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Large-scale metal oxide nanostructures on template-patterned microbowls: A simple method for growth of hierarchical structures

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Abstract

Hierarchical structures–metal oxide nanostructures on desired patterns of metal oxide microbowls have been successfully fabricated by combining the unique advantages of two simple techniques: template assisted self-assembly technique by which polystyrene micro/nanospheres could be readily patterned and positioned on a large scale and hot-plate technique by which metal oxide nanostructures could be easily formed. Instead of using microspheres as mask to locate the catalyst for subsequent nanostructure growth, in this work we directly employed the patterned polystyrene microspheres as a template where the metal films (Fe, Cu, Zn and Co) were deposited and the hierarchical structures were formed subsequently by a one-step low temperature (250 °C–400 °C) heating process in atmosphere. With the feasibilities like patterning, positioning and fabricating the hierarchical structures with large surface area, this simple and practical method exhibits potentials for the synthesis of a unique building block: nanostructures on the desired patterns of micro/nanobowls, for future nanoscience and nanotechnology.

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1. Introduction

Fabrication of nanostructures with a plethora of morphologies is currently a very active field of research [1–11]. To date, in addition to the simple one-dimensional (1D) or 2D nanostructures [1–6], many complicated and exciting nanoscale architectures [7–11] have also been synthesized. Hierarchical structures can even be built as a hybrid system. Once control over the synthesis of simple nanostructures and hierarchical architectures is achieved, development of rational approaches for patterning, positioning and multidimensional assembling such nanoscale building blocks into desired structures will become a significant challenge in the realization of advanced nanodevices.

One of the most favorable and developed techniques for the purpose mentioned above is the assembly of spherical colloids. Recently, in contrast to the aim of depositing materials on the surroundings of spherical colloids, 2D ordered TiO_2 nanobowl arrays have been successfully synthesized by using a monolayer of polystyrene spheres as template [12,13]. In this work, by utilizing the unique advantages of self-assembly of colloid spheres and our hot-plate method [6,14,15], we developed a straightforward and efficient method for fabrication of hierarchical metal oxides (α-Fe_2O_3, Co_3O_4, CuO and ZnO) structures with large-scale and well-controlled 1D, 2D and 3D patterns. The method reported here may open an alternative approach to effectively achieve both morphological and positional control of growth, and consequently may be exploited to fabricate hierarchical structures and controllably assemble such unique building blocks into desired functional structures.

2. Experimental section

The patterning of polystyrene microspheres, sputtering of metal films and heating process have been described elsewhere [6,14–16]. In this work, V-shaped micron sized channels with

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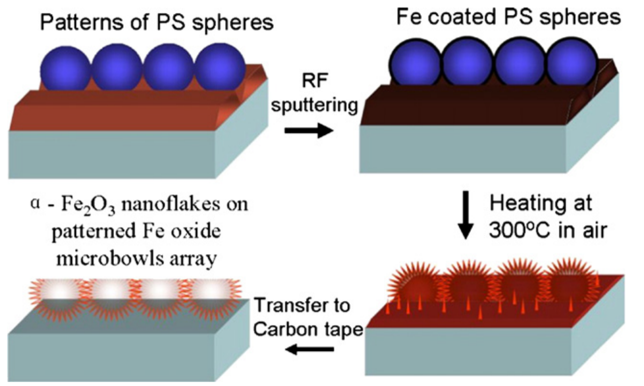

Fig. 1. Schematic illustration of the process of fabricating nanostructures on a desirable pattern of microbowls. Here, Fe oxide is taken as an example.

controllable width and depth on the SU8 film were created by moving the film with respect to the fixed laser beam (λ=532 nm), with speed of 50 μm/s. Monodispersed colloidal solution of polystyrene microspheres (Polyscience, Inc.) was spin coated on the SU8 template at a speed of 700 rpm. The hydrophobic nature of the SU8 and centrifugal force prevented the particles from resting on the SU8 surface. On the other hand, physical confinement provided by the channel effectively trapped the spheres and the lateral capillary force between the colloidal particles drove the spheres to form closely packed configurations in the channels during the drying process. Before a thermal treatment, a RF sputtering process (Denton vacuum Discovery 18 system) was employed to deposit metal films on the patterned polystyrene spheres template. The metal coated spheres were heated from 250 to 400 °C in air for 2 h. The size of the polystyrene microspheres for fabrication of Fe oxide microbowls is 1.5 μm in diameter (Polyscience, Inc.). To demonstrate the material diversity and sphere dimensional feasibility of this method Zn, Co and Cu oxide hierarchical structures were also fabricated by using a mixture of polystyrene microspheres with diameters of 1.5, 2.5, 3.5, and 5 μm as template. The morphologies of the as-grown samples and their inverted top layers which were transferred to the carbon tape were investigated by a scanning electron microscope (SEM, JEOL JSM-6700F). The Raman scattering investigations of individual microbowls was performed using a WITec system with a solid state laser (λ=532 nm) and photoluminescence (PL) spectrum was recorded by a Renishaw 2000 system with a HeCd laser (λ=325 nm).

3. Results and discussion

Taking Fe oxide as an example, Fig. 1 summarizes the process of generating hierarchical structures–metal oxide nanostructures on the patterned metal oxide microbowls. The microsized polystyrene spheres were first patterned on the substrate with a SU8 photoresist layer by a simple template assisted self-assembly method [16].

A sputtering deposition process was carried out to deposit Fe thin film on the polystyrene spheres and SU8 film. Subsequently, the sample was heated on a hot-plate at 300 °C for 2 h in air. This one-step thermal treatment induced the formation of the α-Fe_2O_3 nanoflakes on the flat surface of substrate and the patterned Fe oxide microbowls which were resulted from the evaporation of polystyrene microspheres and oxidization of Fe particles during heating. By using carbon tape, the patterned Fe oxide hierarchical structures could be inverted and transferred.

Fig. 2 shows the scanning electron microscopy (SEM) images of the samples corresponding to each step depicted in Fig. 1. As shown, the

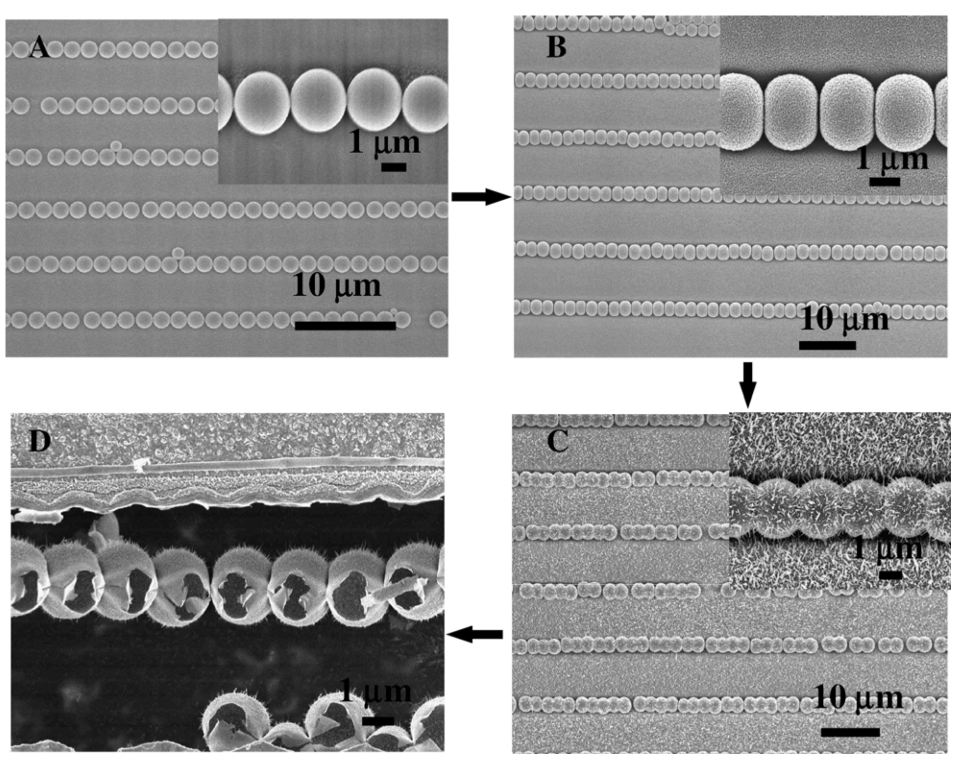

Fig. 2. SEM images of Fe oxide samples corresponding to each step shown in Fig. 1. High magnification SEM images were shown in A, B and C insets.

large-scale linear pattern of polystyrene microspheres was formed by the temp late assisted self-assembly technique [16]. After sputtering deposition, the SU8 photoresist and polystyrene spheres were coated with a thin layer of Fe film. The nanoflakes with similar morphologies as reported in our previous work [6] were fabricated on the flat surface and linearly patterned “microballs” after a simple one-step heating process on a hot-plate. As the glass transition temperature of polystyrene (~100 °C) is less than the heating temperature (300 °C), the polystyrene may be evaporated and the “microballs” where the α-Fe_2O_3 nanoflakes grown may be hollow. This was evidenced by inverting the linearly patterned “microballs” using a carbon tape. Fig. 2D presents the SEM image of α-Fe_2O_3 nanoflakes grown on the linearly patterned Fe oxide microbowls. It was noted that the edges of the bowls were very thin compared with the bottom. This is due to the lack of Fe particles deposited onto the bottom of the polystyrene microsphere, which are inside the microchannels of SU8. Thus, the parts with very thin layer coating, normally which is porous and especially those uncoated parts provided an obvious route for the evaporating polystyrene during the heating process. With careful observation, the nanoflakes could be observed inside the microbowls. This may be promising for future bio/chemical sensing applications as the growth of nanoflakes on both sides of microbowls could significantly increase the surface area. The Raman spectrum (not shown) of individual hierarchical structures indicates that the nanoflakes and the surface layer of microbowls are α-Fe_2O_3 [6].

The monolayer of TiO_2 nanobowls has been fabricated by Wang et al. and showed promising application properties [12,13]. The unique advantage of template assisted self-assembly of colloids is the ease with which the polystyrene microspheres can be assembled into desired patterns in addition to forming a monolayer [12,13]. Base on this strategy, it should be feasible to fabricate the nanoflakes on a patterned microbowls. The SEM images presented in Fig. 3 demonstrate the success of this supposition. Fig. 3A1 and A2 shows the Fe particles coated 2D and 3D ordered structures of polystyrene microspheres, respectively. Fig. 3A3 presents the monolayer of polystyrene microspheres coated with a thin layer of Fe particles. After the heating process, α-Fe_2O_3 nanoflakes were successfully synthesized on the patterned microbowls (Fig. 3B1–B3). Fig. 3C1–C3 shows the SEM images of the patterned hierarchical structures after being transferred onto a carbon tape. It is obvious that the α-Fe_2O_3 nanoflakes were formed on both sides of the microbowls. In addition to the hierarchical structures, micro/nanobowls with desired patterns and compositions

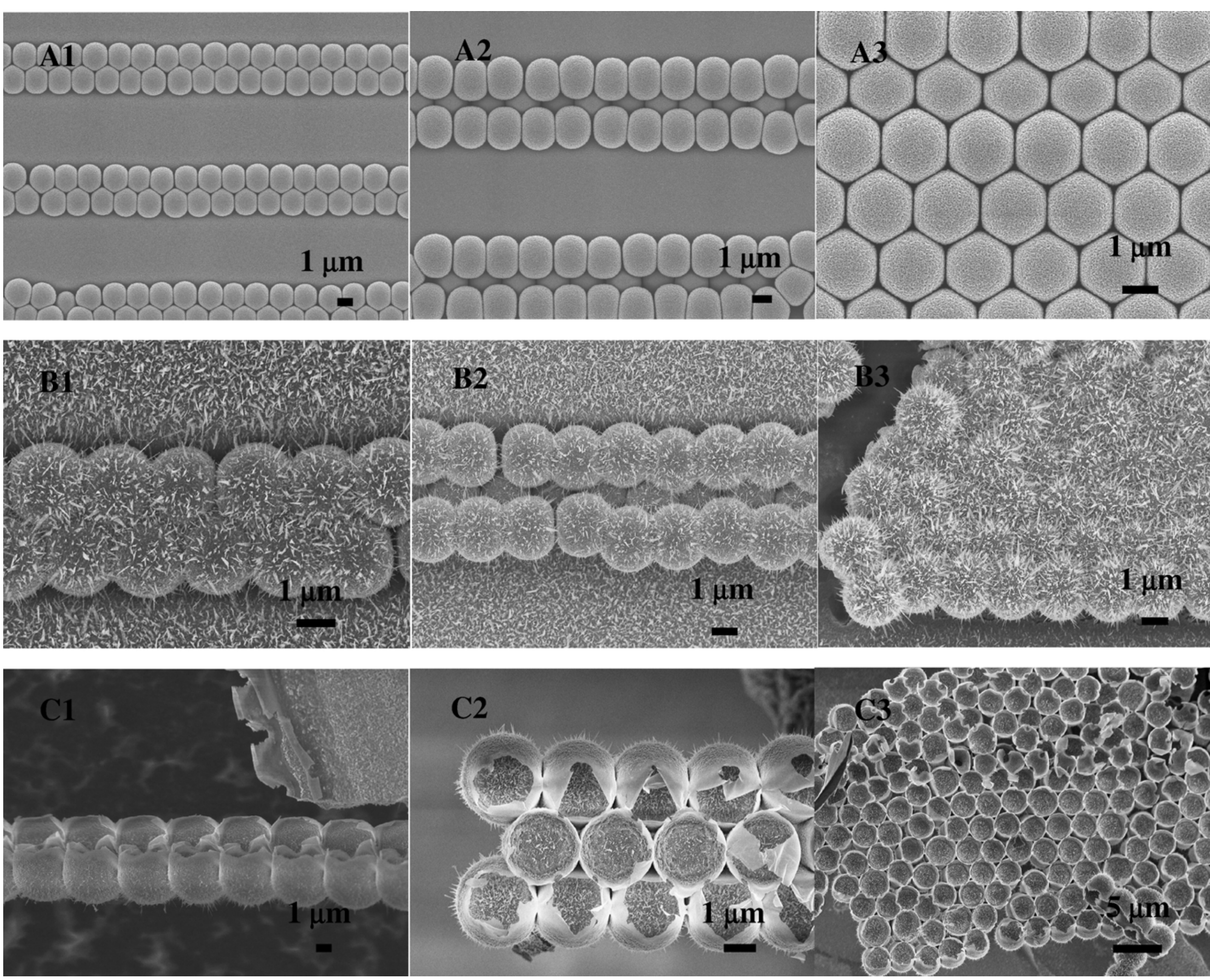

Fig. 3. A1–A3 SEM images of thin layer of Fe particles deposited on the desired patterned polystyrene microspheres. B1–B3 SEM images of α-Fe_2O_3 nanoflakes grown on the flat surface and patterned “microballs”. C1–C3 SEM images of inverted “microballs” transferred onto the carbon tape, indicating the hollow properties of “microballs” and the growth of nanoflakes on both sides of microbowls.

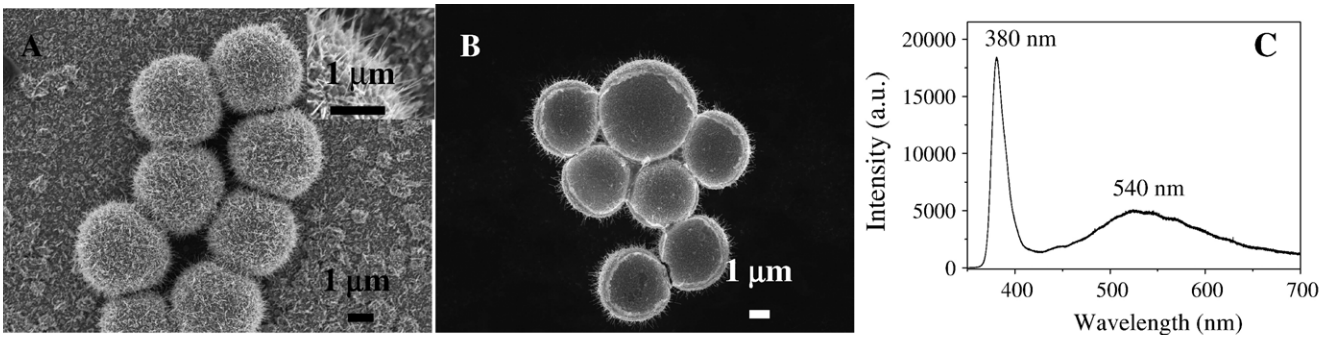

Fig. 4. A and B SEM images of ZnO nanowires grown on both sides of Zn oxide microbowls. C PL spectrum of individual microbowls attached with nanostructures.

could be readily fabricated by controlling the heating temperatures and it is believed that this method can be extended to form pure metal micro/nanobowls which may exhibit promising potential in enhanced near field Raman scattering due to their ultrasharp edges [17,18].

Besides Fe oxide, we extend this strategy to other metal oxides such as Zn, Co and Cu oxides. To demonstrate the material diversity and sphere dimensional feasibility of this method Zn, Co and Cu oxide hierarchical structures were also fabricated by using a mixture of polystyrene microspheres with diameters of 1.5, 2.5, 3.5, and 5 μm as template. Fig. 4A and B shows the SEM images of ZnO hierarchical structures: nanowires grown on microbowls. As shown, under the experimental conditions here (375 °C, 2 h), the as-grown ZnO nanowires with an average length of 600 nm and diameter of 20 nm are radially pointed outwards. It is not implausible that these metal oxide hierarchical structures could be desirably patterned in 1D, 2D or 3D as Fe oxide. A similar structure, ZnO nanorod-based hollow-hemispheres

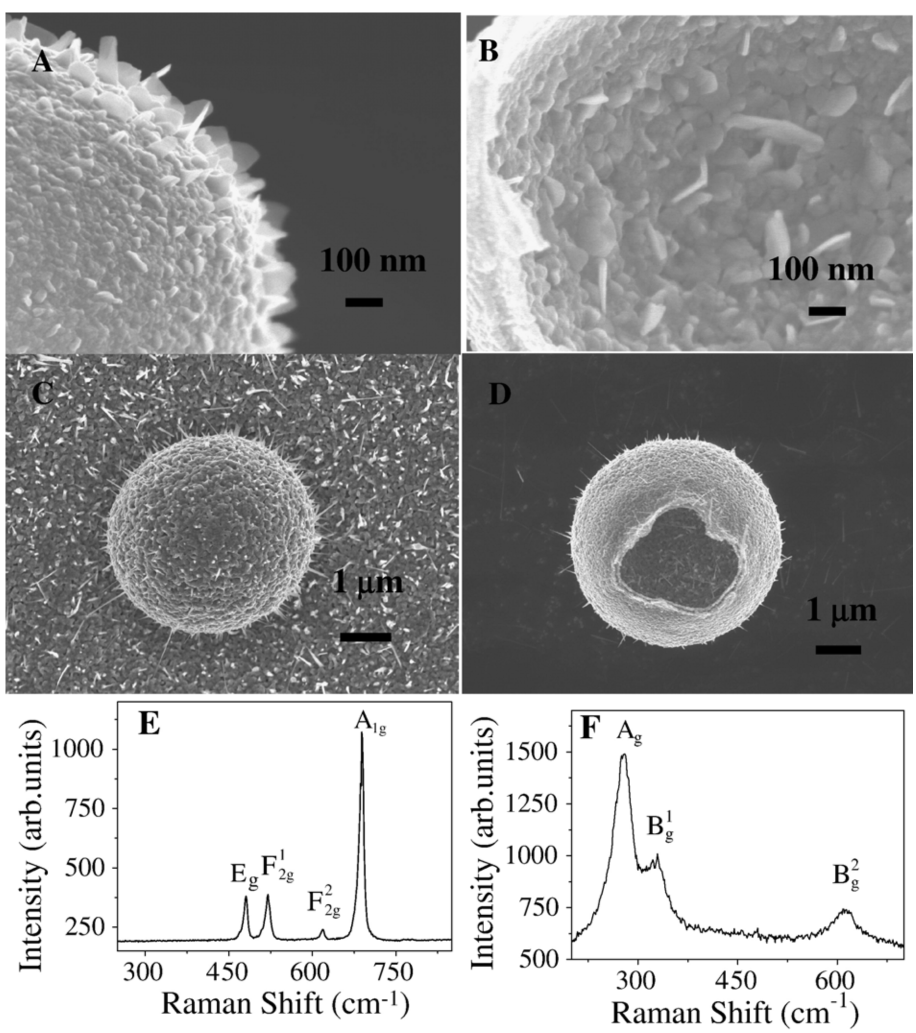

Fig. 5. A and B SEM images of Co_3O_4 nanowalls grown on both sides of Co oxide microbowls. C and D SEM images of CuO nanowires grown on the Cu oxide microbowls. The Raman spectra of individual Co and Cu oxide microbowls were shown in Fig. 5E and F respectively.

have been synthesized by a wet-chemical route [19], where the assemblies of ZnO nanorods were randomly distributed and aggregated together. The micro-photoluminescence (PL) spectrum of individual hierarchical structures was shown in Fig. 4C. The relatively sharp UV peak with full width at half maximum as narrow as 14 nm and high ratio (~4) of UV to visible emission in this work imply a good quality of the hierarchical ZnO structures synthesized by this simple method [20].

Fig. 5 shows the SEM images of Co oxide (Fig. 5A and B) and Cu oxide (Fig. 5C and D) hierarchical structures. By heating the Co coated polystyrene spheres at 250 °C for 2 h, the Co_3O_4 nanowalls with 100 nm in height and several nanometers in thick were formed on the Co oxide microbowls. Rather than 2D wall-like attachments, CuO oxide hierarchical structures fabricated by heating Cu coated spheres at 350 °C for 2 h exhibit 1D wire-like attachment. The Raman spectra (Fig. 5E and F) of the individual of Co oxide and Cu oxide hierarchical structures present the pure spectra of crystalline Co_3O_4 and CuO respectively [14,15], indicating the pure phase of the nanostructures and the top surface layer of microbowls.

Two mechanisms may be responsible for the growth of metal oxide nanostructure attachment. For those starting metals with high melting points like Fe and Co, considering the huge contrast between their melting points (Fe, 1538 °C and Co, 1495 °C) [21] and low formation temperatures (α-Fe_2O_3 nanoflakes, 300 °C and Co_3O_4 nanowalls, 250 °C) and the absence of observation of catalyst terminators in electronic microscopy, surface diffusion may be the dominated growth mechanism. The growth process may be proposed as (i) at the initial heating stage, a very thin top layer of metal film was oxidized and the polystyrene began evaporating; (ii) with the lapse of time, the polystyrene fully escaped and the corresponding metal oxides nucleated at some locations with more defects for example grain boundary and further formed the certain shaped nanostructures with energy preferred directions, for example [110] of α-Fe_2O_3 [3,6]; (iii) with further increase of heating duration, the nanostructures continue to grow by surface diffusion of metal atoms along the edge of the grown structures [3]; (iv) the growth stopped when the samples were cooled down to room temperature. For Cu and Zn, the main growth mechanism could be vapor solid (VS) process. After evaporation of polystyrene and formation of metal oxide bowls, the oxide vapors with a relatively low pressure solidified on the both sides of bowls and formed the CuO and ZnO nanowires [2,6].

4. Conclusions

A simple and efficient method for fabrication of metal oxide hierarchical structures on desired 1D, 2D and 3D patterns has been developed. This method successfully combines the unique advantages of two simple techniques: template assisted self-assembly technique by which polystyrene micro/nanospheres can be readily patterned and positioned on a large scale and hot-plate technique by which metal oxide nanostructures can be easily formed. Novelly, this method offers a feasibility to evaporate the polystyrene, oxidize the metal particles, grow nanostructures attachment, and results in hierarchical structures by one-step heating process in air. By controlling the heating temperature, it is believed that this method can be successfully employed to fabricate patterned pure metals or metal oxides micro/nanobowls without nanostructure attachments. Thus, this simple and efficient method may open an alternative approach for the synthesis of nanostructures on the desired patterns of microbowls, a unique building block for future nanoscience and nanotechnology.

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