A Facile Way to the Generalized Synthesis of Mesoporous Rare Earth Oxide Thin Films via Amphiphilic Ionic Block Copolymer Templating

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A new concept to achieve the generalized synthesis of crystalline mesoporous rare earth (RE) oxide thin films templated by an ionic amphiphilic block copolymer is developed. As a demonstration, mesoporous La₂O₃, Eu₂O₃, Tb₂O₃, and Yb₂O₃ thin films representing the light and heavy rare earth groups are synthesized using polystyrene-*block*-poly (acrylic acid) (PS-*b*-PAA) as a templating agent. The impact of PS-*b*-PAA concentration on the morphology change of the mesopores is investigated. It shows that a certain concentration limit is present to generate homogenous mesoporous thin films with a narrow pore size distribution. The local, long range lateral structures, vertical structures, and crystallinity of the mesoporous thin films are probed with scanning electron microscopy (SEM), atomic force microscope (AFM), grazing incidence small Angle x-ray scattering (GISAXS), x-ray reflectivity (XRR), and transmission electron microscope (TEM). The mechanism about the formation of the mesoporous rare earth oxide thin films is discussed.

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The combination of amphiphilic block copolymer templating agents and sol-gel chemistry has proven effective to synthesize nanostructured oxide thin films including silica, titania, and other transition metal oxides^[7]. The amphiphilic block copolymer undergoes microphase separation in solution to form nano-sized domains. The precursors of the oxides are integrated into the nanostructured domains composed of the hydrophilic block, where the sol-gel reaction proceeds to form the network of oxides. As a result, the morphology of the organic nano-sized domain is replicated by the inorganic oxide network.^[7a, 7b, 8]

Despite the great success of this strategy to synthesize nanostructured transition metal oxide thin films, the morphological control over rare earth oxide thin films still remains a challenge^[9]. Current attempts to synthesize rare earth oxide thin films are mainly based on amphiphilic block copolymers with the non-ionic hydrophilic poly (ethylene oxide) (PEO) block^[7a, 7b, 8, 10]. A major limit of this strategy roots from the fact that no electrostatic interaction or strong coordination bond can be formed between the PEO block and the rare earth ions, the precursor of the rare earth oxide. This feature yields two effects. First, it is hard to integrate the rare earth ions into the PEO domain effectively; second, the sol-gel reaction of the rare earth salts within the PEO domain tends to proceed beyond the boundary of the domain. Both effects together makes it tricky and difficult to use such non-ionic block copolymers as templating agents to synthesize nanostructured rare earth oxide thin films. To our best knowledge, only a few results regarding the morphology control over particular rare earth oxide species have been reported^[9, 11]. A common strategy to achieve the generalized synthesis of the nanostructured rare earth oxide thin films of the whole family is yet to be developed.

Here we present a new concept using an ionic amphiphilic block copolymer as a templating agent to synthesize nanostructured rare earth oxide thin films. The ionic amphiphilic block copolymer demonstrated here is polystyrene-*block*-poly (acrylic acid), denoted as PS-*b*-PAA. Compared to the non-ionic amphiphilic block copolymer, PS-*b*-PAA has advantages being used as a templating agent. First, the PS/PAA pair is supposed to have a bigger hydrophobicity/hydrophilicity contrast than the PS/PEO pair,

Introduction

Nanostructured rare earth oxide thin films have attracted considerable interests due to their wide applications in microelectronics^[1], catalysis^[2], optics^[3], magnetic^[1b, 4]. The morphology including the shape, size, and organization of the nanostructures significantly influences the performance of the rare earth oxides^[5]. Therefore, it is of vital importance to develop an effective method to control the morphology of the rare earth oxide thin films. Furthermore, the rare earth oxide is a family consisting of multiple elements with versatile properties^[6]. It would be very useful to identify a reliable way to achieve the generalized synthesis of the nanostructured thin films covering the whole rare earth oxide family.

which implies a larger Flory-Huggins interaction parameter (χ). It is possible to form stable large sized micro-phase separated nanostructures with the same molecular weight of the individual block. Second, according to the hard-soft-acid-base (HSAB) theory, the rare earth ions are ‘hard’ acid and the carboxylic functional group belongs to ‘hard’ base. Both of them have a very good affinity towards each other^[12]. As a result, potentially the rare earth ions can be integrated into the PAA domain effectively by forming strong coordination bonds. Third, the carboxylic acid group can possess negative charge in a polar solvent or under high pH, forming electrostatic interactions with rare earth ions. The formation of electrostatic interaction further strengthens the association between the rare earth ions and PAA domain.

By using PS-*b*-PAA as a templating agent, a series of representative rare earth oxide mesoporous thin films including La₂O₃, Eu₂O₃, Tb₂O₃, and Yb₂O₃, are prepared. The local and long range lateral structures and vertical structures of the thin films are investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), grazing incidence small angle x-ray scattering (GISAXS), and x-ray reflectivity (XRR). The effect of block copolymer concentration on the morphology of the thin films is investigated as well. The mechanism for the formation of the mesoporous rare earth oxide thin films templated by PS-*b*-PAA is discussed.

Results and Discussion

An amphiphilic ionic block copolymer of PS-*b*-PAA has been designed and synthesized via ATRP in house with 60 repeating units of the PS block and 100 repeating units of the PAA block (details in supporting information, see Scheme S1 and Figure S1, S2, S3). **Figure 1** shows the SEM images of four different rare earth oxide thin films templated by 0.5 wt% PS-*b*-PAA. The XPS data confirms the presence of the rare earth oxide on Si substrate (Figure S4a-S4d). The co-existence of C1s peak is supposed to be the residual carbon from PS-*b*-PAA after calcination.

Figure 1. SEM images of the mesoporous rare earth oxide thin films. a: La₂O₃, b: Eu₂O₃, c: Tb₂O₃, d: Yb₂O₃. Insets are the FFT patterns of each image.

These four rare earth oxide species represent the so-called light (La, Eu), and heavy (Tb, Yb) rare earth element groups^[13]. The sol-gel precursors of the light and heavy rare earth groups (for example, rare earth nitrate used in this work) exhibit slight different

hydrolysis/condensation behavior and affinity towards PAA^[14]. Therefore, they have been selected to evaluate the general templating applicability of PS-*b*-PAA to the whole rare earth family. Figure 1a shows the mesopores of the La₂O₃ thin film with a smeared FFT pattern indicating a broad size distribution. A careful examination of the SEM image shows that the average pore size is roughly 11 nm with a wall thickness of around 10 nm. The thin film prepared without PS-*b*-PAA for control is featureless (Figure S5a); however, the XPS profile proves the presence of La₂O₃ layer on the substrate (Figure S4e). By comparing the control and templated La₂O₃ thin film, it can be concluded that PS-*b*-PAA does template the morphology of the La₂O₃ thin film. Regarding the Eu₂O₃ thin film (Figure 1b), mesopores with an average pore size of 10 nm and wall thickness of 9 nm coexist with macro-pores with the diameter of hundreds nanometers. The formation of the macro-pores is likely due to the de-wetting effect of the sol solution on the Si substrate. The reason why the de-wetting process happens in the case of Eu sol may be due to the very hydroscopic nature of the Europium nitrate. Due to the coexistence of meso- and macro-pores, the FFT pattern of Figure 1b is totally smeared. Without PS-*b*-PAA, the Eu₂O₃ thin film shows a very different structure, where large crystalline particles coexist with a non-structured layer (Figure S5b). Unlike the La₂O₃ and Eu₂O₃ thin films, the structure and organization of the mesopores within the Tb₂O₃ (Figure 1c) and Yb₂O₃ (Figure 1d) thin film is significantly improved. The ring-like FFT pattern of Figure 1c indicates that the mesopores are organized isotropically within the film with a narrow distribution of the characteristic center-to-center distance (*ca.* 17 nm). The average pore size and wall thickness measured in the SEM image are around 12 nm and 9 nm respectively, which is consistent with the value derived from the FFT pattern. The featureless Tb₂O₃ control thin film proves the addition of PS-*b*-PAA in solution effectively guides the formation of mesoporous Tb₂O₃ structures (Figure S5d). Similar to Tb₂O₃, Yb₂O₃ also shows a seemingly ordered mesoporous feature with an average pore size of 13 nm and wall thickness of 7 nm (Figure 1d) with a ring-like FFT pattern indicating a narrow center-to-center distance of 19 nm. The dramatic differences in the structure between the templated and non-templated Yb₂O₃ thin films prove that PS-*b*-PAA is able to template the morphology of the heavy rare earth oxide thin film (Figure S5d). In summary, by comparing the structures of a series of rare earth oxide thin films templated with/without PS-*b*-PAA, it can be concluded that PS-*b*-PAA exercises an effective templating effect to produce mesoporous structures covering the light and heavy rare earth groups. Besides the common feature of mesopores, the detailed mesoporous structures are slightly different from La₂O₃ to Yb₂O₃. This may be due to the different sol-gel reaction behavior and interactions with PS-*b*-PAA among these rare earth salts.

The formation of mesoporous rare earth oxide thin films is due to the microphase separation process of PS-*b*-PAA in the mixed solution of DMF and CH₂Cl₂. PS-*b*-PAA forms spherical core-shell micelles in solution with the core composed of the PS block and the shell composed of the PAA block (**Scheme 1**), which is partially proven by dynamic light scattering (Figure S6)^[15]. The PAA shell integrates the rare earth salts by forming coordination bonds and electrostatic interactions with the rare earth ions as indicated by the size increase of the micelles in solution from the DLS result (Figure S6) and the powder FTIR spectrum as well (Figure S7)^[16]. Sol-gel reaction of the rare earth salts proceeds within the PAA shell to form the oxide network. The hybrid micelles are self-assembled on the Si substrate and form continuous network induced by both the solvent evaporation process and shear force during spin coating^[7g]. Because the micelle core is only composed of the organic PS block, pores are formed

after PS is removed by calcination. Regarding the PAA block, because it forms the hybrid network with the rare earth oxide, the calcination process removes the PAA block while crystallization of the inorganic rare earth oxide network occurs simultaneously. As a result, mesoporous structures with continuous network are formed. Furthermore, from the SEM images it can be seen that the calcination procedure applied in this work does not deteriorate the continuous mesopores significantly. It implies that the mesoporous structures are quite stable even at high temperatures.

Scheme 1. Formation of rare earth oxide mesopores.

With the identical concentration of PS-*b*-PAA (0.5 wt% over total solvent mass), and PAA/RE³⁺ concentration ratio (molar ratio of PAA/RE³⁺: ca.5.4 mmol/0.1 mmol), and film post-treatment protocol, the templating effect of PS-*b*-PAA is mainly influenced by the balance between the integration and sol-gel process of the rare earth salts. According to the hard-soft-acid-base theory (HSAB), rare earth ions belong to the hard acid group due to their high charge state and small ionic radius, which is partially determined by the ionic potential, Z/r (charge over ionic radius). The rare earth ions tend to form strong coordination bonds with the carboxylate/carboxylic acid functional group, which is a hard base^[12]. Due to the lanthanide contraction effect, the rare earth ions have progressively decreasing ionic radius from light to heavy rare earth group^[14]. Therefore, from La³⁺ to Eu³⁺, Tb³⁺, and Yb³⁺, the rare earth metal ions are supposed to have increasing coordination ability to the carboxylic ligand, leading to better integration of the rare earth ions into the PAA shell. Regarding the sol-gel process of the rare earth salts, in our system, rare earth nitrates are used as sol-gel precursors, which have a moderate hydrolysis and condensation property. As a result, even though the hydrolysis/condensation ability is enhanced with decreasing ionic radius from La³⁺ to Yb³⁺. The hydrolysis/condensation of the rare earth salts still do not go beyond the boundaries of the PAA domain. Therefore, for the particular templating system addressed in this work, the templating effect of PS-*b*-PAA is mainly determined by the integration of the rare earth salts into the PAA shell. Consequently, under the specific combination of the templating system and film post-treatment protocols addressed in this manuscript, a better morphology control has been achieved within the Tb₂O₃ and Yb₂O₃ mesoporous thin films as compared with the La₂O₃ and Eu₂O₃ thin films.

The impact of block copolymer concentration on the morphology control is investigated focusing on the Tb₂O₃ system. The concentration of PS-*b*-PAA over the total amount of DMF/CH₂Cl₂ was varied from 0.25 wt% to 1.0 wt%, while keeping the concentration of the rare earth nitrates over the total amount of solvents constant. In **Figure 2** the SEM images (a-c), AFM height images (d-f), and AFM phase images (g-i) of the Tb₂O₃ thin films templated with 0.25 wt% (a, d, g), 0.5 wt% (b, e, h), and 1.0 wt% (c, f, i) PS-*b*-PAA are shown. The SEM image (Figure 2a) shows that the mesoporous structures are deposited in patches onto the substrate. This is likely due to the lack of sufficient amount of PS-*b*-PAA in solution. The average pore size and wall thickness

measured in SEM is around 11 nm and 9 nm, respectively. The AFM height images and phase images show similar mesoporous structures consistent with the SEM image. With the PS-*b*-PAA concentration increased to 0.5 wt%, homogeneous mesoporous structures are observed in the SEM image (Figure 2b), where a ring-like FFT pattern appears, indicating a narrow center-to-center distance distribution of the mesopores (17 nm). The AFM height image shows a small height fluctuation on the film surface. However, further examination of the AFM height and phase images reveals that the mesopores are homogeneously distributed over the entire image with an average pore diameter of 12 nm and wall thickness of 9 nm. With further increasing the block copolymer concentration to 1.0 wt%, besides the spherical mesopores, worm-shaped mesopores appear within the film. However, a ring-like FFT pattern still exists in the SEM image indicating a characteristic center-to-center distance of 18 nm (Figure 2c). The wall thickness is measured in the SEM image, which is around 9 nm. Based on the characteristic center-to-center distance from FFT and wall thickness measured in SEM, the average pore size is calculated to be around 9 nm. The AFM height (Figure 2f) and phase (Figure 2i) images show that the mesopores are distributed on the substrate more homogeneously than the film prepared with 0.5 wt% PS-*b*-PAA. As a consequence, it can be concluded that a sufficient amount of PS-*b*-PAA in solution is needed to obtain homogeneous mesoporous rare earth oxide thin films. The increase of PS-*b*-PAA concentration does not modify the dimension of the mesopores significantly, but tends to change the shape of the mesopores. In case of an insufficient PS-*b*-PAA amount in solution, not all of the rare earth salts can be integrated within the PAA shell. As a result, only patches of the mesoporous structures are formed on the substrate. The free hydrolyzed/condensed Tb₂O₃ species are deposited in a featureless fashion on the substrate. With increasing amount of PS-*b*-PAA in solution (for example, 0.5 wt%), the integration of terbium salts into the PAA shell is improved, leading to a better morphology control of the mesoporous Tb₂O₃ thin films. However, if the PS-*b*-PAA concentration increases too much (for example, 1.0 wt%), a fusion process of the spherical micelles happens, leading to the formation of worm-shaped micelles in solution and consequent worm-shaped mesopores within the film^[7g].

Figure 2. SEM (a, b, and c), AFM height images (d, e, and f), and AFM phase images (g, h, and i) of the mesoporous Tb₂O₃ thin films templated by 0.25 wt% (a, d, g), 0.5 wt% (b, e, h), and 1.0 wt% (c, f, i) of PS-*b*-PAA. Scale bar: 250 nm, height scale: 10 nm, phase scale: 10 ° for g and h, and 40 ° for i. Insets are the FFT patterns of each SEM image.

Besides the local structure investigated by real space techniques, rare earth oxide thin films have been investigated by grazing incidence small angle x-ray scattering (GISAXS) to get more detailed information about the lateral structure buried under the surface^[17]. Details of the GISAXS technique and experiments are described in the supporting information. The SEM images indicate a homogeneous mesoporous structures over μm scale on the surface (Figure S8). However, it is still not sufficient to reveal the average structure over macroscopic scale and the structure beneath the surface. Image a-f in **Figure 3** shows the 2D GISAXS data of the mesoporous La_2O_3 (a), Eu_2O_3 (b), Tb_2O_3 templated by 0.25 wt% (c), 0.5 wt% (d), 1.0 wt% (e) of PS-*b*-PAA, and mesoporous Yb_2O_3 (f) thin films. The inset of each image shows the experimental (dot) and simulated (line) horizontal line cuts along q_y direction containing the lateral length information. While Figure 3a shows a fairly weak side wing pattern, Figure 3b-3f exhibit well pronounced side wing patterns. Furthermore, it can be seen that the side wing pattern is progressively getting stronger along with the series of La_2O_3 , Eu_2O_3 , Tb_2O_3 , and Yb_2O_3 . The electron density contrast between the rare earth oxides and the air attributes to the visibility of the side wing patterns, which implies the presence of highly ordered upright cylindrical domains within the films.

Figure 3. 2D GISAXS data and horizontal line cuts (insets) of the mesoporous rare earth oxide thin films, a: La_2O_3 , b: Eu_2O_3 , c: Tb_2O_3 templated by 0.25 wt% of PS-*b*-PAA, d: Tb_2O_3 templated by 0.5 wt% of PS-*b*-PAA, e: Tb_2O_3 templated by 1.0 wt% of PS-*b*-PAA, f: Yb_2O_3 . In the insets the measured data (dots) and fits (lines) are shown.

The horizontal line cut of the 2D GISAXS data in case of the La_2O_3 thin film (Figure 3a) only shows a broad peak corresponding to 200 ± 20 nm, which implies a fairly weak long range lateral structural order. In case of Eu_2O_3 , the horizontal line cut (Figure 3b) shows a distinct peak located at 18 ± 1 nm, which implies highly ordered lateral structure. Concerning the Tb_2O_3 mesoporous thin films prepared with increasing PS-*b*-PAA concentration, the film templated with 0.25 wt% PS-*b*-PAA shows a less pronounced peak in the horizontal line cut (Figure 3c) as compared to the Eu_2O_3 film. However, the Tb_2O_3 thin films templated above 0.5 wt% PS-*b*-PAA show a very pronounced peak, which is accompanied with a second-order peak (Figure 3d, Figure 3e). In case of the Yb_2O_3 mesoporous thin film, a pronounced main peak is coexisting with an additional side peak, corresponding to lateral orders of 19 ± 1 nm and 8 ± 1 nm respectively (Figure 3f). This implies that the Yb_2O_3 thin film possesses a very good lateral structural order.

In the measured and simulated horizontal line cuts of the 2D GISAXS data of the Tb_2O_3 mesoporous films templated with increasing PS-*b*-PAA concentration, the distances between neighboring pores remains unchanged at around 18 ± 1 nm,

whereas the peaks are getting progressively more pronounced. When the template copolymer concentration reaches 0.5 wt%, an additional minor peak located at 9 nm appears, which is taken as the second-order peak of the structure. These two phenomena indicate that the long range lateral structural order is improved along with the increasing concentration of PS-*b*-PAA. Thus it can be concluded that the GISAXS results confirm on the one hand a better morphology control from La_2O_3 to Eu_2O_3 , Tb_2O_3 , and Yb_2O_3 and on the other hand an improved morphology control with increasing block copolymer concentration.

The vertical structures of the rare earth oxide thin films normal to the Si substrate are characterized by x-ray reflectivity (XRR) as shown in **Figure 4**.

Figure 4. XRR data (symbols) and fits (lines) of the mesoporous and control rare earth oxide thin films, a: La_2O_3 , b: Eu_2O_3 , c: Yb_2O_3 , d: Tb_2O_3 (templated with different PS-*b*-PAA concentrations); a-c: (square: mesoporous, circle: control); d: (square: 0.25 wt% PS-*b*-PAA, circle: 0.5 wt% PS-*b*-PAA, upper triangle: 1.0 wt% PS-*b*-PAA, lower triangle: control).

According to the data and the applied fitting, there are two common features regarding the rare earth oxide thin films. First, all of the rare earth oxide thin films need to be modeled with two layers. The bottom layer with a thickness of *ca.* 2 nm is ascribed to SiO_x , which is formed due to high temperature calcination and confirmed by XPS in Figure S4; the top layer is the rare oxide thin film. Second, the profiles of all of the control rare earth oxides thin films (without block copolymer templating) do not show clear intensity oscillations, which results from the small film thickness (*ca.* 4 nm) in combination with a relative large surface roughness (*ca.* 2 nm). The XRR data of both the mesoporous La_2O_3 and Eu_2O_3 thin films show a broad intensity oscillation corresponding to a film thickness of 10 nm and 9 nm respectively (Figure 4a, 4b). Unlike La_2O_3 and Eu_2O_3 , the mesoporous Yb_2O_3 thin films exhibits a better defined intensity oscillations indicating a film thickness of 10 nm (Figure 4c). The appearance of the oscillation pattern implies a smooth homogeneous mesoporous Yb_2O_3 layer on the substrate. Concerning the Tb_2O_3 thin films templated by 0.25 wt% of PS-*b*-PAA, the XRR data does not show a clear intensity oscillation due to a small film thickness (4 nm) and large surface roughness. With further increased PS-*b*-PAA concentration to 0.5 wt% and 1.0 wt%, intensity oscillations appear. The corresponding film thickness is around 8 nm and 9 nm respectively (Fig. 4d). The XRR results of the rare earth oxide thin films reveal that a mesoporous rare earth oxide layer is present within the thin films. Particularly, within the Tb_2O_3 and Yb_2O_3 thin films, a distinct

homogeneous mesoporous layer is present resulting in well defined intensity oscillations in the XRR data.

Transmission electron microscopy (TEM) is performed to determine the crystallographic phase of the rare earth oxide thin films. **Figure 5** shows the corresponding TEM images of La_2O_3 (a), Eu_2O_3 (b), Tb_2O_3 (c), and Yb_2O_3 (d) thin films. All of the TEM images show mesoporous structures within the thin films, which is consistent with the SEM results. No obvious preferred crystallographic orientation plane development are observed. It indicates that the thin films are polycrystalline, which is confirmed by the selected area electron diffractions (SAED) patterns.

Figure 5. TEM images of the mesoporous rare earth oxide thin films. a: La_2O_3 , b: Eu_2O_3 , c: Tb_2O_3 , d: Yb_2O_3 . Insets are the corresponding selected area electron diffraction (SAED) patterns of each image.

Conclusions

In summary, a new concept using an amphiphilic ionic block copolymer as a templating agent to achieve the generalized synthesis of crystalline rare earth oxide thin films is developed. Mesoporous La_2O_3 , Eu_2O_3 , Tb_2O_3 , and Yb_2O_3 thin films templated by PS-*b*-PAA are prepared representing the light and heavy rare earth groups. It proves that this strategy has a general applicability to the whole rare earth family. The local and long range lateral structures, vertical structures, and crystallinity of the mesoporous thin films are investigated by AFM, SEM, GISAXS, XRR, and TEM respectively. The systematic structural analysis reveals that a long range lateral structural order is present within the mesoporous thin films, which are consistent with the local structures. Furthermore, it shows that PS-*b*-PAA exercises a better templating effect with Tb_2O_3 and Yb_2O_3 rather than La_2O_3 and Eu_2O_3 , which is likely due to the increasing affinity of the rare earth salts to PAA. The impact of the PS-*b*-PAA concentration on the morphology control has been investigated focusing on Tb_2O_3 . It suggests a sufficient PS-*b*-PAA concentration (above 0.5 wt %) is needed to have a good templating effect, where a homogeneous mesoporous Tb_2O_3 layer is deposited on the substrate. Further systematic studies on the morphology control over the thin films of the whole rare earth family, and applications of the mesoporous rare earth oxide thin films are in progress and will be addressed in a separate paper.

Experimental Section

Typically, 0.01 g PS-*b*-PAA (repeating unit of PS: 60, repeating unit of PAA: 100) was added to a solvent mixture of 1.00 g of DMF and 1.00 g of CH_2Cl_2 , followed by the addition of 0.04 g rare earth nitrate. The solution was stirred for one hour before spin coating onto Si (100) substrates with a rotation speed of 2000 rpm. The as-prepared composite films were calcined at 600°C for 4 hours in air to remove PS-*b*-PAA and crystallize rare earth oxide simultaneously. The structures of the composite films were investigated with AFM, SEM, GISAXS, and x-ray reflectivity measurements. Experimental details are given in the supporting information. **Supporting Information** (see footnote on the first page of this article): the synthesis and characterization of PS-*b*-PAA, detailed sample preparation and characterization procedure, XPS, SEM, DLS, and FTIR data.

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Entry for the Table of Contents

Layout 1:

A strategy to achieve the generalized synthesis of mesoporous rare earth oxide thin films is developed using an amphiphilic ionic block copolymer of PS-*b*-PAA as a templating agent.

((Key Topic))

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A Facile Way to the Generalized Synthesis of Mesoporous Rare Earth Oxide Thin Films via Amphiphilic Ionic Block Copolymer Templating

Keywords: Rare earth oxides/Block copolymers/Self-assembly/Thin films/Mesoporous /Sol-gel

Experiments

1. Synthesis of PS-*b*-PAA Scheme S1. Synthesis of PS-*b*-PAA (n=60, m=100)

1.1. Materials

CuBr (Alfa Aesar, 99.999%), 4,4'-di-*tert*-butyl-2,2'-bipyridine (DTB-bipy) (Alfa Aesar, 98%), 1-bromo-1-phenylethane (BMPE) (Alfa Aesar, 97%) and *o*-xylene (Alfa Aesar, 99%) were used as received. 2-*tert*-Butylacrylate (tBA) (Alfa Aesar, 99%) was rinsed with 5wt. % NaOH, followed by rinsing with water and dried over CaCl₂. It was then distilled under reduced pressure from CaCl₂ and stored under nitrogen at -20 °C. Styrene (St) (Aldrich, 99%) was purchased and purified by distillation under vacuum prior to polymerization.

1.2. Instruments

¹H NMR spectra were recorded on a “Bruker-Spectrospin” instrument (400 MHz) at room temperature. Gel Permeation Chromatography (GPC) chromatograms were conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns in THF as an eluent at 30 °C at a flow rate of 1mL/min, calibrated with linear PSt standards.

1.3. Synthesis of macroinitiator PS-Br

The monomer styrene (8 g, 76.8 mmol) and the initiator BMPE (35.3 mg, 0.192 mmol) were placed in a Schlenk tube and dissolved in *o*-xylene (4 mL). CuBr (27.5 mg, 0.192 mmol) was then added and

the mixture was degassed by three freeze-pump-thaw cycles. The ligand DTB-bipy (103 mg, 0.384 mmol) was added under nitrogen, and the solution was stirred at 25 °C for 10 min. The tube was sealed and placed in a thermostated oil bath at 100 °C to start the reaction. After a specific polymerization time the reaction mixture was cooled down to room temperature and the content was diluted with dichloromethane and passed through a column of neutral alumina to remove the copper salts. The polymer was precipitated from an excess of methanol, filtered and dried under vacuum to give product PS-Br as a white powder (conversion: 15%, r.u.=60, $M_{n,theory}=6425$ g/mol; $M_{n,GPC}=4900$ g/mol, PD=1.13; $M_{n,NMR}=6100$ g/mol, calculated from 1H -NMR spectra of PS-Br in Figure S1).

1.4. Synthesis of block copolymer PS-*b*-PtBA

A Schlenk tube was charged with macroinitiator PS-Br (400 mg, 0.062 mmol, 1 equiv), *t*BA (3.99 g, 31 mmol, 500 equiv) and *o*-xylene (3 mL). After the tube was degassed by three freeze-pump-thaw cycles, CuBr (8.9 mg, 0.062 mmol, 1 equiv) and DTB-bipy (33.4 mg, 0.124 mmol, 2 equiv) were added into the reaction tube followed by a freeze-pump-thaw cycle. A subsequent stirring period of 10 minutes was required to ensure the catalyst completely formed complex. The tube was sealed and placed in a thermostated oil bath at 90 °C to start the reaction. After a specific polymerization time, the solution was poured into excess mixture of methanol and water (v/v=1:1) to precipitate the polymer. The precipitate was dissolved in dichloromethane and purified using an alumina column to eliminate the used copper salt. After drying in a vacuum oven over night at room temperature, the block copolymer PS-*b*-PtBA was obtained as a white powder (Conversion: 20%, PS_{r.u.}=60, PtBA_{r.u.}=100, $M_{n,theory}=19242$; $M_{n, GPC}= 13500$ g/mol, PD=1.18; $M_{n, NMR}=19000$ g/mol, calculated from 1H -NMR spectra of PS-*b*-PtBA in Figure S2).

1.5. Hydrolysis of block copolymer PS-*b*-PtBA

The copolymer PS-*b*-PtBA (880 mg) was placed in a Schlenk flask equipped with a magnetic stirring bar and then dissolved in dichloromethane (20 mL) under nitrogen. The same amount of trifluoroacetic acid (TFA) (20 mL) was then added into the solution under stirring at room temperature. After 24 h, the solvent was removed from the resulting heterogeneous mixture. Further purification was performed by re-dissolving the solid in methanol and then by precipitation from dichloromethane (3 × 40

mL). The precipitate was dried under vacuum at room temperature for 10 h to give rise to the final product PS-*b*-PAA as a white powder ($PS_{r.u.}=60$, $PAA_{r.u.}=100$, $M_{n,theory}=13631$; $M_{n, GPC}= 8200$ g/mol, $PD=1.12$, in Figure S3).

Figure S1. ^1H NMR spectrum (Bruker 400 MHz in CDCl_3) of PS-Br.

Figure S2. ^1H NMR spectrum (Bruker 400MHz in CDCl_3) of PS-*b*-PtBA.

Figure S3. ^1H NMR spectrum (Bruker 400MHz in DMSO- d_6) of PS-*b*-PAA.

2. Thin film preparation and characterization

An asymmetric diblock copolymer of polystyrene and polyacrylic acid (PS-*b*-PAA) was synthesized in house according to the above description. Rare earth complexes of $(\text{RE}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O})$, RE=La, Eu, Tb, Yb) were purchased from Alfa Aesar. Analytical grade of N, N-dimethylformamide (DMF), dichloromethane(CH_2Cl_2) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

Sample solutions were prepared according to the following procedure. 0.01 g PS-*b*-PAA was mixed together with *ca.* 0.043 g rare earth salt, 1.00 g DMF, and 1.00 g CH_2Cl_2 within five minutes. The solutions were stirred for 60 mins before spin coating.

Films were prepared on Si (100) substrate by spin coating for 60.0 s using a spin coater (KW-4A, Institute of Microelectronics of Chinese Academy of Sciences) under ambient conditions (Temperature: 25 °C, relative humidity: 65%-75%, rotation speed of 2000 rpm, lid open)

Calcination of the films was carried out at 600 °C for 4 hours in air with a ramp rate of 5 °C/min starting from 40 °C. After calcination, the samples were cooled to room temperature in the furnace.

AFM images were recorded using a Digital Instruments scanning force microscope (Dimension 3100V, Veeco) in tapping mode equipped with Bruker cantilevers (spring constant ranging between 20 – 80 N/m and resonant frequency of 278 – 327 kHz).

Scanning electron microscopy (FESEM) images were obtained on Hitachi S 4800 scanning electron microscope (Tokyo, Japan) at an accelerating voltage of 4 kv.

Samples for transmission electron microscopy (TEM) analysis were prepared as following. The rare earth oxide thin films were cleaved in diluted hydrofluoric acid (HF) and then transferred to amorphous carbon-coated copper grids. The mesoporous structures and corresponding crystallographic phase of the thin films were performed with a JEOL JEM-2100F TEM operated at 200 kV or Tecnai F20 (America FEI) instrument..

The X-ray photoelectron spectrum (XPS) was recorded on an AXIS UTLTRADLD system (Shimadzu Japan) with Ag radiation.

Grazing incidence small angle x-ray scattering (GISAXS) measurements were carried out at the beamline P03 of the PETRA III storage ring at HASYLAB (DESY, Hamburg, Germany). The selected wavelength was $\lambda=0.0957$ nm. The incident angle was set to $\alpha_i = 0.35^\circ$, which is above the critical angle of the materials in the film, therefore, the X-ray beam can penetrate the whole film and give the scattering information through the full depth of the film. The sample was placed horizontally on a sample stage. A sample-detector distance of 249 cm was used. A beam stop was used to block the direct beam in front of the detector, and a second beam stop was used to block the very high specular reflection intensity for protecting the detector. A 2D detector (487*619 pixels, pixel size $172*172 \mu\text{m}^2$) was used for recording the scattering data. Structural information can be obtained from the horizontal (q_y direction, parallel to the sample surface) and vertical cuts (q_z direction, normal to the sample surface) of the 2D GISAXS data distribution.

X-ray reflectivity (XRR) experiment was conducted using a surface XRD- D8 Discover diffractometer equipped (Bruker AXS). The modeling of the experimental profiles was conducted using the Parratt 32 software (version 1.5 provided by the Berlin Neutron Scattering Center at the Hahn-Meitner-Institute).

Dynamic Light Scattering was performed with a custom built goniometer setup using a laser Verdi V2 (Coherent), wavelength 532nm. The incident light of a maximum power of 100 mW on the sample was vertically polarized with respect to the scattering plane by a Glan prism with extinction ratio of 10^{-5} . Of the scattered light only the vertically polarized component selected by a Glan-Thompson prism with extinction ratio of 10^{-8} was analyzed. Single mode fiber detection was utilized with a beam splitter and two avalanche diodes (Perkin-Elmer) as detectors. The autocorrelator, "ALV-6010 / 160 high speed multiple tau digital Korrelator" (ALV, Langen, Germany), was run in pseudo cross correlation to eliminate correlated noise from the detectors at short times. All samples with the PS-*b*-PAA concentration of 0.5 wt% or 0 wt% were filtered into dust free light scattering cells through a $0.2 \mu\text{m}$ Millipore Teflon filter to remove dust.

Fourier-transform infrared (FT-IR) was employed to investigate the complexation between the rare earth salt and PS-*b*-PAA. The solution of 0.043 g Tb(NO₃)₃·6H₂O and 0.01 g PS-*b*-PAA in the solvent mixture of DMF/CH₂Cl₂ (1.00g/1.00g) was dried at 100°C in vacuum for 12 hours to remove the solvents. The spectra were recorded in solid power-KBr pellets on a Thermo Nicolet 6700 spectrometer (Madison, America) with the wavenumber range from 4000 to 400 cm⁻¹. The spectrum of each sample was an average of 32 scans at 4 cm⁻¹ resolution.

Figure S4. XPS profiles of the nanostructured rare earth oxide thin films. a: mesoporous La_2O_3 thin film, b: mesoporous Eu_2O_3 thin film, c: mesoporous Tb_2O_3 thin film; d: mesoporous Yb_2O_3 thin film; e: control La_2O_3 thin film.

Figure S5. SEM images of the control rare earth oxide thin films. a: La₂O₃, b: Eu₂O₃, c: Tb₂O₃, d: Yb₂O₃.

Figure S6. Dynamic light scattering (DLS) profiles of the PS-b-PAA in solution without (a) and with (b) Terbium(III) nitrate. The insets show the distributions of radii from a CONTIN analysis.

Figure S7. FTIR profiles of the powders of pure PS-b-PAA (red) and PS-b-PAA complex of Terbium (III) Nitrate (orange). The marked regions indicate the shift of the carbonyl stretching band (1716 cm^{-1} vs. 1648 cm^{-1}), the disappearance of the symmetric vibration band of the carboxylic acid dimer (1416 cm^{-1}) and the appearance of the COO-M vibration band (1406 cm^{-1}).

Figure S8. Low magnification SEM images of the mesoporous rare earth oxide thin films. a: La_2O_3 , b: Eu_2O_3 , c: Yb_2O_3 , d-f: Tb_2O_3 templated by PS-b-PAA with different concentrations (d: 0.25 wt%, e: 0.5 wt%, f: 1.0 wt%).