

Large-Size Lifiable Inverted-Nanobowl Sheets as Reusable Masks for Nanolithography

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ABSTRACT

A low-cost procedure is introduced for fabricating large-area, liftable, ordered TiO₂ nanobowl sheets. The sheet is made using the template of self-assembled polystyrene spheres, followed by atomic layer deposition (ALD), ion milling, and etching. By introducing a thin organic layer between the nanobowls and the substrate, the whole sheet can be lifted-off in full size. The dimension of the holes at the bottom of the nanobowls is controlled by additional ALD; thus, the sheet has been applied as a reusable mask for producing nanodot patterns with designed sizes. This technique demonstrates a simple and economic nanolithography approach for producing various designed patterns without using a clean room, and it has a great potential for scale-up, mass production, and commercial applications.

Nanotechnology is experiencing a fast development in laboratories as well as in industry. Both bottom-up and top-down approaches have been employed for fabrication of nanometer-scale materials and devices.¹ To take advantage of both approaches and eventually lower the cost of production, techniques can be combined to generate patterns utilizing a top-down process, such as lithography, and control the local structure through a bottom-up process, such as self-assembly. However, challenges still remain in integrating bottom-up and top-down processes for economical large-scale fabrication of nanodevices. Since the cost increases exponentially when the pattern size created by lithography drops below 100 nm, it will greatly facilitate the commercialization of nanotechnology if a low-cost large-scale bottom-up process can be developed to extend or replace lithography techniques in the nanometer size range. As a successful example, monolayer self-assembly (MSA) of polystyrene (PS) submicrometer spheres has been adopted in large-scale pattern generation for quantum dots arrays^{2,3} or selective growth of quasi-one-dimensional (1D) nanostructures.^{4,5} Most recently, a combination of MSA and atomic layer deposition (ALD) has created a brand new nanobowl array structure,⁶ which further extended the applications of this low-cost self-assembly technique. Although the nanobowl arrays have been demonstrated as a good candidate for surface-reaction-related nanodevices as well as a size selector, their inflexibility on substrates limits their adaptability and applications.

In this paper, we report an improved bottom-up process for fabrication of large-scale, free-standing nanobowl arrays

with high flexibility in operation and manipulation. By introducing an organic buffer layer between the nanobowls and the substrate, a full layer (in the centimeter range) of nanobowl arrays can be lifted up and deposited on any other substrate or even placed upside-down forming small chamber arrays. Coating a copper transmission electron microscopy (TEM) grid with this nanobowl sheet will be demonstrated, which can be utilized as a reusable mask for making catalyst or quantum dot arrays with precisely controlled sizes, distribution, and density.

In our experiments, the basic fabrication strategy is based on our previous reported procedures. However, to eventually separate the nanobowl sheet from the substrate, a ~300 nm poly(methyl methacrylate) (PMMA) layer was first spin-coated onto a silicon substrate, which was used for supporting the nanobowl sheet, as illustrated in the inset of Figure 1a. A monolayer of PS spheres was self-assembled on a water surface using a surfactant, sodium dodecyl sulfate (SDS). Since this monolayer is easily destroyed when contacted by a hydrophobic surface, the PMMA-coated silicon substrate was preimmersed into a 2% SDS solution for 2 h. After this treatment, a monolayer with an area of a few square centimeters can be smoothly transferred from the water surface onto the PMMA layer without any distortion. A TiO₂ coating was then grown to a thickness of ~25 nm through a low-temperature ALD process. It should be noted that the growth of TiO₂ occurred both around the PS spheres and on the PMMA layer, which composed spherical shells and a flat bottom surface, respectively. The top-half of the TiO₂-coated PS spheres was evenly milled away by an argon ion beam in an ion milling machine. The residual hemispheres

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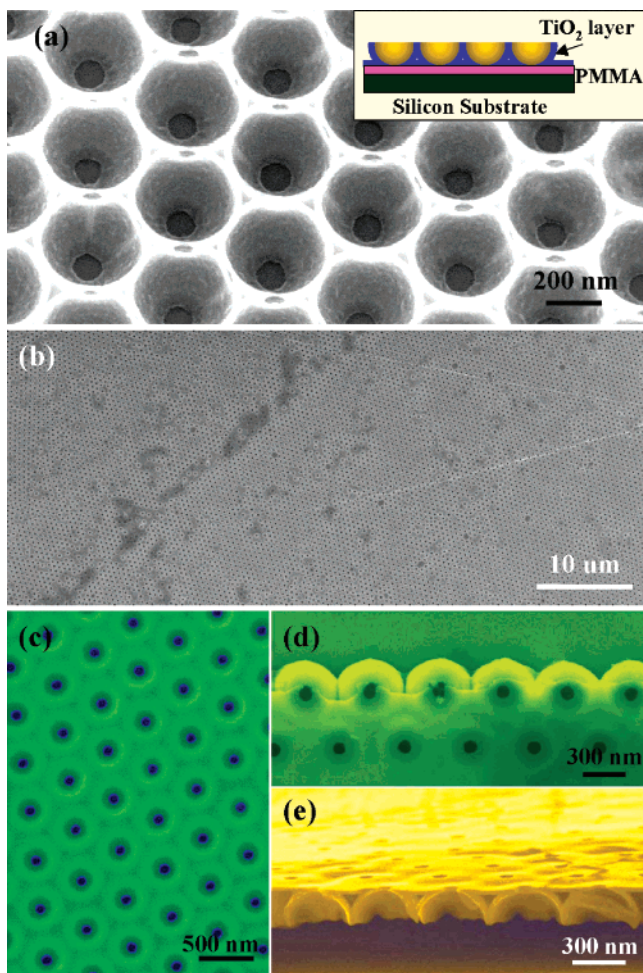


Figure 1. (a) A SEM image of TiO₂ nanobowl arrays on a PMMA layer. Inset: schematic of the modified configuration for fabricating free-standing nanobowl sheets. (b) A low magnification SEM image of a bowl-side-down nanobowl sheet on a silicon substrate. (c) A high magnification SEM image of the backside of a nanobowl sheet. (d) Edge of a bowl-side-down nanobowl sheet. (e) Cross section of a bowl-side-down nanobowl sheet.

of PS spheres were removed by toluene to achieve the nanobowl morphology. To ensure the remaining spheres were completely removed, the substrate was normally sonicated in toluene for 2–3 min until bright optical diffraction from the ordered structure became clearly visible again. Although the PMMA is also soluble to toluene, it was protected by the TiO₂ coating and was not dissolved. By immersion of the substrate in acetone overnight, the PMMA layer was slowly removed, creating a free-standing TiO₂ nanobowl sheet. The free-standing nanobowl sheet floated to the acetone surface and could be lifted up by any other substrate with the bowls facing either away or toward the substrate.

A LEO HF 1530 scanning electronic microscope (SEM) was used to examine the experimental results. Figure 1a shows the as-synthesized TiO₂ nanobowl array on a PMMA layer. Due to the good wetting between PS and PMMA, an almost identical and perfect small open circle was formed at the center of each nanobowl, from which the underneath PMMA layer can be seen. This shows that sonicating in toluene for a short period of time can completely remove the PS hemispheres while leaving the PMMA layer unaf-

ected, even though both polymers are soluble to toluene. Similarly for the lift-off process in lithography, immersing in acetone for a long time (normally around 10 h) can slowly dissolve the PMMA layer away through the small open circles. Once the PMMA is completely removed, the nanobowl sheet separates from the supporting silicon substrate and is ready for further applications.

A piece of bowl-side-down nanobowl sheet is shown in Figure 1b, which was lifted from the acetone surface by another silicon substrate. The TiO₂ surface exhibits high flatness inherited from the supporting substrate. The open circles at the center of each nanobowl now become a hole-array when they are observed from the backside, while the high periodicity of the nanobowls remains unchanged. Behind the TiO₂ layer, all of the nanobowls are facing down and are actually supporting the whole layer from substrate. Owing to the identical height of each nanobowl attributing to the ion milling process, no fluctuation of the top layer can be observed. A high-resolution SEM image of the backside is shown in Figure 1c, from which the identical shape and size of the holes are clearly demonstrated. Since the TiO₂ layer is only ~25 nm in thickness, the spherical nanobowl shape can still be seen by the electron beam through the top layer. This bowl-side-down configuration of the nanobowls is more clearly revealed by a view of the edge area (Figure 1d), where the smooth back of the nanobowls is exposed.

From a side view of a cross section, as shown in Figure 1e, a good contact between the nanobowls and the substrate is evident. In this configuration, each nanobowl forms a dome with a size of a few hundred nanometers and there is only one “window” opened on the top of each dome. These domes are highly ordered and separated from each other, forming a two-dimensional nanocell array. The cell is interconnected by a tiny tunnel at the bottom, which is actually the notch between the nanobowls resulting from the contact point between the PS spheres. On the other hand, it is also possible to completely separate each cell by milling over the contacting spot during ion milling process. Considering that the “window” is ~100 nm, which is comparable to the size of a single virus, this nanocell array can be a good candidate for housing, filtering, and separating viruses.

Because of the thin shell, the nanobowl sheet broke due to high stress when the size of a single piece was larger than ~0.3 mm² despite the high flexibility of amorphous TiO₂ layer. The general dimension was 0.5 mm × 0.5 mm for a free-standing sheet, which contained ~1 million ordered nanobowls. This is a reasonably large number considering the quantity of nanocells that can be formed and used. However, it is still necessary to improve the size limit in order to achieve real large-scale fabrication and manipulation and eventually commercialization. The key issue is how to bind the entire sheet to an unbreakable framework, which can also be easily removed when needed.

By considering that PS does not dissolve in acetone while PMMA does, PS was chosen to be a binding material. As shown in the inset of Figure 2a, on top of the PMMA layer, another layer of PS (~100 nm in thickness) was spin coated before loading the monolayer template of PS spheres. After

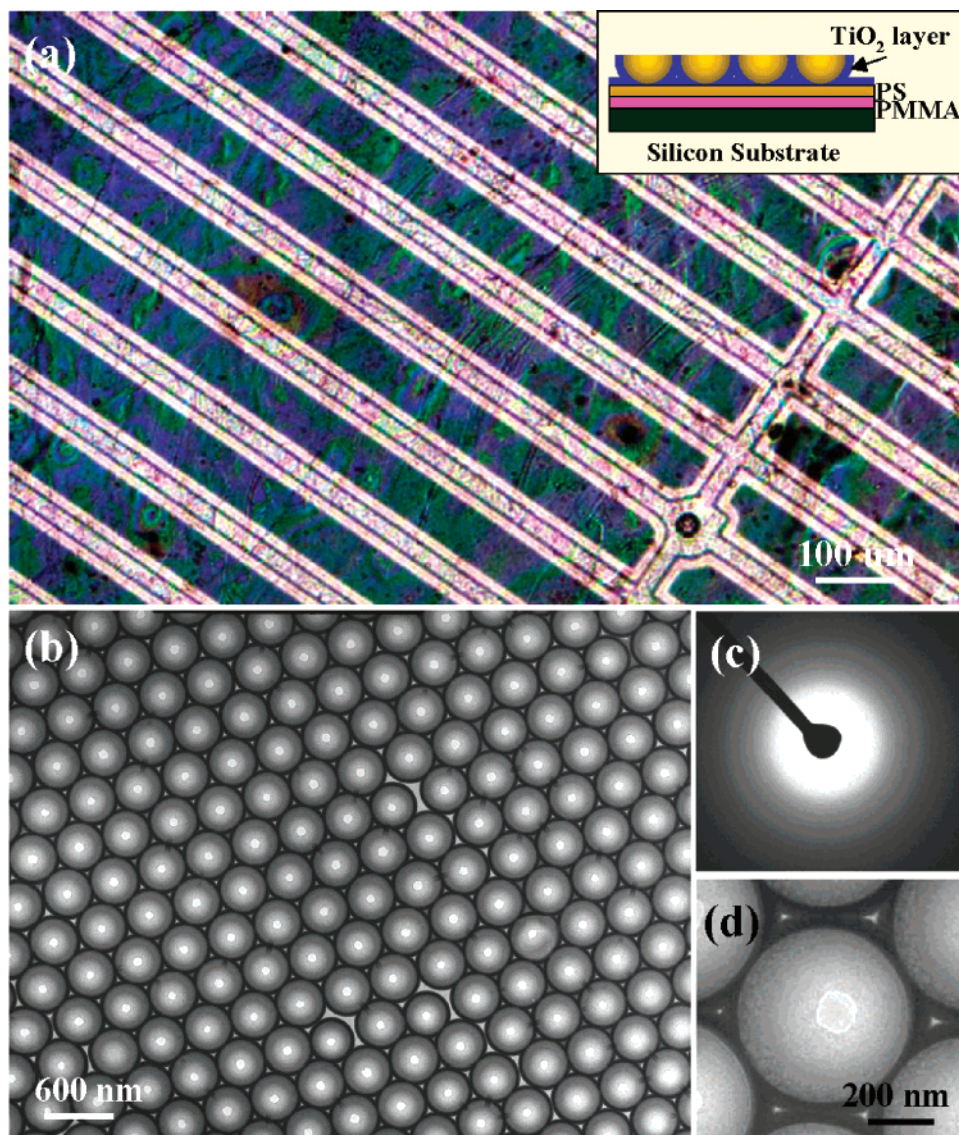


Figure 2. (a) Optical image of a copper TEM grid covered by a large-area nanobowl sheet. Inset: schematic of the modified configuration for fabricating stable large-area nanobowl sheets. (b) A TEM image of the nanobowl sheet loaded on a TEM grid. (c) Electron diffraction of the amorphous TiO₂ nanobowl sheet. (d) A closer view of a single nanobowl in TEM.

the procedure described above was used to form the hemispheres shown in the inset of Figure 2a, the substrate was first immersed in acetone overnight. Due to their different solubility, the PMMA layer between the silicon substrate and PS layer was completely removed so as to separate the half-sphere layer from substrate. Held together by a very flexible PS layer on the bottom, the thin TiO₂ nanobowl sheet can be made as big as a few square centimeters. This free-standing composite sheet can then be lifted up by another substrate or even a TEM grid. The final morphology of the nanobowl sheet was achieved by using toluene to remove the residual PS half spheres and the bottom PS layer. The resulting large-area nanobowl sheet did not break once supported by a solid substrate.

An optical microscope image of the nanobowl sheet supported by a copper TEM grid is shown in Figure 2a. The green and blue colors were from light scattering upon the ordered structure. The total size of this nanobowl layer is 10 mm², which completely covered a standard TEM grid

with a diameter of 3.05 mm. Van der Waals forces held the nanobowl sheet attached to the TEM grid, owing to the flat surface on the bottom of the nanobowls. The open space between the copper bars is $\sim 80 \mu\text{m}$, which is within the size range that the TiO₂ layer itself can hold the nanobowls together without falling apart. The nanobowl arrays can therefore be easily observed inside a transmission electron microscope, and a typical TEM image is shown in Figure 2b. Changing of contrasts clearly demonstrated the spherical shape, the circular holes, and the walls of nanobowls, while the flat amorphous TiO₂ layer is not easily distinguished due to the absence of Bragg reflections from the sample (Figure 2c,d). This image also proves that the improved fabrication process has successfully transferred a large-area nanobowl sheet to a substrate without damaging its morphology and distribution.

Attaching the nanobowl sheet onto a TEM grid facilitated the easy manipulation and application of this nanobowl arrays. The 20-nm-thick sheet could be moved, tilted, and

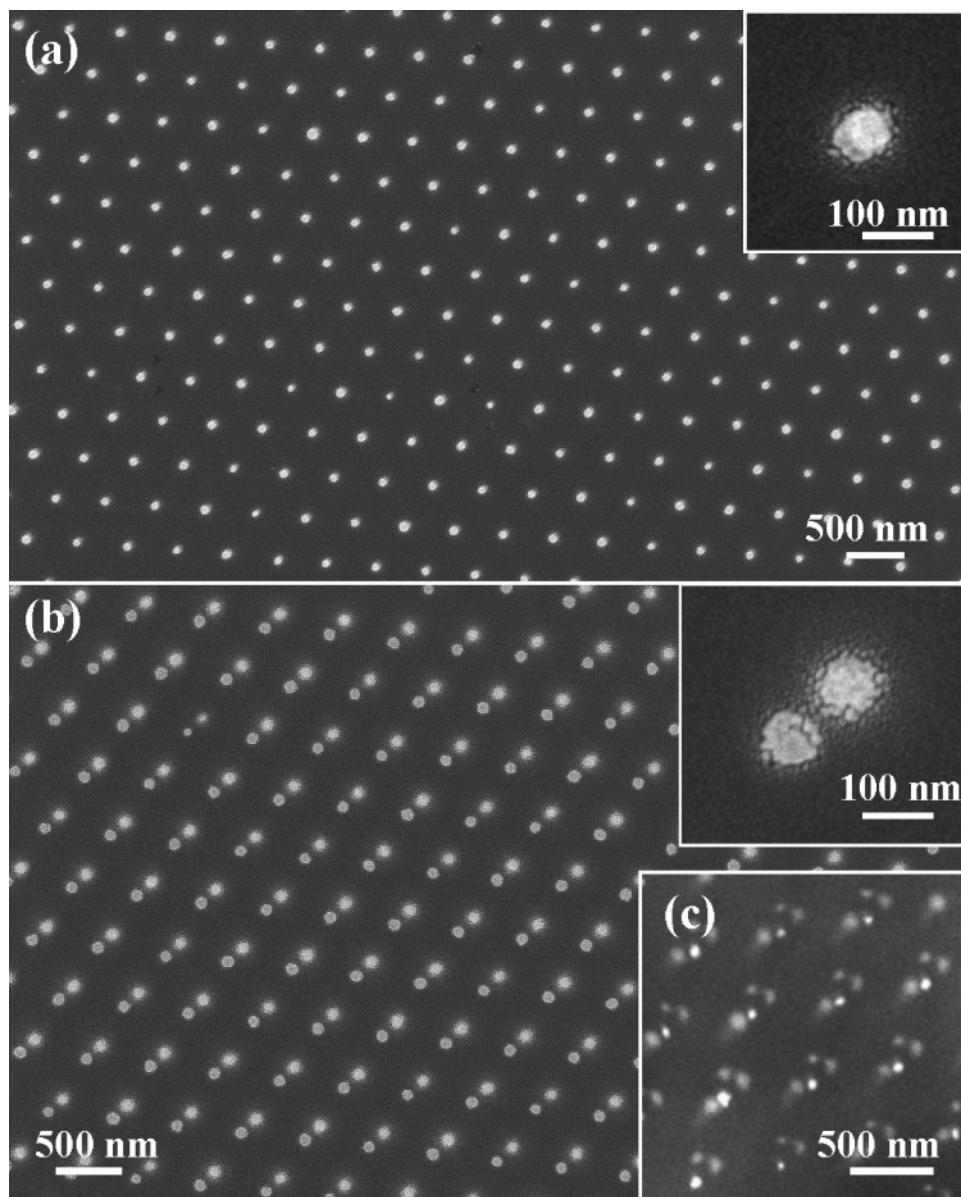


Figure 3. Gold dot patterns made through the nanobowl masks: (a) a triangular single-dot pattern; (b) a triangular double-dot pattern; (c) a multidot pattern.

placed by simply controlling the supporting TEM grid. In this configuration, the top-down (TEM grid) and bottom-up (nanobowl sheet) processes have been successfully united and provide a very promising example for a low-cost and high-efficiency fabrication process for nanoscale features.

Taking advantage of the open hole at the bottom of each nanobowl, the nanobowl-coated TEM grid is demonstrated as a reusable mask for generating catalyst or quantum dot arrays with precise control of size and distribution. As mentioned previously, the open bottom is caused by the contact point between the spheres and substrate. Since the contacts between the PS spheres and the PS layer are fairly uniform, the size variation of the holes is within 5% (Figure 2b). Using the uniform and highly organized holes as a mask, triangular gold nanoparticle patterns were generated through thermal evaporation of a 20 nm gold layer, as shown in Figure 3a. Each gold dot exhibits a circular shape with a diameter of ~ 100 nm determined by the size of the holes

(inset in Figure 3a). The distance between the gold dots is ~ 500 nm corresponding to the size of the PS sphere template (505 nm in diameter). Once the nanobowl mask was put upside-down on the substrate, the walls of the nanobowls, whose height was precisely controlled by the time of ion-milling, separate the holes from the target substrate with a certain distance so that various patterns can be generated through the mask by changing the deposition angle,⁷ such as double-dot and multidot patterns (Figure 3b,c) or even circles by angularly rotating the substrate.⁸ More important, this mask can be reused multiple times owing to the support from the TEM grid, which can be simply removed after deposition and put on another substrate manually without damaging the mask. This cannot be achieved by photoresist-based lithography techniques.

In addition to the reusability, the hole size on the mask can also be tuned precisely so as to achieve different particle sizes. The hole diameter can be controlled by depositing

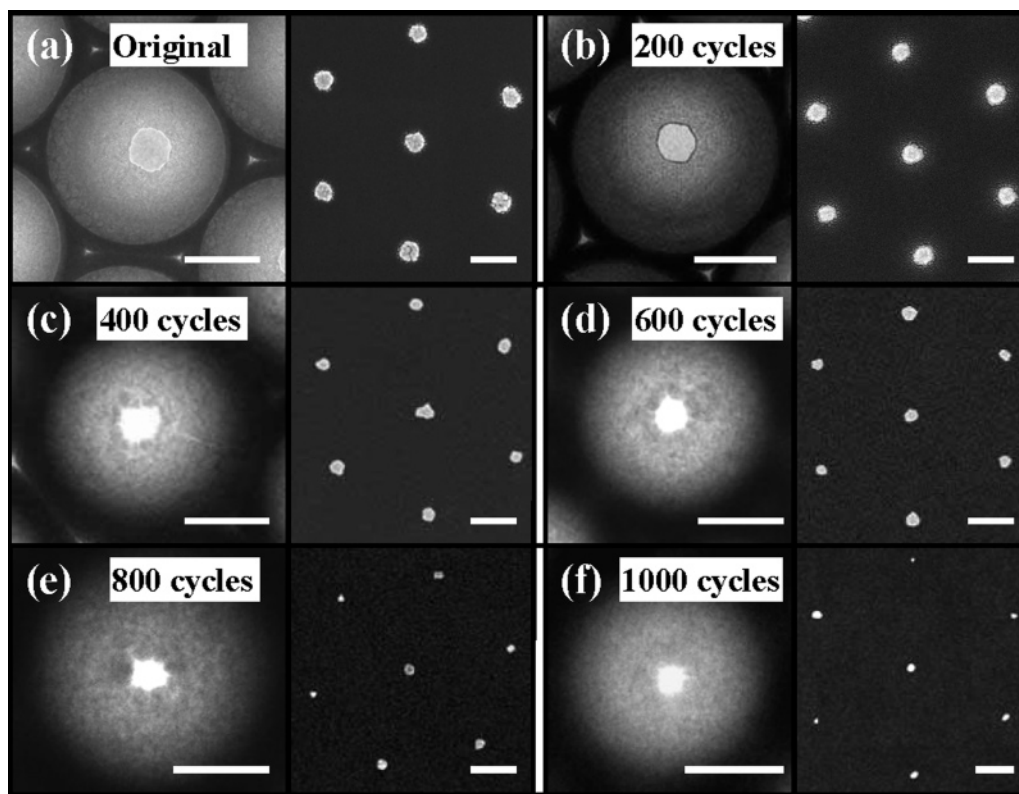


Figure 4. TEM images of the nanobowls after additional ALD growth of 0 (a), 200 (b), 400 (c), 600 (d), 800 (e), and 1000 (f) cycles. Besides each TEM image is the gold dot pattern generated through the corresponding nanobowl masks. All the scale bars represent 200 nm.

additional TiO_2 on the nanobowls through low temperature ALD, in which the holes are gradually closed by the conformal TiO_2 coating. This additional ALD coating allows uniform control of the hole size with sub-nanometer precision. Figure 4 shows a series of TEM images of nanobowls after additional ALD growth with different numbers of cycles. The average diameter of the original hole was 110 nm (Figure 4a), and after each increment of 200 ALD cycles, the average hole diameter was tuned to 105, 86, 64, 48, and 37 nm, as shown in parts b–f in Figure 4, respectively. Besides each image is a SEM image of the gold dots made through the corresponding nanobowl mask in a thermal evaporation process. Obviously, the dimensions of gold dots were very well determined by varying the hole diameters. Furthermore, this size control is practically continuous. According to the ALD growth rate, which is $\sim 0.5 \text{ \AA}/\text{cycle}$ on average,⁹ the precision in size control can be as good as a few angstroms. However, the size uniformity might decrease when the dots get smaller. This is because the uniform ALD growth keeps the absolute size deviation unchanged in any hole dimensions; e.g., if the mask starts with a hole size of $110 \pm 5 \text{ nm}$, it will end up with $37 \pm 5 \text{ nm}$ after additional ALD growth, in which the variation is more significant in percentage.

In summary, this paper introduces a procedure for fabricating free-standing, large-area, ordered TiO_2 nanobowl sheets at low cost and without using clean-room facilities. Nanocell arrays and reusable nanoscale masks are two new structures fabricated by manipulating the free-standing nanobowl sheets. Applications of the structures as masks

have been demonstrated for fabricating nanodot arrays with controllable size and distribution on a substrate. The formation of both bowl-side-down nanobowls and nanobowl masks presents successful examples of integrating top-down and bottom-up processes, which is the future of nanotechnology. The process has a great potential for scale-up, mass production, and commercial applications.

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