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Facile Patterning of Periodic Arrays of Metal Oxides**

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Highly ordered arrays of periodic nanostructures[1] show interesting characteristics for applications in photonics,[2] electronics,[3] optoelectronics,[4] sensing,[5] biochips,[6] and catalysis.[7] The array properties are determined by the choice of material and can be tuned further by varying the geometry, chemical composition, periodicity, and the size of the nanostructures.[4,8] Such controlled and elaborate arrays are commonly fabricated by X-ray or electron-beam lithography. However, there are limitations to patterning over large areas using these lithographical techniques due to long processing times, which result in higher costs. Relatively simple and cost-effective nanopatterning processes have been developed to address these inherent limitations, including interference lithography,[9] nanosphere lithography,[10] and soft lithography.[11] In order to pattern metals or metal oxides, however, the non-conventional methods still require multistep processing as does conventional photoresist lithography. In this paper, we demonstrate a novel but simple methodology for the fabrication of periodic structures comprising metal oxides at the sub-100 nm scale using polymeric templates, colloids, and common laboratory equipment. Thus, this nanopatterning technique does not require high-vacuum deposition, etching, or photoresists, which are common in other processes. The patterns produced with this method were periodic and composed of 1D or 2D arrays of nanostructures over large areas. Fabrication of these metal oxide nanostructures required only a few hours once the nanometer-sized colloid of the metal oxide and polymeric templates were available. The structural resolution of the resulting pattern was determined by the amount of colloidal deposition onto the grooves (or grating) of the templates used. Although this process utilized microstructured templates, it is possible to fabricate features of metal oxide at the 100 nm scale. The geometry and periodicity of the structure can be well defined and controlled through selection from a wide variety of polymeric templates fabricated by numerous techniques. This unique strategy to achieve controlled nanopatterning can utilize a wide variety of inorganic colloids and/or intricate templates (or masks) available from various established lithographic methods.

Microstructured polymeric templates have been prepared using a single-step holographic patterning process by exposing films of azobenzene-functionalized polymers (AFPs) on substrates to an argon-ion laser (488 nm) interference pattern.[12] The interference pattern produced photoinduced mass transfer in the polymer film giving rise to a surface-relief structure without additional processing.[13] Such surface modulation leads to 1D or 2D periodic arrays of surface-relief-grating (SRG) structures on the polymeric films. A variety of holographic surface structures can be designed and fabricated with good control over the modulation and periodicity of the patterns.

In this work, SRG structures from thin films of AFP on quartz and glass substrates were prepared by exposing the films to a 488 nm laser interference pattern. Titania nanoparticles, with a mean diameter of less than 10 nm, were then deposited selectively on the surface of the SRG using sequential electrostatic layer-by-layer deposition (ELbL) with the polyelectrolyte, poly(4-styrene sulfonate) (SPS). The nanolayered assemblies of SPS and titania (SPS/titania) were then heated to a suitable temperature in air to aggregate the colloids further along the grooves of the SRG. At higher temperatures, the colloidal particles sinter together to form 1D or 2D arrays of metal oxide and the polymeric template eventually degrades. The resulting line features were composed of titania and extended over several tens of micrometers or longer with line widths of 100 nm. This quick and cost-effective process took only a few hours to pattern more than one square centimeter using ordinary laboratory equipment under ambient conditions. Scheme 1 illustrates the stepwise process used to prepare these titanium dioxide nanopatterns on the surface of a glass substrate.

Figure 1A and B show 3D views of the SRG patterns of the AFP films that were typically used in this approach. The AFP used in this work was a copolymer of bisphenol A diglycidyl ether and disperse orange 3 (PDO3). Both structures were used as the templates for the ELbL layering of SPS/titania but

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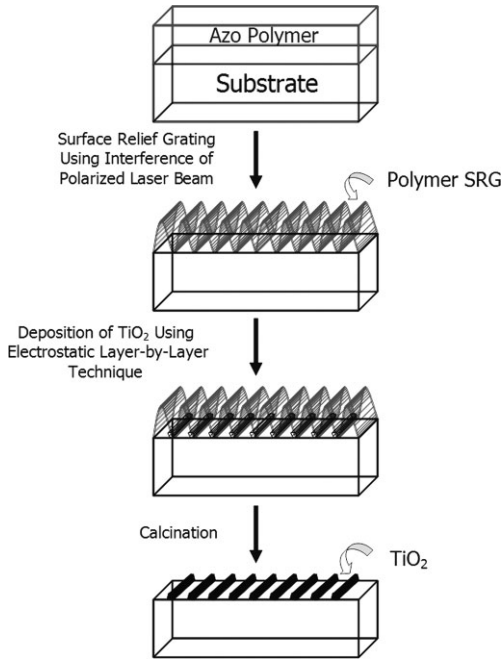

Scheme 1. Schematic illustration of the procedure used for the fabrication of periodic arrays of titania wires with a microstructured polymer template and colloid.

each resulted in different titania patterns. The sinusoidally modulated SRG shown in Figure 1A was used to fabricate a periodic array of titania wires and the orthogonal grating shown in Figure 1B was used to fabricate periodic arrays of titania dots. This egg-crate-like structure in Figure 1B was fabricated by recording two gratings orthogonally to each other at the same point. The morphology of the AFP grating templates was characterized using contact-mode atomic force microscopy (AFM). AFM height profiles of both SRG patterns showed an average modulation amplitude of 300 nm and a periodicity of 1 μm. However, the periodicity of the gratings is controllable, ranging from 0.35 to 3 μm with an amplitude of up to 0.5 μm, by simply adjusting the laser-writing setup.[13]

Optically transparent, colloidal particles were dried on a carbon-film-coated copper grid and examined by transmission electron microscopy (TEM, JEOL FasTEM). TEM images in Figure 1C and D show the presence of crystalline titania nanoparticles with an average diameter of less than 10 nm. The titania powder was dried and collected for X-ray diffraction (XRD) analysis using a rotary evaporator. The XRD powder pattern confirmed the exclusive presence of anatase[14] in the powder with *d*-spacings of 3.52, 2.38, and 1.89 Å.

AFM images in Figure 1E and F show a 3D view of a three-bilayer assembly of SPS/titania on the SRG templates prepared using sequential ELbL as previously described. It was interesting to note that the SPS/titania settled and agglomerated selectively into confined places, such as grooves or hollows in the templates. The surface modulation of the SRG was 300 nm, with the bottom of the SRG being approximately 200 nm from the substrate. The average thickness of SPS/titania deposited on an SRG for a three-bilayer assembly is 70 nm. For the case of a seven-bilayer assembly, the thickness value ranges between 120 and 150 nm. The average advancing contact angles of a plain surface and SRG on films of PDO3 with amine groups at terminal ends[15] were found to be 92° and 88°, respectively, using deionized (DI) water. These values are similar to reported values of hydrophobic bulk polystyrene.[2b,16a] The hydrophobic surface of the SRG template was modified with sulfonic acid or sulfonate groups by dipping the template in a pH 1.0 SPS solution for 10 min followed by soaking in pH 1.0 DI water. The average advancing contact angle of the surface-modified template was determined with DI water to be 72°. This value confirmed that the surface of the SRG had been modified and should provide sufficient counterion charge for subsequent deposition of the titania nanoparticles. However, the wettability of the polymeric film can be simply controlled by the deposition or removal of polyelectrolytes on the surface.[16] The hydrophobicity of the SRG recovers close to the average contact angle value of 86°, subsequent to dipping in pH 10 DI water for 30 min.

As described previously, the first bilayer assembly of SPS/titania was prepared using a pH 1.0 SPS solution. Here, the sulfonyl and/or sulfonate groups of the SPS anchored to the protonated amines of the PDO3 terminal groups that were present at the surface of the SRG template. The surface-modified SRG template was then rinsed in pH 6.0 DI water for 10 min and dried with a gentle flow of nitrogen normal to the film surface. The film was then dipped into a colloidal suspension of titania nanoparticles at pH 1.0 to electrostatically layer titania onto the sulfonyl groups of SPS.[17] This one cycle (or one bilayer) of the ELbL titania-deposition process was then followed by washing with DI water and drying. During the process, the adhesive strength of the deposited SPS to the SRG decreases due to complexation (or charge interaction) with the titania colloid and deprotonation of amines as the SRG was dipped in pH 6.0 DI water. As a result, the surface of the SRG recovers hydrophobicity during the drying step, because the SPS/titania layers become so loosely bound to the SRG substrate that they migrate and deposit into grooves or hollows of the template.[18] Thus, the pH of the dipping solutions dictates the final morphology by strengthening or weakening the ionic bonds between the deposited SPS/titania layers and the amine groups in the substrate. Depositing two bilayers after an initial single bilayer using a pH 5.0 SPS solution preferentially deposited SPS onto the surface of the first SPS/titania bilayer assembly at the bottom of the SRG grooves. No deposition was observed when a pH 10.0 SPS solution was used after the preparation of the first SPS/titania bilayer. When a pH 1.0 SPS solution was used without a drying step, deposition of SPS/titania was observed over the entire surface of the SRG, not just within the confines of the depressions.

In the sintering process, the polymeric templates were thermally removed through degradation and oxidation to volatile products. At the same time, the titania nanoparticles aggre-

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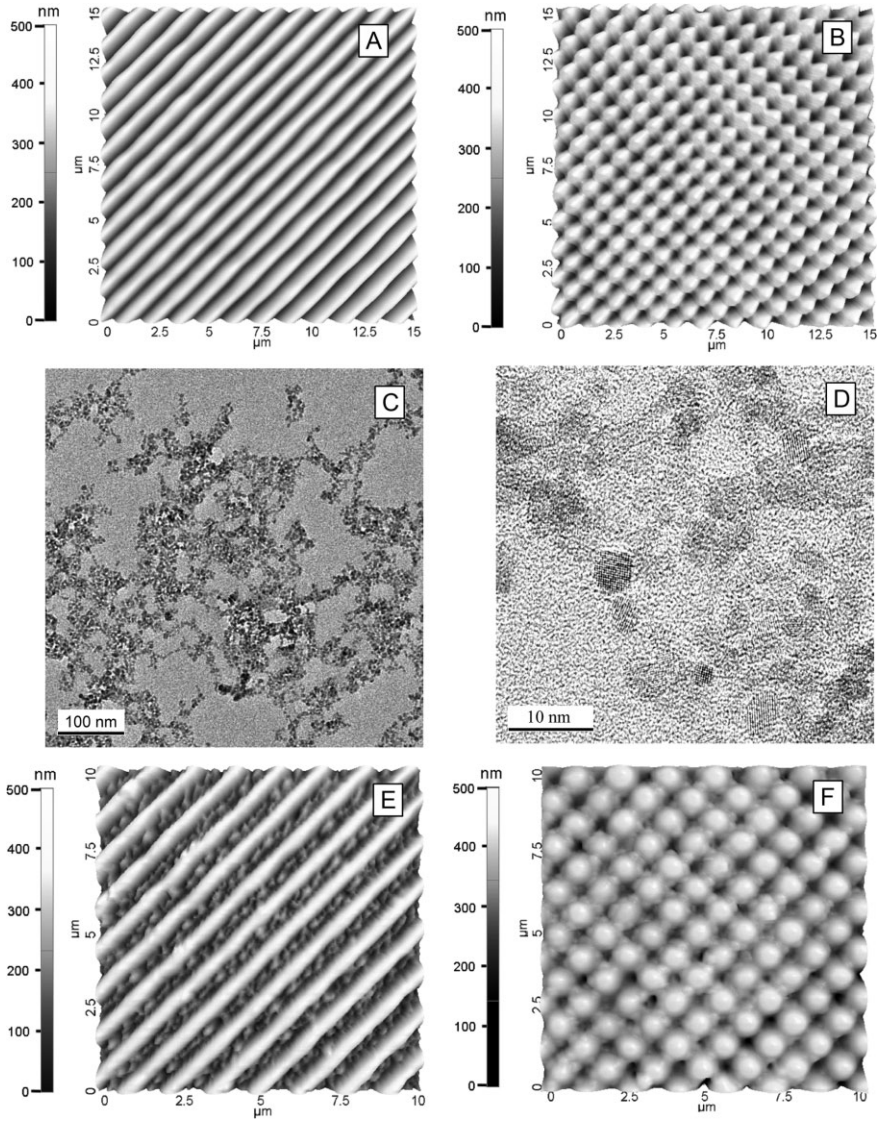

Figure 1. 3D views of polymeric templates show sub-microstructured SRGs fabricated by exposing AFPs to a visible laser interference pattern. A) A typical SRG template used for periodic arrays of titania lines and B) for periodic arrays of titania dots. TEM images of sub-10 nm sized anatase particles prepared by hydrolysis of titanium(IV) isopropoxide: C) homogeneous size distribution of titania nanoparticles and D) a magnified image of titania. 3D views of three bilayers of SPS/titania assembled in depressions on different SRG templates: E) deposition occured at the bottom of grooves of the template (refer to Fig. 1A) and F) in hollows in the template (refer to Fig. 1B).

gate and fuse together to form either sintered titania arrays of periodic features or gratings depending on the processing conditions. Three different SPS/titania assemblies on SRG polymeric templates were prepared by depositing three, seven, and thirty bilayers using the templates shown in Figure 1A to generate line features on the substrates. All were prepared similarly, with the exception that the thirty-bilayer assembly was prepared without the drying step. After thirty bilayers had been assembled, the film was sintered in air at 500 °C for 2 h to create a titania grating. While the images are not presented here, the grating mimics the typical modulation of the polymeric template as was observed using AFM or scanning electron microscopy (SEM). The titania replica has a periodicity and amplitude of modulation of approximately 1.0 and 0.1 µm, respectively, and a morphology comparable to that reported for titania films prepared by a sol–gel process.[19] In addition to fabrication of a grating of titania (or a replica), periodic arrays of titania lines can be fabricated by controlling the amount of colloidal deposition using the ELbL technique. SEM and AFM images in Figure 2 show periodic arrays of titania lines on glass which were generated by pyrolyzing the seven-bilayer assembly in an oven. The periodic line arrays of the titania have an average height of 80 nm (inset of Fig. 2C) and a line width of about 100 nm (inset of Fig. 2A). Here, the periodicity of the arrays of titania lines is also 1 µm (Fig. 2C) and matches the periodicity of the polymeric template (Fig. 1A). Each line exposed in the SEM image of Figure 2B extends to longer than 50 µm and most lines are observed to be several hundreds of micrometers in length. We have performed measurement of the diffraction efficiency at different portions of the TiO_2 periodic arrays to measure the variation of height over much larger areas than is accessible through AFM measurements. The diffraction efficiency in the first order varies almost by 15 % over a square centimeter. Since the diffraction efficiency is small, and in this regime the diffraction efficiency is known to scale as a square of the surface-height modulation, we conclude that the average variation of the height of TiO_2 arrays is approximately 7.5 %. The three-bilayer assembly of SPS/titania after sintering also results in line arrays of titania, as observed using AFM. While the AFM images are not presented here, these lines extend many tens of micrometers with an average height of around 50 nm.

These results show that the height of the line arrays may be controlled through adjustment of the number of deposition cycles and that the type of pattern (array lines or gratings) can be controlled through the pH of the deposition solution and the template morphology. 2D arrays of titania dots may be prepared by pyrolyzing a seven-bilayer assembly of SPS/titania on the type of SRG template shown in Figure 1B. Figure 3A shows a periodic array of titania dots deposited uniformly over a 50 µm × 50 µm area. Each dot has a diameter of

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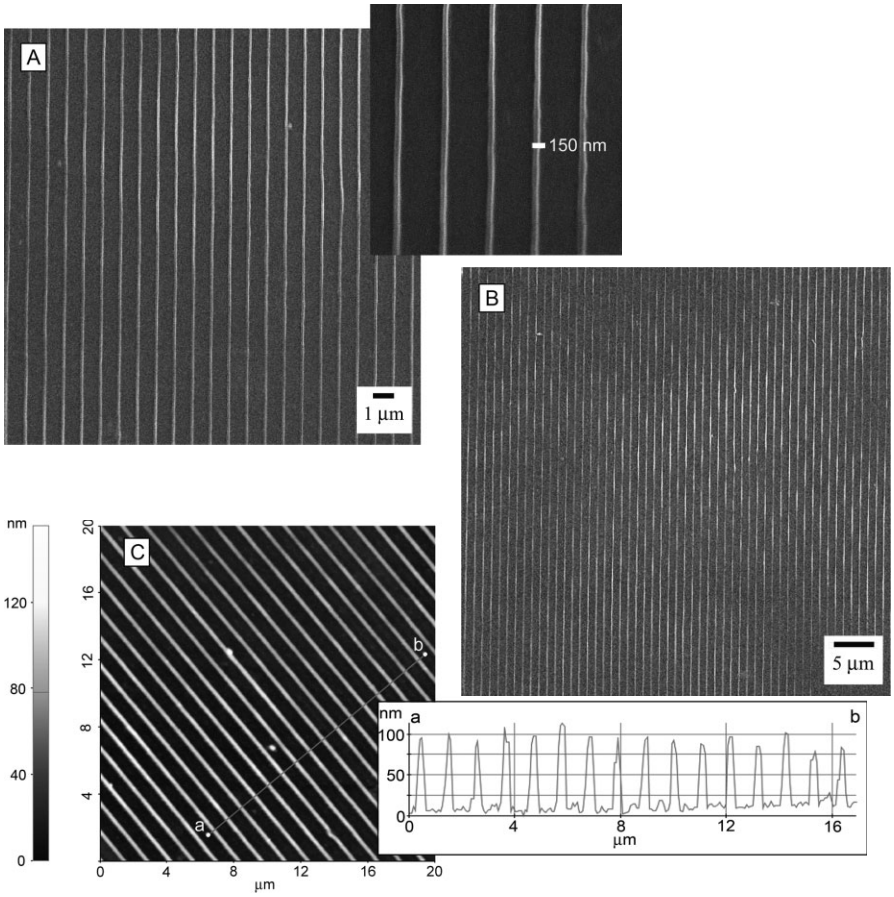

Figure 2. SEM images and an AFM image of periodic arrays of titania lines prepared by pyrolyzing a seven-bilayer assembly of SPS/titania: A) inset is a magnified image of titania lines with a line width of about 100 nm, B) arrays of titania lines over a 50 µm × 50 µm area. C) AFM image of arrays of titania lines shows a periodicity of 1 µm and an average height of 80 nm (inset diagram) after pyrolyzing a seven-bilayer assembly.

about 250 nm with a height of 250 nm as shown in Figure 3B. The periodicity (or pitch) of the arrayed titania dots is in good agreement with that of the polymeric SRG template shown in Figure 1B. Further optimization of this procedure is being studied to achieve more fine control over the dimensions and types of pattern features.

The chemical composition and crystalline structure of the titania line features after sintering has been monitored by X-ray photoelectron spectroscopy (XPS) and XRD. The XPS of a sintered seven-bilayer assembly on a glass substrate shows the following signals in reference to the weak carbon signal (C 1s) at 285.0 eV: Si signals from the glass substrate at 154.5 and 103.5 eV (Si 2p) and Ti signals near 458.5 eV (Ti $2p_{3/2}$), 61.5 eV (Ti 3s), and 36.5 eV (Ti 3p). The nitrogen peak (N 1s), which would be a signature of the residual polymeric template, was not observed. Due to the small sample quantity, XRD of the nanometer-sized patterns showed only *d*-spacings of 3.52, 2.38, and 1.89 Å for the nanowires on glass. However, when a mixture of plain titania colloids and SPS were pyrolyzed, XRD showed *d*-spacings of anatase such as, 3.52, 2.38, 1.89, 1.68, and 1.47 Å after thermal treatment at 500 °C for 2 h in air. The results from XPS and XRD indicated that the line features of titania were composed of anatase and that no significant traces of the polymeric template remained.

This paper describes a simple, reliable, cost- and time-effective approach to fabricating periodic arrays of anatase wires at the nanometer scale over a relatively large area (greater than 1 cm × 1 cm). Titania nanoparticles were sequestered within the confines of the grooves of a periodic microstructured template using modified ELbL deposition methodology. The feature size of the nanopatterning can be controlled on the order of tens of nanometers with simple adjustment of the number of colloidal deposition cycles. This nanopatterning is carried out under common laboratory conditions, without the need for specialized equipment such as high vacuum or chemical vapor deposition. These titania nanopatterned structures are expected to have interesting applications as sensors and optical elements. The approach presented here is general and can be extended to the nanopatterning fabrication of a variety of other metal oxides, metals, or novel materials. The technique could also be readily combined with other templates and patterning techniques such as photoresist templates, conventional optical masks, scratching on the nanometer scale, indentation, and interferometric lithography to design and fabricate more complicated structures.

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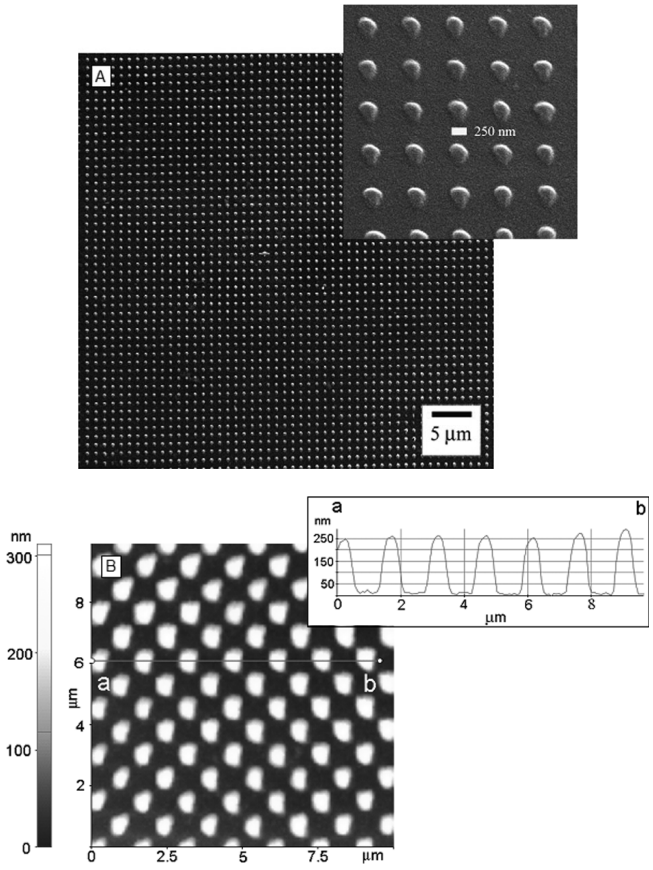

Figure 3. A) SEM images of arrays of titania dots over a 50 µm × 50 µm area with a diameter of about 250 nm (inset diagram) after pyrolyzing a seven-bilayer assembly of SPS/titania. B) AFM image showing each dot has a height profile of about 250 nm (inset diagram) after pyrolyzing a seven-bilayer assembly of SPS/titania.

Experimental

An epoxy-based AFP, PDO3, has been prepared with a diglycidyl ether of bisphenol A, aniline, and 4-nitroaniline using a post azo-coupling reaction as described previously [20]. Aniline was added in slight excess relative to the diglycidyl ether of bisphenol A with a molar ratio of 1.05 to 1, such that the synthesized polymer had amine groups at the terminal ends [15]. The AFP was dissolved in spectroscopic grade 1,4-dioxane and filtered through a 0.45 µm membrane. The solution was then spin-coated on a quartz or glass substrate with a thickness of approximately 0.5 µm through adjustment of the solution concentration and spin speed. The AFP film was then dried in a vacuum oven overnight at 60 °C. SRGs were inscribed using two interfering argon-ion laser beams at 488 nm with an intensity of 50 mW cm^{-2}.

Colloidal titanium dioxide was prepared based on the modification of a reported method [21]. Titanium(IV) isopropoxide 37.76 mL (0.125 mol) was transferred into the mixture of 100 mL of anhydrous ethanol and 1 mL of concentrated HCl using a double-tipped needle under argon. The resulting solution was mixed with 500 mL of 0.1 M perchloric acid solution and refluxed for 36 h.

Assemblies of SPS/titania were prepared using alternate deposition of the polyelectrolyte SPS and a colloidal suspension of the titania by the ELbL deposition technique. The titania colloidal suspension used was 2 wt % at pH 1.0, and was filtered through a 0.1 µm membrane prior to use. The concentration of the SPS solution used was 0.1 wt % with pH 1.0 for the deposition of the first layer, and then with pH 5.0 for all subsequent layers. In the assembly process, the SRG template was first modified by dipping it into the pH 1.0 SPS solution for 10 min to obtain the appropriate amount of sulfonyl groups on the surface. The SPS surface-modified SRG was dipped in pH 6.0 DI water for 10 min and dried with a gentle stream of nitrogen normal to the SRG template. Subsequently, the template was dipped into the pH 1.0 titania colloidal suspension for 10 min, again followed by further identical rinsing and drying steps. This completed one cycle, or a deposition of one-bilayer assembly of the SPS/titania. Thereafter, the process was repeated, by alternating the deposition of SPS in a pH 5 solution and titania in a colloidal solution of pH 1.0 until the desired amount of titania was deposited in the assembly. The final template assembly was then heated at 500 °C for 2 h whereupon the polymer template softened and the adsorbed titania aggregated and fused into the grooves of the grating [18].

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