Fabrication and Photocatalytic Activities of Morphology-Controlled Titania Nanoobject Arrays by Block Copolymer Templates

Juan Peng, Xue Li, Dong Ha Kim,* Wolfgang Knoll

We report a simple scheme to fabricate organic/inorganic hybrid nanostructures with extraordinary morphologies by one-step spin coating, using a PS-\(b\)-PEO diblock copolymer as template coupled with sol-gel chemistry. The shape and size of the titania nanoobject can be fine-tuned by controlling the amount of sol-gel precursor relative to PS-\(b\)-PEO and the composition of the precursor. Ordered arrays of nanoscopic titania objects such as nanodots, nanobowls, and nanonetworks were obtained from the initial hybrid nanostructures by removing the organic matrix by UV treatment. Photocatalytic activities of the resulting titania nanoobjects were investigated in terms of the degradation of a typical dye.

Introduction

The design of advanced nanostructured materials with diverse composition and tailored morphology is of immense interest in the field of recent nanoscience and nanotechnology. Numerous strategies were proposed to develop target-oriented nanomaterials and still more efforts have been devoted to suggest simpler, cost-effective means of fabrication.[1] In this regard, self-assembly has been recognized as one of the most effective pathways toward functional nanomaterials.[2] Block copolymer (BCP) self-assembly constitutes one typical example of self-assembly systems whereby a wide range of nanoscopic morphology spectrum can be obtained from spontaneous organization into ordered nanostructures induced by the microphase separation of chemically distinct constituent polymers covalently connected at one end.[3–5]

Titanium dioxide (\(\text{TiO}_2\)) nanomaterials have gained significant attention due to their potential applications in the fields of chemical and alternative energy industries, for example, photocatalysts,[6–8] semiconductors in solar cells,[9,10] and fuel cells.[11,12] Over the past few years, various routes to nanostructured \(\text{TiO}_2\) have been reported, such as hydrothermal synthesis,[13,14] metal-organic chemical vapor deposition,[15] and sol-gel template methods,[16–25] etc., in which the most critical issue is the control of their shape, size, and spacing.

Combining the BCP self-assembly process with sol-gel chemistry, Kim et al. recently reported that ordered arrays of hybrid BCP/titania nanostructures could be prepared by...
one-step spin coating a common solution composed of asymmetric polystyrene-block-poly(ethylene oxide) diblock copolymer (PS-b-PEO) and sol-gel precursor onto a solid substrate. Hexagonally packed arrays of titania nanodots with controlled lateral spacing were obtained after removing the organic template by appropriate means.

Herein, we extend this methodology to fabricate a series of PS-b-PEO/titania nanohybrid films and pure titania nanopatterns with extraordinary morphologies by manipulating the experimental parameters involved in the solution preparation step. It is found that the relative amount of acid in the precursor solution plays a critical role in inducing morphological changes similar to the results of Eisenberg et al. Specifically, the increased amount of acid in the precursor solution plays a critical role in inducing morphological changes similar to the results of Eisenberg et al. Specifically, the increased amount of acid induces a systematical change of the PEO-titania domains from cylinders to bowl-like structures further to interconnected networks, as schematically depicted in Figure 1. Thus, ordered arrays of unprecedented, extraordinary-shaped titania nanopatterns with controlled size are obtained after removing the PS-b-PEO template by exposing to deep UV light. The photocatalytic activity of these titania nano-objects is also demonstrated using a typical dye as a photocatalytic reactant.

**Experimental Part**

**Materials**

An asymmetric PS-b-PEO diblock copolymer with a total molecular weight of $M = 25400$ ($M_{\text{PS}} = 19000$ and $M_{\text{PEO}} = 6400$, $\frac{M_{\text{PS}}}{M_{\text{PEO}}} = 1.05$) was purchased from Polymer Source, Inc. Titanium tetraisopropoxide (TTIP, 97%) and methylene blue (MB) were purchased from Aldrich. Analytical grade benzene, isopropanol, and hydrochloric acid (HCl, 37%) were purchased from Laborbedarf GmbH.

**Film Preparation**

The PS-b-PEO was dissolved in benzene (overnight to reach complete dissolution) with a concentration of 1 wt.-%. Sol-gel precursor solutions were prepared as previously described. By fixing the amount of TTIP and changing HCl amount, the molar ratio of TTIP/HCl in the sol-gel solutions was adjusted from 0.19 to 2.19. The desired amount of sol-gel precursor solution was mixed with the PS-b-PEO solution and stirred for 30 min. The amount of precursor solution relative to the BCP solution was adjusted from 10.3 to 72.1 wt.-%. Thin films were prepared by spin-coating the mixed solution onto silicon wafers at 2000 rpm for 60 s. The obtained PS-b-PEO/titania hybrid films were dried under ambient conditions to induce crosslinking of the sol-gel precursor. The samples were irradiated by UV light at 254 nm with a dose of 25 J cm$^{-2}$ (XX-155, UVP, Inc.) at room temperature for 48 h in air to remove the organic matrix, leaving behind titania domains.

**Characterization**

Atomic force microscopy (AFM) images were obtained using a Digital Instruments Dimension 3100 scanning force microscope in tapping mode with an Olympus cantilever (spring constant in the range of 33.2–65.7 N m$^{-1}$ and resonant frequency of 277.3–346.3 kHz). Field emission scanning electron microscopy (FESEM) images were obtained on a field emission SEM (LEO 1530 “Gemini”) under 1 kV accelerating voltage.

**Photocatalytic Activity Measurements**

The photocatalytic activities of these titania films on the photooxidation of MB were investigated. The titania thin film ($1 \times 1$ cm$^2$) was immersed in the 5 mL MB aqueous solution with a concentration of $10^{-5} \text{M}$, and the solution was irradiated by UV light at 254 nm (XX-155; UVP, Inc.). The change of absorption at 665 nm was applied to identify the concentration of MB using a UV-Vis spectrophotometer (Perkin-Elmer, Lambda 900) with a 30 min interval for a total irradiation time of 270 min.

**Results and Discussion**

Figure 2 shows a series of PS-b-PEO/titania hybrid films with different amounts of sol-gel precursor by keeping the
The TTIP/HCl ratio was set at 0.60. The amounts of precursor relative to the BCP (4) were 10.3, 20.6, 41.2, 51.5, and 72.1% by weight [Figure 2(a)–2(e), respectively]. For the films with 10.3% sol-gel, an ordered array of nanocylinders with nanodepressions at the surface [Figure 2(a)] is observed with the diameter, center-to-center distance, and a depth of 25.4, 35.6, and 1.1 nm, respectively. The titania sol-gel precursor is located in PEO domains surrounded by PS blocks. With increasing the sol-gel amount to 20.6 and 41.2%, hexagonal arrays of nanoholes with the diameters of 35.6 nm [Figure 2(b)] and 42.1 nm [Figure 2(c)] are seen, respectively, which are much larger than that of nanoholes in Figure 2(a). FESEM image at low magnification shows that the ordered arrays of nanoholes cover a wide area of the surfaces (see Supporting Information). In addition, the depths of the holes in Figure 2(b) and 2(c) is ≈12.6 nm and 18.1 nm, respectively, which are much deeper than that in Figure 2(a). There are distinct differences between the two types of nanostructures, as manifested in Figure 2(a’) and 2(c’), which are the corresponding perspective FESEM images of Figure 2(a) and 2(c), respectively. The former shows very shallow depressions while the latter illustrates the holes span deeply through the film-like bowl shape. The cylindrical morphology with depressions at the surface and bowl-like one are also compared in Figure 1. We note at the 41.2% ratio, macrophase separation between

*Figure 2.* High-contrast AFM images of PS-b-PEO/titania hybrid films with different amount of sol-gel precursor: (a) 10.3, (b) 20.6, (c) 41.2, (d) 51.5, (e) 72.1%. All AFM images are 1 × 1 μm² in size. (a’) and (c’) are the corresponding side-view FESEM image of (a) and (c), respectively.
the copolymer and the sol-gel solution is observed. When the sol-gel amount is 51.5%, the shape of individual nanohole becomes irregular and the lateral correlation between the nanoholes is lost [Figure 2(d)]. With further increase in the sol-gel amount to 72.1%, irregular network is formed [Figure 2(e)].

The formation of various PS-b-PEO/titania hybrid morphologies described above can be understood by the following mechanism. The morphology evolution can be rationalized by analyzing the role of sol-gel precursor solution in the system. The acid HCl is believed to be the crucial factor to induce morphological changes from nanocylindrical domain to nanobowl-like one. In order to support this hypothesis, only HCl except for the titania precursor is added to the PS-PEO solution. As the HCl concentration increases from 0 to 0.08 M, further to 0.24 M, it is observed that the thin film morphology changed from disordered worm-like patterns to nanocylindrical structure and at last to nanobowl-like structure (see Supporting Information). Such a systematic transition of the morphology can also be induced by the change of the inherent amount of the acid, using sol-gel solutions with different molar ratio of TTIP/HCl with keeping the ratio of the sol-gel solution to PS-b-PEO solution the same (see Supporting Information). Both experiments prove that the relative content of the HCl induces the morphological transformation from nanocylinder structure to nanohole structure.

At the same time, TTIP is incorporated into the hydrophilic PEO domains through coordination bonds, hydrolyzed, and then condensed into Ti–O– nanostructures. Furthermore, Ti–O– covalent bonds between neighboring PEO domains can be formed when hydrolysis and condensation of TTIP occur between adjacent PEO domains. When the sol-gel amount is low, each PEO domain contains a certain amount of titania precursor. We notice that the size of the nano-objects is quite uniform in either nanoscopic cylindrical or bowl-like structures. This indicates that the precursor is uniformly distributed in each PEO domain. With increasing the amount of titania precursor, the circular-shaped nanobowls become deformed and the walls (PS domains) become thinner due to the overswelliness of PEO domains [Figure 2(d)]. Some PEO domains merge together due to the contact between neighboring titania precursors. Finally, the presence of the excess amount of the precursor induces more junctions among PEO domains, leading to irregular interconnected network [Figure 2(e)].

In terms of the role on acids of the morphological change, it has also been reported that acetic acid or hydrofluoric acid selectively swells minor domains in polystyrene-block-poly(vinyl pyridine) leading to depression or opening of pores in poly(vinyl pyridine) nanodomains. Considering all these reports and interpretation, it is reasonable to conclude that the extra amount of HCl in the present system is responsible for the morphological transformation of PEO nanodomains.

From the series of hybrid BCP/titania nanostructures defined by the above-mentioned procedures, one can obtain pure titania nanostructures with controlled shape and size after removal of the organic template. It is well known that free radicals and activated species, which have been generated in situ from the coupling between atmospheric oxygen and UV light, remove organic polymer. Figure 3 shows a series of AFM and FESEM images of titania nanopatterns with various morphologies after exposing the initial films (Figure 2) to deep UV light. It is clearly observed that highly dense arrays of \( \approx 27.3 \) nm wide titania dots [Figure 3(a) and (a')] covering a wide area of the substrate surface are generated from the original cylindrical hybrid film with 10.3% precursor, which are consistent with the observation of Kim et al. The formation of nanobowl structures after the removal of polymer matrix is obvious. The average size and depth of the titania nanobowls are \( \approx 53.3 \) and 7.8 nm in Figure 3(b), and \( \approx 83.2 \) and 15.1 nm in Figure 3(c), respectively. Figure 3(d) and 3(e) show that the corresponding titania granulas are formed after UV treatment of the hybrid samples with 51.5 and 72.1% precursor, respectively.

Titanium dioxide is widely utilized photocatalyst as a strong redox agent, having the ability to oxidize water to hydroxyl radicals and to reduce molecular oxygen to superoxide radical anion. These radical intermediates can in turn decompose organic compounds or oxidize inorganic ions. Photocatalytic performance of titania nanostructures was evaluated for degrading MB under UV irradiation. Among these titania nanostructures, the UV-treated nanodot and nanobowl-like samples with 10.3 and 20.6% precursor, respectively, were chosen to investigate their photocatalytic activities. Figure 4(a) shows the evolution of MB absorption spectra in the presence of nanobowl-like titania catalyst, from which we can see that the absorbance peaks at 247, 294, and 665 nm associated with MB decreased with irradiation time. The titania nanodot catalysts with different size and lateral spacing degraded the MB with similar trend (data not shown). After irradiation for 270 min, the absorption peak at 665 nm almost disappeared, and the blue color of the solution vanished completely. Based on the linear relationship between the concentration and the absorption of MB according to the Lambert-Beer equation, the variation in absorption of MB at 665 nm was used to determine the change of the concentration of MB as a function of irradiation time as shown in Figure 4(b). For comparison, the photodegradation without catalyst (curve 1) and in the...
presence of nanodot catalyst (curve 2) was also measured. It is revealed that the photo-degradation rate of MB is the fastest in the presence of nanobowl-like TiO₂ catalyst among the various nanostructures examined in this study. Electrons and holes generated by UV irradiation in TiO₂ react with reductants (e.g., H₂O) and oxidants (e.g., O₂), producing various radicals such as HO₂ and OH, respectively. These active species react with MB molecules adsorbed on the TiO₂ surface, resulting in their decomposition. The blank test shows that MB can also be degraded under UV irradiation without catalyst with a slower rate, where the observed gradual decrease in the absorption of MB over time is attributed to the direct decomposition of the dye upon UV irradiation.

In summary, the presence of titania nanostructures exhibits enhanced photocatalytic property and the performance was found to be most active in the case of nanobowl catalyst. It should be pointed out that the nanobowl catalyst may contain slightly larger amount of TiO₂ than the nanodot catalyst because the former was prepared using larger amount of TTIP precursor (20.6%) than the latter (10.3%). Thus, it is reasonable to explain the nanobowl catalyst with larger surface area, along with more amount of TiO₂, exhibits higher photocatalytic property than the nanodot one.

Conclusion

A simple fabrication route to PS-b-PEO/titania hybrid films and pure titania films with tailored morphologies and domain
size was demonstrated. Thin films of PS-b-PEO with a titania precursor incorporated in PEO domains were obtained by one-step spin-coating from the common solution. By varying the relative amount of titania precursor to the PS-b-PEO BCP, different morphologies of PS-b-PEO/titania hybrid films such as nanoscopic cylindrical domains, nanobowls, nanonetworks, etc. can be obtained. The overall relative content of the acid is found to be the crucial factor to induce the morphological transformation. Subsequent UV treatment to remove the organic template resulted in the corresponding pure titania nanostructures with controlled morphology and size. Such titania nano-patterns exhibited enhanced photocatalytic activity for the decomposition of MB. The protocol suggested by this work may open up a facile way to fabricate a broad range of inorganic or composite nanostructures with diverse morphologies and unique properties which may be useful in a variety of functional devices.

Acknowledgements: Financial support from the Max Planck Society is acknowledged. J. P. is grateful to the financial support of Alexander von Humboldt Foundation. This work was supported by the Seoul Research and Business Development Program (10816), the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2006-003-D00138), and the National Natural Science Foundation of China (20674030). The authors are indebted to Mr. Gunnar Glasser for FESEM analysis.

Received: June 13, 2007; Revised: August 6, 2007; Accepted: August 8, 2007; DOI: 10.1002/marc.200700430

Keywords: diblock copolymers; nanobowl; self-assembly; sol-gel; titania