt% PS-*b*-PEO/PMMA toluene solution containing 1.18 wt% HCl solution (37%).

4. Conclusion

The micelle-templated nanostructured titania thin films can be formed via co-assembly of PS-*b*-PEO copolymers, titania sol–gel precursor, and other additives (such as PMMA and $HAuCl_4$) in a selective solvent. It is found that addition of PMMA or $HAuCl_4$ has an important influence on the morphologies of the hybrid PS-*b*-PEO/sol–gel films. Both of them can be selectively sequestered into the PEO domains during co-assembly and induce the morphology transition from spherical micelles to vesicles. The changes of mixture compositions give control over the nanostructure morphologies formed on silicon substrate surfaces, allowing access to nanoparticles or contiguous nanoporous films. After removal of organic matrix, nanoparticle aggregates or nanobowls are left behind on the substrate surface. For producing nanobowls in particular, this may be a relative simple method.

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