Periodic Titania Nanostructures Using Block Copolymer Templates

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ABSTRACT The deposition of periodic titania nanostructures, templated by a polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer, is reported. When cast as a thin film (30—50 nm thick), the PS-*b*-P4VP forms a morphology that consists of P4VP cylinders that are orientated perpendicular to the substrate. The P4VP phase was lightly cross-linked by exposing the film to diiodobutane. When the block copolymer film was exposed to the sol—gel titania precursor, titanium(IV) bis(ammonium lactate) dihydroxide (TALH), titania was formed in the P4VP phase. The resulting titania structures were identical in size to the P4VP cylinders and only formed (under the deposition conditions used in this study) when the block copolymer film was present on the substrate, thus providing evidence that the block copolymer indeed acts as a template. The process works for both silicon and indium tin oxide substrates.

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For some time now, it has been recognized that phase separation within block copolymer thin films has significant potential in various fields.[1−5] The morphology achieved by such phase separation is based on molecular weight, volume fractions, and interaction parameters of the specific block copolymers being used and can lead to structures and/or patterns on a length scale of tens of nanometers. Geometries such as lamella, bicontinuous cubic double gyroid, hexagonally packed cylinders, and bcc packed spheres are all possible.[1−4] Furthermore, orientation of the microdomains can also be achieved by applying external fields[6] or by additives,[7−10] selective solvents or solvent vapors[11−15] to generate a pattern of arrays with densities of 10^{11} elements per square centimeter. Such block copolymer thin films can form a template which can be later removed or by further reactions, for example, by cross-linking of the minor component, be altered to give specific structures or patterns.[14,16−18] These templates can be used for surface chemistry, electrodeposition, and pattern transfers. Using block co-

polymers as templates can be cost-effective, in terms of production of large-area optoelectronic devices, because block copolymers are solution processable and can be potentially used in roll-to-roll printing of electrodes.

In terms of block copolymer templating, arrays of vertical cylinders have been of considerable interest because of their potential in creating high aspect ratio nanostructures which might be used in a wide range of potential applications. However, creating vertically aligned cylinders within diblock copolymer films has proved challenging because typically one block preferentially wets the substrate which leads to horizontal cylinders. Several approaches have been developed in order to produce the vertically aligned cylinder morphology.[5] In early work, Hawker *et al.* showed that, by growing a thin film of a random copolymer of styrene and methyl methacrylate on the substrate, a diblock copolymer of these two monomers would phase separate into vertically orientated cylinders.[19,20] Nealey *et al.* have generalized this approach to other block copolymer systems.[21] Other workers solved the issue by the addition of small molecules that would act as complexing agents, thus inducing vertical cylinder formation,[7−10] or rendered the substrate neutral toward the block copolymer segments *via* self-assembled monolayers.[22] Russell *et al.* have used solvent annealing to produce vertical cylinders.[23,24] Furthermore, recent work has shown that square arrangements of cylinders may be formed, as opposed the more common hexagonal nanopatterns.[25,26]
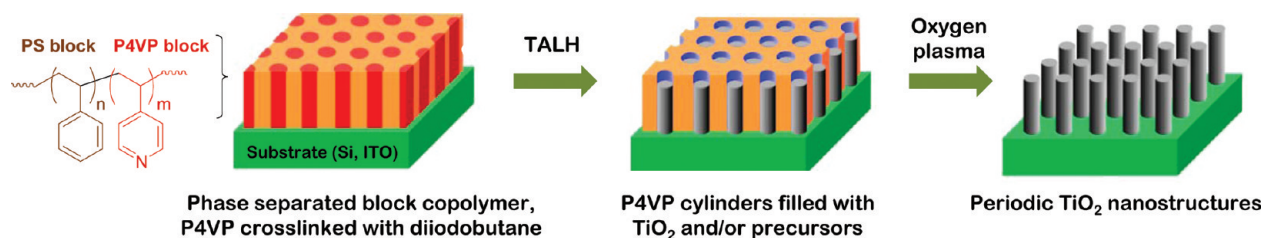
The development of well-ordered semiconductor nanostructures, especially of titania (TiO_2) for photovoltaic (PV) applica-

Scheme 1. Outline of the preparation of an ordered, cross-linked PS-*b*-P4VP template followed by deposition and formation of titania nanostructures.

tions, is currently an area of intense interest. However, there are many barriers to overcome if well-ordered structures are to become widely applicable. This is particularly so when attempting to get TiO₂ nanostructures which have been problematic in terms of forming well-ordered structures due to the high reactivity of the crystalline surfaces.[27,28] In spite of the high reactivity, many approaches such as anodized aluminum oxide (AAO) template-assisted sol−gel,[29−31] various electrodeposition methods,[32,33] electrochemical anodic oxidation of pure titanium sheets,[34,35] and chemical treatment of fine titania particles[36] have all been used to produce titania nanostructures. Some publications document the preparation of TiO₂ nanorods[31] or nanotubes,[37] but these are not particularly ordered when deposited onto a substrate. Several authors reported using polysiloxane-based soft lithography stamps[38] or block copolymers to template titania deposition. Examples of the latter include work by Park *et al.*,[39] who made TiO₂ nanoposts using a block copolymer mask coupled with selective oxygen plasma etching. This multistep procedure gave high aspect ratio TiO₂ nanoposts, whose widths and heights could be altered *via* changes in the block copolymer composition and etch time. Crossland *et al.*[40] have used poly(4-fluorostyrene)-*block*-poly(D,L-lactide) to template the electrodeposition of TiO₂ and then examined these materials in a PV device. However, because of the use of plasma etching and/or electrodeposition methods, these approaches may have difficulty in being applied to large-scale production.

In this paper, we report the preparation of high-density arrays of titania nanostructures on silicon and indium tin oxide (ITO) glass substrates using polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer template and titanium(IV) bis(ammonium lactate) dihydroxide (TALH) as the TiO₂ precursor. The procedure can exclusively involve solution processing and can be applied to a variety of substrates. The use of the PS-*b*-P4VP block copolymer, which forms P4VP cylinders that orientate perpendicular to the substrate, builds from work by Russell *et al.*[11−14,16,17,41] Various analytical methods, such as field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM), show that well-aligned arrays of titania nanostructures are produced and the block copolymer acts as a template for these nanostructures.

RESULTS AND DISCUSSION

High-density arrays of titania nanostructures on silicon substrate (with a native oxide layer) were prepared as shown in Scheme 1. First, a 1.0 wt % polymer solution was spin-coated onto the silicon substrate. The polymer films were then annealed, primarily through exposure to tetrahydrofuran (THF) vapors but in some cases *via* heating at 160 °C for 24 h, which resulted in P4VP cylinders surrounded by a polystyrene matrix. Second, the film was exposed to diiodobutane (DIB), which will selectively react with the P4VP, in order to lightly cross-link the P4VP cylinders while the TiO₂ is deposited. Our concern was that the thin film might rearrange into a morphology other than cylinders during the exposure to the aqueous TALH solution. Indeed, samples with no DIB treatment did show disordering (data not
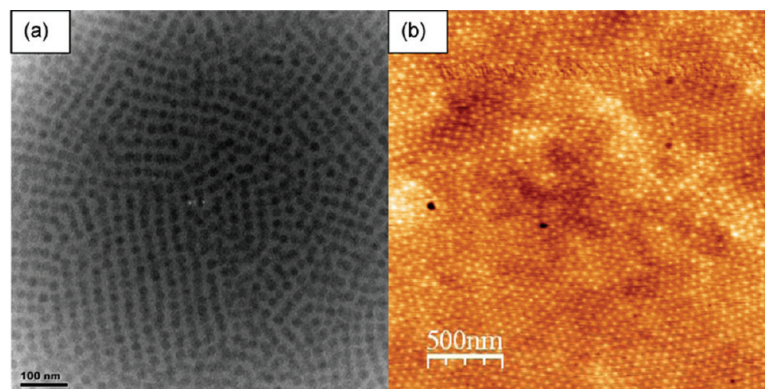

Figure 1. TEM (a) and AFM (b) images of the 41.5K/17.5K (PS/P4VP) block copolymer thin film on silicon after solvent annealing.
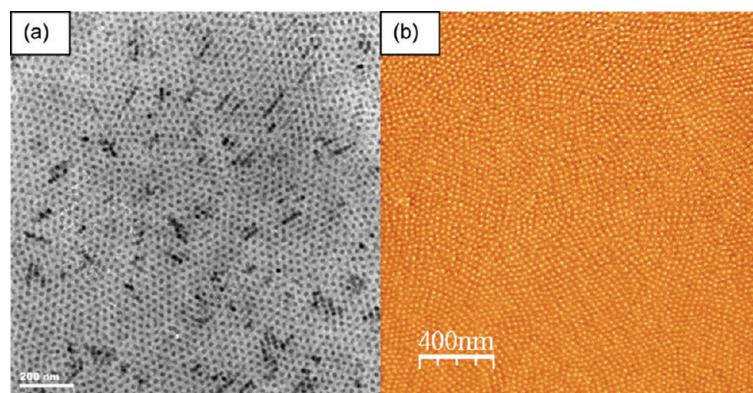
Figure 2. TEM (a) and AFM (b) images of the 25K/7K (PS/P4VP) block copolymer thin film on silicon after solvent annealing.

shown). Third, the cross-linked template was placed in the TALH precursor solution. The final step involved the removal of the polymer template by oxygen plasma treatment, resulting in titania nanostructures on the substrate.

The first step was to obtain evidence that, under our conditions, the PS-*b*-P4VP would provide the cylindrical morphology seen in the work of Russell *et al.*[11] Two PS-*b*-P4VP samples were used; these had number average molecular weights (M_n) of 41 500/17 500 (41.5K/17.5K; PS/P4VP) and 25 000/7000 (25K/7K), respectively. The block copolymers were dissolved in 75/25 toluene/THF mixtures at a concentration of 1.0 wt % and spin-coated (2000 rpm) onto the silicon substrate. The films were then exposed to THF for 12 h to induce mobility for the polymer chains and result in better alignment of the cylindrical structures. Ellipsometry results showed that under these spin-coating conditions the film thickness was 30 ($\pm$5) nm.

Figure 1 shows transmission electron microscope (TEM) and atomic force microscopic (AFM) images of the higher molecular weight block copolymer film after solvent annealing. To increase contrast for the TEM imaging, the films were exposed either to iodine or to di-iodobutane (DIB), both of which would result in staining the P4VP cylinders. The DIB additionally will act to cross-link the P4VP cylinders.[18] As discussed in the literature,[11] the use of the THF/toluene solvent during spin coating followed by annealing produces cylinders that

are oriented perpendicular to the substrate. Our data are similar to those published previously, and thus we conclude that our films are also composed of vertically orientated P4VP cylinders in the PS matrix. However, it is interesting to note that the cylinders do not form an ideal hexagonal packing seen in similar systems but, in Figure 1b in particular, seems to be a mix of square-like and hexagonal packing. This mixed packing is only seen in the higher molecular weight block copolymer we used and was consistently formed regardless of annealing conditions. While not necessarily the focus of the current paper, we believe this could be due to the relatively high P4VP content ($\sim$30 wt/%) in the block copolymer, which could be bordering on the cylinder-lamella phase transition. In any case, the approximate diameter of the cylinders is 25 $\pm$ 5 nm, and intercylinder distance is around 10 $\pm$ 5 nm. Figure 2 shows the TEM and AFM images of the lower molecular weight block copolymer. In this case, the packing is observed to be hexagonal. As expected for this sample, the diameter of each cylinder smaller than the higher molecular weight block copolymer, at approximately 15 $\pm$ 5 nm, and has an average intercylinder distance of around 10 $\pm$ 5 nm. For both polymer samples, there was no difference in the TEM images between the films exposed to iodine or DIB.

The polymer films were also spin-coated onto ITO substrates and solvent annealed. Figure 3 shows the TEM and AFM images of the low molecular weight
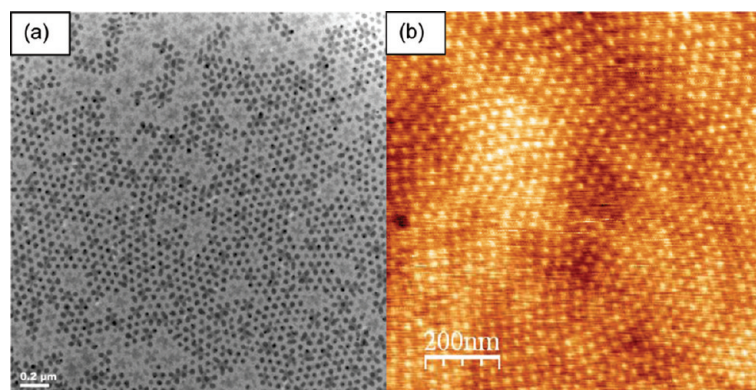

Figure 3. TEM (a) and AFM (b) images of the 25K/7K (PS/P4VP) block copolymer thin film on ITO after solvent annealing.
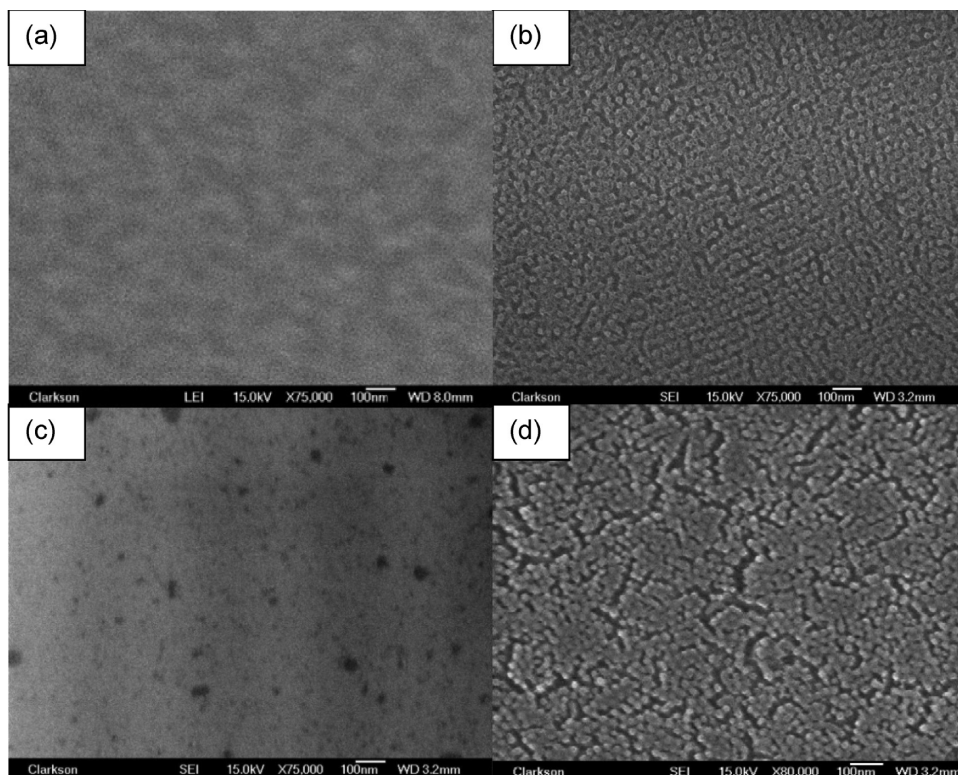
Figure 4. SEM images of (a) TiO$_2$−polymer nanocomposite (41.5K/17.5K PS/P4VP block copolymer) on silicon, (b) then after polymer was removed by O$_2$ plasma, (c) attempted deposition of TiO$_2$ without any block copolymer film present, and (d) TiO$_2$ nanostructures using the 25K/7K PS/P4VP block copolymer template.

block copolymer film on ITO. The images show a well-ordered packing of the cylinders, similar to those films cast onto the silicon, with a slightly less uniformity over an area of 50−100 nm, presumably due to the rougher crystalline surface of the ITO. The cylinder diameter was again in the 15 ± 5 nm range. Similar results were found for the higher molecular weight block copolymer (*e.g.*, see Figure SI-1 of Supporting Information). Thus we conclude that the cylindrical morphology within both block copolymer samples can be obtained on either the silicon or ITO substrates.

The next step was the addition of the TiO$_2$ to the block copolymer film. This was achieved by exposing the films to an aqueous solution containing TALH. We found that for the silicon substrate the optimum pH for this process was in the range of 1.9−2.4, while for the ITO substrate the best pH was 2.1. The time for the deposition procedure was varied from 4 to 12 h, with shorter times providing better results for the lower molecular weight sample and the longer times preferred for the higher molecular weight block copolymer. A scanning electron microscope (SEM) image of the film after the TiO$_2$ deposition process is shown in Figure 4a. This particular image shows very little by way of structure. However, after the TiO$_2$/polymer film nanocomposite was exposed to O$_2$ plasma treatment for 2 h, removing the polymer template and leaving the TiO$_2$ material, a nanostructured TiO$_2$ film was observed (Fig-

ure 4b). The nanostructured TiO$_2$ structures seen in this image are approximately 25 nm in diameter, the same diameter as the P4VP cylinders in the block copolymer film, and again the square-like packing is observed (using the high molecular weight block copolymer).

To substantiate that the block copolymer is actually acting as a template, we also attempted to deposit TiO$_2$ onto a silicon substrate without any block copolymer film present. All other conditions (*e.g.*, concentrations, times, oxygen plasma treatment) were kept the same as those that resulted in the material shown in Figure 4b. The SEM of this surface is presented in Figure 4c. Clearly,
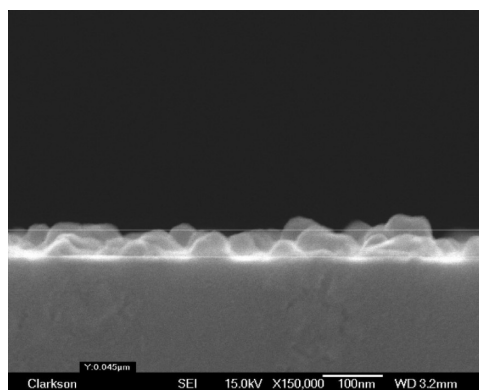

Figure 5. Cross-section SEM image of TiO$_2$ nanostructures using the 41.5K/17.5K PS/P4VP block copolymer template on silicon after oxygen plasma treatment.
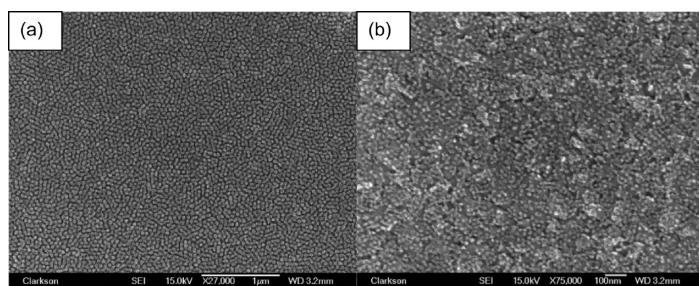
Figure 6. SEM images of TiO_2 nanostructures using the (a) 41.5K/17.5K PS/P4VP block copolymer and (b) 25K/7K PS/P4VP block copolymer template on ITO.
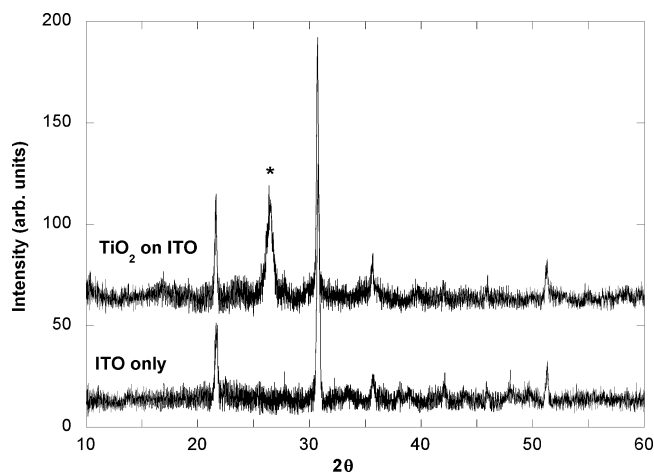

Figure 7. XRD patterns of TiO_2 nanostructures on ITO and ITO only.

this surface has no nanostructuring and no TiO_2 film, thus we conclude that the block copolymer is indeed acting as a template and in fact is necessary for the formation of TiO_2 film on the substrate under the conditions we are using. The lower molecular weight block copolymer was also used to template the deposition of the TiO_2 onto the silicon substrate. A SEM image of the resulting nanostructured TiO_2 is seen in Figure 4d. The titania made from these deposition conditions is expected to be anatase.[18,42,43]

The TiO_2 nanostructures' heights were examined by cross-section SEM. As shown in Figure 5, the height of the TiO_2 ($\sim$30−40 nm) is approximately the same as the thin film template ($\sim$30 nm). These match the thicknesses of the block copolymer template films. Furthermore, we have been able to increase the block copolymer films by using a more concentrated polymer solution and/or slower spin coater speed. Thick block copolymer films (e.g., 350 nm thick) resulted in block co-

polymer film−TiO_2 composites that were slightly swollen (e.g., a 350 nm polymer film gave 429 nm thick composite). After the polymer was removed, the TiO_2 nanostructures were thinner relative to the composite (e.g., the 429 nm thick composite gave TiO_2 nanostructures of $\sim$260 nm in height). This shrinkage is due to condensation to form the titania and the removal of the polymer template and is more pronounced with the thicker films. However, the fidelity of the thicker nanostructures suffered, especially as their aspect ratio increased.

Lastly, we were also able to deposit nanostructured TiO_2 onto ITO, as seen in Figure 6, for both block copolymer samples. As can be seen in comparing these two images, the size of the nanostructures is clearly dependent on the size of the P4VP cylinder domains. The structure of the ITO can just be seen underneath the TiO_2, particularly for the lower molecular weight template. Wide-angle X-ray diffraction (XRD) analysis of the TiO_2 on ITO primarily showed peaks due the ITO (Figure 7), but evidence that TiO_2 was also present could be observed through the appearance of the peak at approximately $2\theta = 26°$. However, because of the small amount of TiO_2 on the ITO surface, resulting in low peak intensity, we are unable to differentiate between anatase and rutile forms of the titania. However, our spectra are consistent with those of Baskaran et al.,[42] who found that TALH deposition into thin films of TiO_2 resulted in anatase and TiO_2 (B).[44]

CONCLUSIONS

In summary, we reported a convenient way of preparation of nanostructured titania films on silicon and ITO substrates using a block copolymer template. These titania nanostructures have potential application in catalytic and photovoltaic applications. Furthermore, because of low temperatures and mild precursor solution, this approach can be potentially applicable to the preparation of large-area, such as roll-to-roll printing. Fundamentally, the results are of interest in examining the effect of well-ordered titania nanoposts on photocatalytic activity, particularly in photovoltaic applications. Recent work in ordered nanostructures of silicon,[45] CdTe/CdS,[46] and modeling[47] has clearly shown the benefits in improved PV performance, and as such, our approach to the production of ordered TiO_2 nanostructures may also enhance solar efficiencies in TiO_2-based PV cells.

EXPERIMENTAL SECTION

Block Copolymer Thin Film Preparation. Two PS-b-P4VP samples (Polymer Source, Inc.) were used; these had number average molecular weights (M_n) of 41 500/17 500 (41.5K/17.5K; PS/P4VP) and 25 000/7000 (25K/7K), respectively. The block copolymers were dissolved in 75/25 (v/v) toluene/THF mixtures at a concentration of 1.0 wt % and spin-coated (2000 rpm) onto either silicon or ITO substrates. The films were then exposed to THF vapor for

12 h in a closed system composed of 300 mL in the bottom of a 5 L glass container. Ellipsometry on a Multiskop null-elipsometer (Optrel, Germany), equipped with a He−Ne laser (λ = 633 nm), showed that under these spin-coating conditions the film thickness was 30 ($\pm$5) nm. The films were exposed to di-iodobutane (Aldrich, Milwaukee, WI) vapor for 3 h.

Titania Deposition. The thin films were immersed in an aqueous solution containing 0.2 M titanium(IV) bis(ammonium lac-

tate) dihydroxide (TALH; Aldrich, Milwaukee WI), using 1.0 M HCl to adjust the pH to 1.9 for silicon substrates and 2.1 for ITO substrates. Deposition times were varied from 4 to 12 h. After deposition, the substrates were flushed with deionized water to remove excess TALH on the surface, then placed in a vacuum oven at 90 °C overnight. Finally, the polymer−titania hybrid films were placed in an oxygen plasma (Harrick Plasma) for 2 h.

Materials Characterization. A JEOL 2010 high-resolution transmission electron microscope (TEM) was used to analyze morphology of polymer thin films after the film was removed from the substrate by etching the underlying oxide layer with a 5 wt % HF solution. A JEOL 7400 high-resolution field emission scanning electron microscope (SEM) was used to image the titania nanostructures. Atomic force microscopy (AFM) was performed on a Dimension 3100 (Veeco Instruments, NY) operating in tapping mode. Silicon probes with a tip radius of about 20 nm, a spring constant of 1.5−6.3 N m^{-1}, and frequency of 63−100 kHz were used.

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