

Large-Scale Fabrication of Ordered Nanobowl Arrays

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Received August 31, 2004; Revised Manuscript Received September 17, 2004

ABSTRACT

A novel approach is presented for the large-scale fabrication of ordered TiO₂ nanobowl arrays. The process starts with a self-assembled monolayer of polystyrene spheres, which is used as a template for atomic layer deposition of a TiO₂ layer. After ion-milling, toluene-etching, and annealing of the TiO₂-coated spheres, ordered arrays of nanostructured TiO₂ nanobowls have been fabricated. The nanobowls exhibit smooth interior and exterior surfaces and uniform sizes and thickness. The nanobowl arrays have been demonstrated to be useful for selecting spheres smaller than the inner diameter of the bowls. This approach can be extended to a wide range of coating materials and substrates (ceramics, metals, polymers, glasses) with controlled wall thickness and size.

Monolayer self-assembly (MSA) of polystyrene (PS) sub-micron spheres on a flat substrate^{1,2} is an effective and economical technique for fabricating patterns on a relatively large scale.^{3,4} The catalyst pattern created by MSA has been applied for growing aligned and spatial-distribution controlled carbon nanotubes⁵ and oxide nanorods.⁶ Atomic layer deposition (ALD), in which film growth is a cyclic, multistep process of alternating surface-limited chemical reactions, has been demonstrated to be a powerful technique for fabrication of high-quality and multifunctional thin films on various substrates.^{7,8} A diversity of nanostructures can be synthesized using ALD owing to its wide operation temperature and precursor adaptability. For example, by controlling the thickness of the uniformly deposited films, a template-assisted ALD process has been applied to the fabrication of inverse opal structures^{9,10} and quasi-one-dimensional (1D) nanostructures.^{11,12}

In this paper, we present a process that utilizes MSA and ALD for fabricating arrays of TiO₂ nanobowls. The TiO₂ nanobowls exhibit smooth surfaces and uniform size and thickness. The nanobowls may be used as ultra small containers for holding fluid of nanoscale volume, and are also demonstrated to be useful for the size selection of submicron spheres. The approach presented could be extended to a wide range of coating materials and substrates with controlled wall thickness and size.

The experimental procedures are schematically illustrated in Figure 1. First, a monolayer of highly ordered PS spheres (505 nm in diameter) was self-assembled onto a sapphire substrate (5 mm × 5 mm) using a technique we reported

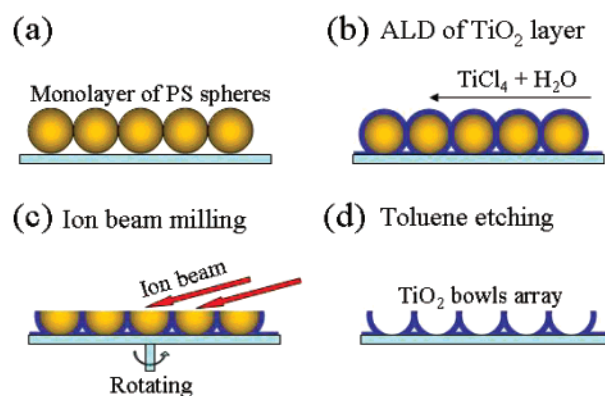


Figure 1. Experimental procedure for fabricating TiO₂ nanobowl arrays.

previously⁶ (Figure 1a). The substrate was placed at the center of an ALD chamber, which was kept at 80 °C during the entire growth process. Then, pulses of TiCl₄ vapor and H₂O vapor were introduced sequentially into the chamber under a vacuum of 4.5×10^{-3} Torr. The pulse duration was 4 s for each precursor, and the pulses were separated by a N₂ purging gas for 10 s. A TiO₂ layer was slowly grown on the surfaces of the PS spheres and the substrate (Figure 1b). The growth was terminated after 200 pulse cycles, which produced a uniform amorphous TiO₂ layer ~20 nm in thickness. The estimated growth per cycle was 0.1 nm, which was determined experimentally from the planar growth per cycle of TiO₂ on natively oxidized Si(100) substrates at 100 °C.¹³

Second, an ion milling machine was used to remove the top half of the TiO₂-coated PS spheres. A 5 kV, 15 mA ion

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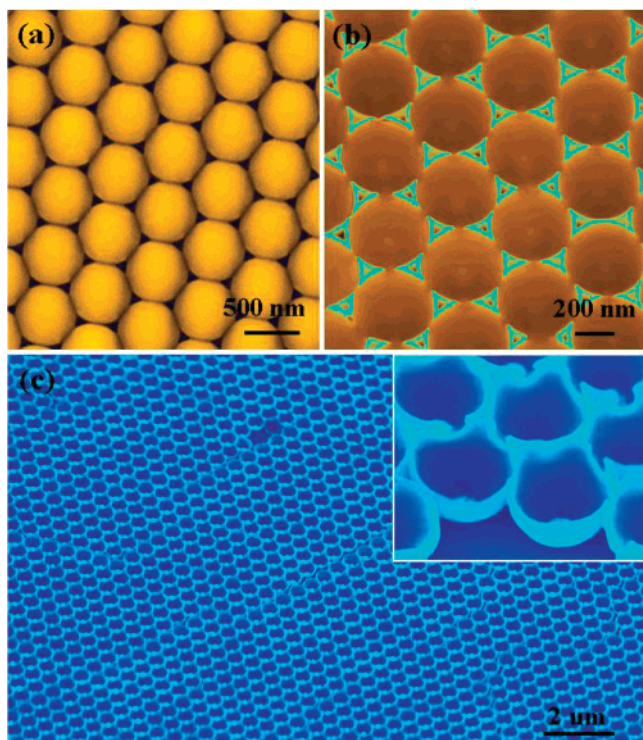


Figure 2. SEM images at each step of the fabrication process. (a) Monolayer self-assembly of polystyrene spheres coated with TiO₂. (b) Ion beam milled surface of TiO₂ coated polystyrene spheres. (c) Low and high (inset) magnification SEM image of TiO₂ nanobowl arrays.

beam was incident on the sample surface at an angle of 10° while the sample was continuously rotated without cooling (Figure 1c). After 20 min of continuous milling, the top half of the spheres was evenly removed. Finally, the PS hemispheres left on the substrate were etched by toluene, resulting in a highly ordered array of TiO₂ nanobowls (Figure 1d). Annealing at 850 °C for 2 h transformed the amorphous film into polycrystalline anatase TiO₂.

Scanning electron microscope (SEM) images are shown in Figure 2 to demonstrate the result of each step described above. Figure 2a shows a monolayer of self-assembled PS spheres coated with TiO₂, which exhibits a very smooth surface due to the low growth temperature. The spaces between the spheres are partially filled as a result of the TiO₂ growth. The sample surface after ion milling is shown in Figure 2b. The blue triangles are TiO₂ shells with a uniform thickness of ~24 nm. This reveals that the growth per cycle of amorphous TiO₂ on the PS spheres is about 0.12 nm at 80 °C, a little higher than growth at 100 °C, as expected from the increased number of hydroxyl groups present on the surface at low temperatures. The brown region among the triangles is the milled polystyrene surface, which is slightly lower than the TiO₂ surfaces owing to a higher milling rate of polystyrene.

Highly ordered arrays of TiO₂ nanobowls were fabricated after toluene etching. As shown in Figure 2c, the periodic structure was well preserved during the entire process. No distortion was observed on the thin walls of TiO₂ after sonicating in toluene for 1.5 min. The bright spot at the center

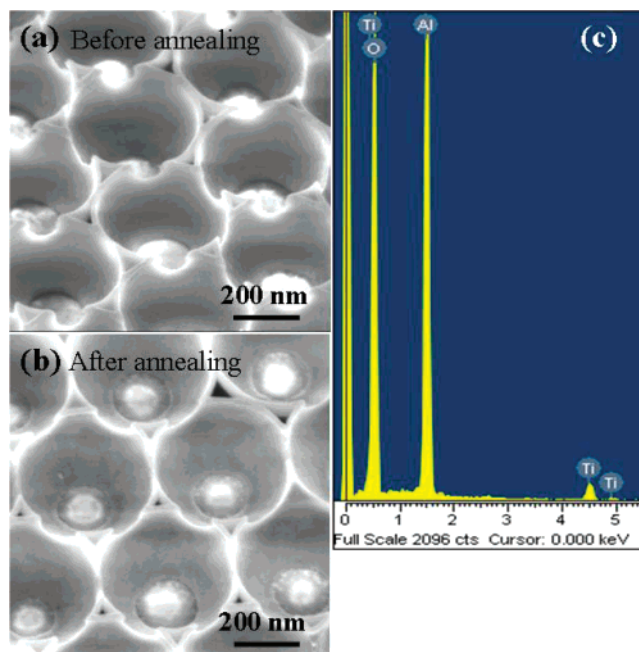


Figure 3. High-temperature annealing was used to transform the amorphous structured walls into polycrystalline walls. TiO₂ nanobowls before (a) and after (b) annealing at 850 °C. (c) EDS spectra recorded from the TiO₂ nanobowls after annealing.

of each bowl is the exposed Al₂O₃ substrate, which was masked from TiO₂ deposition at the PS sphere contact points. The inset in Figure 2c is a high-magnification image of the TiO₂ bowls, from which the spherical shape and the smooth interior surface of the bowls can be clearly seen. The notches between the bowls are the result of the contact point between PS spheres.

The amorphous TiO₂ nanobowls can be converted into polycrystalline nanobowls by annealing. After annealing at 850 °C for 2 h in air, nanobowls composed of nanocrystallites were produced. Representative images of the TiO₂ bowls before and after annealing are shown in Figure 3a and b, respectively. By comparing these two pictures, no obvious size shrinkage was induced: the diameter of the bowls remains at ~460 nm and the thickness of the TiO₂ wall measured at the triangular region is also constant at 24~25 nm. Furthermore, the annealing process does not obviously change the smoothness of the interior surface, although there is a small roughness around the contact region between the TiO₂ bowls and the substrate. The chemical composition of the bowls after annealing is confirmed by energy-dispersive X-ray spectroscopy (EDS) (Figure 3c). In addition to Ti and O peaks, Al is also shown, which attributed to the substrate.

The crystallography of the annealed TiO₂ was examined using a Hitachi HF2000 transmission electron microscope (TEM). A low-magnification TEM image is shown in Figure 4a. The TiO₂ bowls were broken for the TEM specimen preparation. However, their spherical shape can still be seen. The strong contrast of the wall is due to the larger projected mass thickness. The inset in Figure 4a is a typical diffraction pattern recorded on the TiO₂ bowls, indicating their polycrystalline structure. The anatase crystal structure is confirmed by the diffraction pattern.¹⁴ Although the TiO₂ bowls

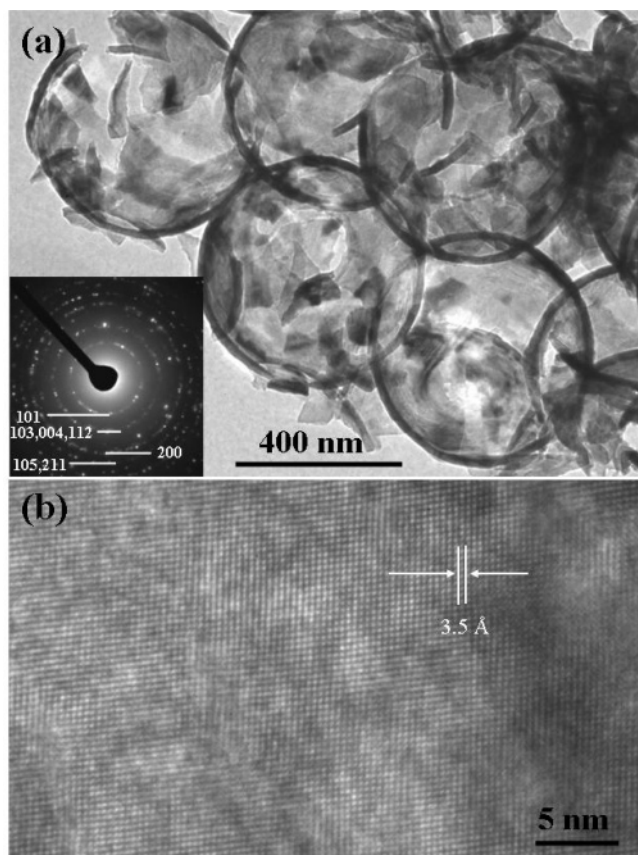


Figure 4. Crystallographic structure of the TiO₂ nanobowls. (a) Low magnification TEM image of TiO₂ nanobowls. (inset) Diffraction pattern recorded from TiO₂ nanobowls. (b) High-resolution TEM image of the wall of a TiO₂ nanobowl.

exhibit a polycrystalline structure, their grain size is fairly large, typically 50 nm. A high-resolution TEM image recorded from a TiO₂ nanocrystal is shown in Figure 4b. The uniform lattice fringe spacing is indicative of the high quality of the nanocrystal. The distance between each fringe is about 3.5 Å, corresponding to the interplanar distance of {101}.

As one of the important functional semiconductors, TiO₂ exhibits promising applications in solar cell,^{15,16} photocatalytic,¹⁷ photonic crystal,^{18,19} and photovoltaic²⁰ technology. As described above, robust and highly ordered anatase TiO₂ nanobowl arrays have been successfully fabricated, and their larger open surface area could significantly increase the efficiency of surface related phenomena. The fabrication technique could also be applied to different substrates that have smooth and hydrophilic surfaces, such as silicon, glass, metals, or even polymers. This will broaden its application in various fields. The nanobowls could also be lifted off the substrate to form monolayer submicron filters. Moreover, the thickness of the TiO₂ wall can be precisely tuned by varying the number of ALD cycles, and the bowl size can be adjusted by using different sized PS spheres during the formation of the templates. Therefore, these nanobowl arrays could be good candidates as size separators and containers for fine particles, or even for bio species such as cells if the interior surface is coated with functional groups. The following experiment demonstrates a potential application.

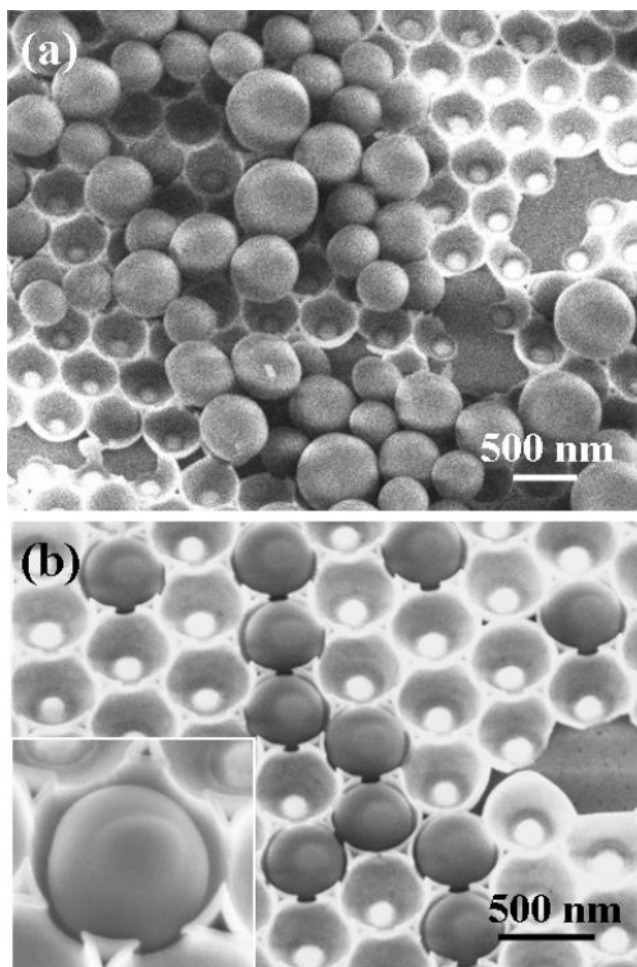


Figure 5. (a) Different sized PS spheres lying on the top of a TiO₂ nanobowl array after applying a drop of PS spheres with mixed sizes. (b) Only the smallest PS spheres remain after washing with ethanol. (inset) A 450 nm PS sphere confined inside a TiO₂ nanobowl.

A mixture of PS spheres with different sizes was used to demonstrate that the TiO₂ bowls can be used for selecting monosized submicron spheres. In the following experiment, equal amounts of PS spheres of diameters 450 nm, 590, 680, and 820 nm were added into 10 mL of ethanol, forming a 0.5% (by weight) PS sphere suspension. One droplet of the suspension was applied onto the crystallized TiO₂ bowls and sonicated for 15 s. As shown in Figure 5a, PS spheres that are larger than the inner diameter of the TiO₂ bowls (~460 nm), are distributed on the top of the bowls. Only the smaller PS spheres with a diameter of 450 nm fell into the TiO₂ bowls. Then, a small amount of ethanol was sprayed onto the substrate to wash away the PS spheres. All of the larger spheres were flushed away, and only the small sized spheres remained inside the bowls (Figure 5b). The inset in Figure 5b shows that a PS sphere that is located inside a TiO₂ bowl is well surrounded and protected so that it was not flushed away by the ethanol. Due to the low concentration of PS spheres in suspension, only a small percentage of the TiO₂ bowls were occupied. A repeat of the above process may select all of the smaller spheres. This simple experiment illustrates that TiO₂ bowl arrays are useful for selecting particles smaller than their inner diameter.

In summary, we presented an effective approach for fabricating highly ordered anatase TiO₂ bowl arrays. The process utilizes a self-assembled monolayer of PS spheres as a template. TiO₂ walls are uniformly coated on the sphere surface by atomic layer deposition, with which the thickness of TiO₂ walls can be precisely controlled. The final nanobowl arrays were achieved after ion milling, etching, and annealing. In addition to their inherited well-ordered arrangement, the nanobowls also exhibit smooth interior and exterior surfaces and uniform size and thickness. TiO₂ nanobowls could potentially be applied to solar cell, photocatalysis, and photovoltaic technology. The nanobowls have been demonstrated for selecting spheres smaller than the inner diameter of the bowls. The approach presented in this paper could be extended to a wide range of coating materials and substrates, with controlled wall thickness and size.

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NL048589D