

Unconventional Lithography for Hierarchical Micro-/Nanostructure Arrays with Well-Aligned 1D Crystalline Nanostructures: Design and Creation Based on the Colloidal Monolayer

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ABSTRACT We have developed a strategy for designing and fabricating hierarchical micro-/nanostructured arrays based on the combination of a colloidal monolayer substrate and the pulsed laser deposition (PLD) process. In this approach, microstructures are provided by the colloidal monolayer and can be tuned by changing colloidal monolayer periodicities, while crystalline nanostructures are supplied by PLD and can be controlled by PLD experiment parameters (e.g., ambient gas pressure). In comparison with the traditional lithography techniques, the proposed method has the obvious advantage of low cost. More importantly, the complicated hierarchical micro-/nanostructure arrays obtained by the present strategy cannot easily be designed and synthesized by traditional lithography techniques. This fact suggests that the proposed method can be a quite powerful alternative to fabricate complicated hierarchical arrays by complementing the weakness of traditional lithographic routes. In addition to these, the strategy also features uniform surface morphology, room-temperature reaction, and pure sample surfaces that are highly valuable to build a new generation of microdevices or nanodevices in nanophotonics, energy storage, etc. on the basis of these special hierarchical micro-/nanostructured arrays.

KEYWORDS: hierarchical • micro-/nanostructure arrays • aligned • one-dimensional nanostructures • room temperature

1. INTRODUCTION

Hierarchical micro-/nanostructures have recently attracted much attention due to their unique properties and applications in optoelectronic devices, microfluidic devices, biomedical science, field emission, and self-cleaning surfaces (1). Generally, such interesting structures could be synthesized by replication induced by chemical vapor deposition (CVD) (2), template techniques (3), or solvent thermal synthesis (4). However, most of these methods are based on reactions in liquid medium or physical or chemical deposition at high temperature. In the reactions in liquid, surfactants, reductants, or other additives are required for the synthesis of hierarchical micro-/nanostructures, resulting in the presence of impurities in the final products. Chemical or physical deposition (e.g., CVD) requires a high-temperature environment, leading to high costs. The alignment of hierarchical micro-/nanostructures into regular arrays would be helpful in devising new micro/

nano devices based on these ordered arrays. The traditional methods for periodic arrays focus mainly on the lithographic technique (5), which most laboratories cannot afford. Therefore, unconventional lithography to fabricate the micro- or nanopatterns has attracted interest recently and the development of a new technique to fabricate hierarchical micro-/nanostructured arrays to overcome the above disadvantages is crucial (6).

Recently, monolayer colloid crystals have attracted considerable interest, owing to their many applications in optical gratings, optical filters, and antireflective surface coatings. Until now, large-area monolayer colloid crystals have been fabricated by controlling the operating parameters; the monolayer colloidal crystal with an area of several square centimeters can easily be synthesized by self-assembly (7–10), for instance, a continuous convective assembling technique (7), a spin coating method (8), or self-assembly at the liquid–gas interface (9). A monolayer colloid crystal is naturally composed of microspheres with a hexagonal close-packed arrangement on the substrates using the latex microsphere aqueous suspension by careful control of the operation parameters (11). Thus, it can supply periodic arrays with microstructures if one designs and constructs hierarchical micro-/nanostructured arrays using them. In our previous work, we demonstrated that TiO₂ could form the

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amorphous nanostructured arrays on the substrate and grew a micro-/nanostructured array based on the colloidal monolayer (12). Our recent research found that crystalline 1D nanostructures (nanorod or nanobelt) of some metal oxides (e.g., CuO, Fe₂O₃, and ZnO) can easily be fabricated on the flat substrates by pulsed laser deposition (PLD) at room temperature (without heating substrates) using corresponding materials as targets (Figure S1, Supporting Information). The nanostructures of the obtained materials are highly pure without surfactants or additives. These 1D nanostructured rods or belts are well aligned on flat substrates, and their length may be tuned by controlling the deposition time. Most importantly, these 1D crystalline nanostructures tend to grow along the normal direction of substrates (13).

Therefore, we propose that if we use the colloidal monolayer of microsphere as a substrate to supply the microstructures and fabricate the 1D nanostructures on it by PLD, we may easily find an efficient method to fabricate highly pure, large-sized hierarchical micro-/nanostructured arrays. Fortunately, our experimental result successfully proves our hypothesis. More importantly, the complicated hierarchical micro-/nanostructure arrays cannot easily be designed and synthesized by traditional lithography techniques. This indicates that the presented route can be a quite powerful alternative to fabricate the complicated hierarchical arrays by complementing the weakness of traditional lithographic routes. In addition to these, the strategy also features uniform surface morphology, room temperature reaction, and pure sample surfaces that are highly valuable to build a new generation of microdevices or nanodevices in nanophotonics, energy storage, etc. on the basis of these special hierarchical micro-/nanostructured arrays.

2. RESULTS AND DISCUSSION

Figure 1 presents the field emission scanning electron microscope (FE-SEM) images of the ordered structured array obtained by PLD on the colloidal monolayer with a polystyrene (PS) sphere size of 350 nm using CuO as a target in oxygen at 6.7 Pa. The sample presents a hexagonal close packed array observed from the top, and each arrayed unit in micrometer size appears to be composed of many particles with trigonal pyramidal shapes (Figure 1a) (14). The section image indicates that each unit consists of a PS sphere at the bottom and deposited materials on the PS sphere top (Figure 1b). Additionally, deposited materials do not exhibit round shapes but radially aligned nanorods having tips with trigonal pyramidal shapes on the PS sphere. The X-ray photoelectron spectroscopy (XPS) survey spectrum indicates that the deposited materials are composed of Cu and O, like the composition of the CuO target (Figure 2a). The Cu2p core level peaks reveal the presence of CuO (Figure 2b). These results indicate that a hierarchical CuO micro-/nanostructured array was successfully fabricated, further proving the feasibility of the proposed strategy. In the corresponding XRD spectrum, and all the observed diffraction peaks can be assigned to CuO, indicating that the deposited materials are crystalline CuO (Figure 3). Additionally, in comparison with the standard data for bulk CuO (JCPDS 801268), the

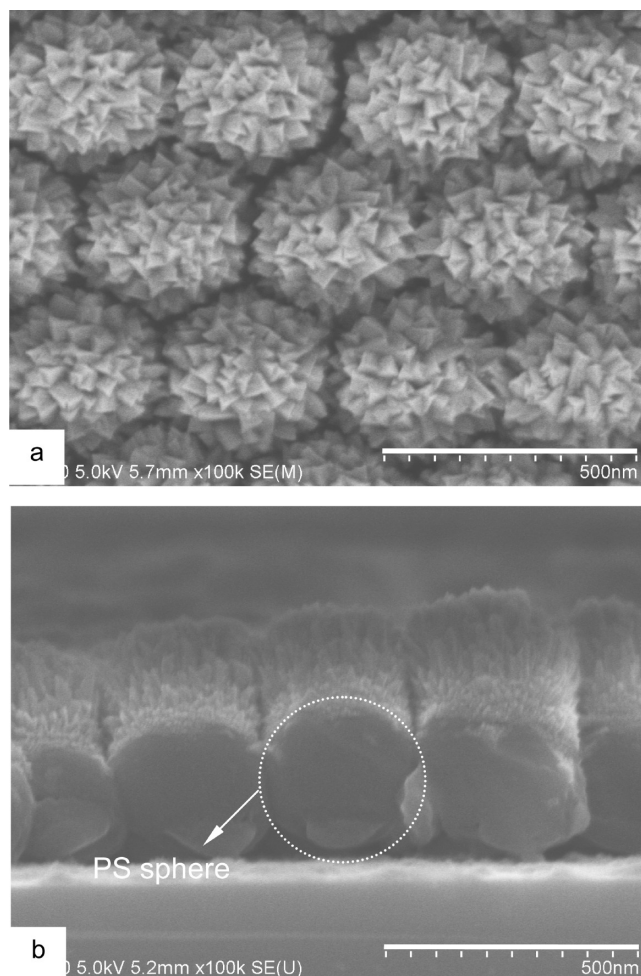


FIGURE 1. FE-SEM images of a periodic structured array obtained by combining the PS colloidal monolayer and PLD process using CuO as a target (PS sphere size 350 nm, deposition time 2 h, ambient oxygen pressure during deposition 6.7 Pa): (a) top-view image; (b) section view. Scale bars in parts a and b indicate 500 nm.

relative intensity of the (002) peak is much higher in the XRD spectrum, suggesting that the CuO nanostructures are well aligned and have preferential orientation along the *c* axis, which is attributed to a template-induced fabrication process. A similar orientation has been also observed by a lithography-induced growth process (15).

The corresponding TEM results are presented in Figure 4. A top-view observation of the periodic structured arrays indicates that each unit consists of radially aligned nanorods emanating from the center (Figure 4a). The image of some separated units in the array agrees well with the SEM sectional image of the sample, and the whole unit has aligned nanorod structures that grow almost vertically on the PS sphere surface (Figure 4b). The aligned nanorods on the PS sphere surface indicate that the unit in the array has a hierarchical micro-/nanostructure (i.e., the nanostructures are supplied by aligned nanorods and the microstructures are provided by microsized PS spheres). The selected area electron diffraction (SAED) pattern demonstrates that the nanorods deposited on PS spheres by PLD are polycrystalline CuO (inset in Figure 4b).

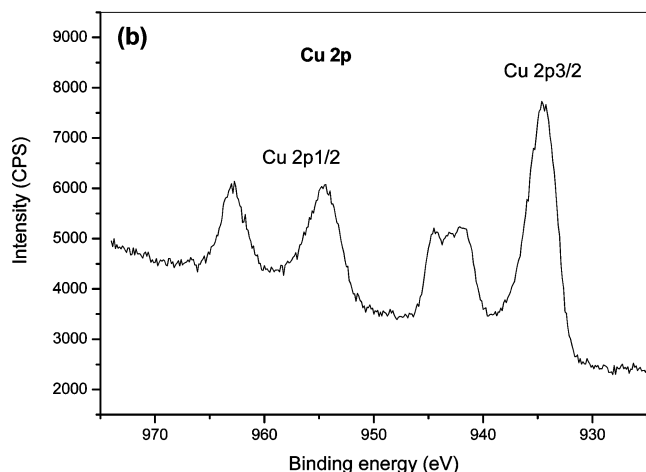
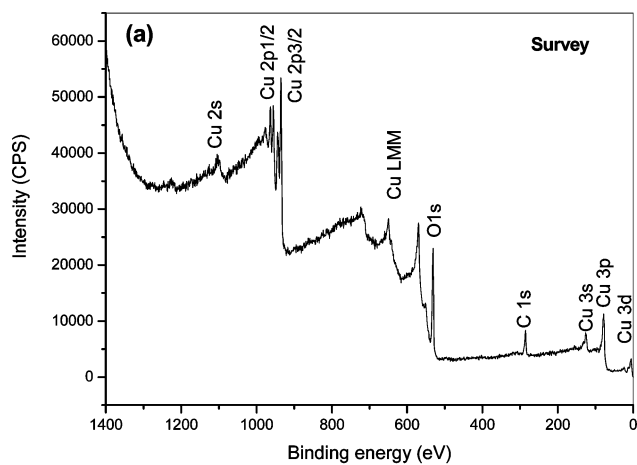


FIGURE 2. XPS spectra of the sample obtained by PLD using a CuO target: (a) survey spectrum; (b) Cu 2p core level spectrum.

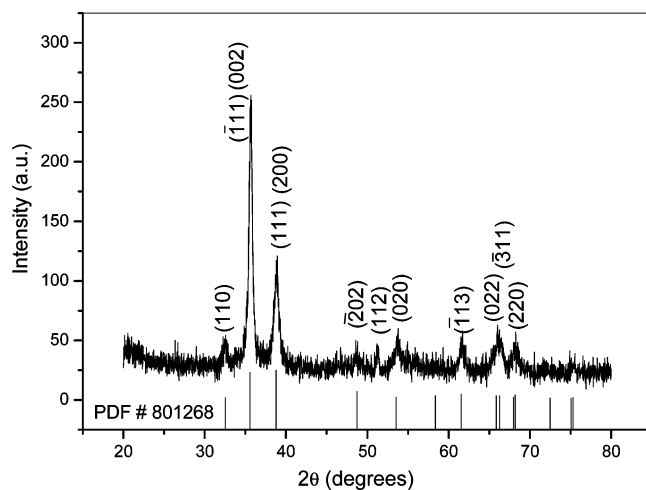


FIGURE 3. Corresponding XRD pattern of a prepared sample.

In the proposed strategy, the microstructures in hierarchical micro-/nanostructured arrays can be tuned by changing the periodicities of the monolayer colloidal crystals. For instance, just by changing the PS sphere size for monolayer colloidal crystal from 350 to 750 nm without any other alteration of the fabrication process, we obtained a similar hierarchical micro-/nanostructured

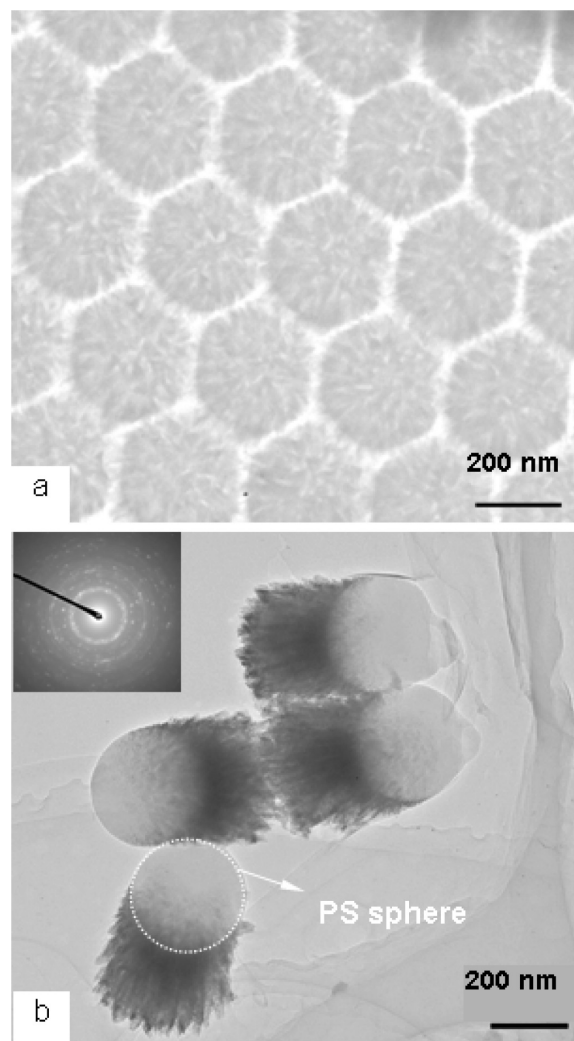


FIGURE 4. TEM images of a prepared sample: (a) periodic array observed from the top; (b) several separated units from the periodic array and the corresponding selected area electron diffraction (SAED) pattern.

array with the same nanostructures but different microstructures (Figure S2, Supporting Information).

In addition, nanostructures can be controlled by varying ambient gas pressures during the PLD process. Figure 5 presents the FE-SEM and TEM images of samples obtained by deposition in higher ambient gas pressures during the PLD process using the monolayer colloidal crystals as substrates. When oxygen pressure increased from 6.7 to 26.7 Pa, the morphology did not appreciably change and exhibited similar hierarchical structures (Figure 5a). However, when the oxygen pressure increased to 53.3 Pa, the morphology changed and was completely different from those at lower pressures. The tips of nanorod structures on the PS sphere formed imperfect trigonal pyramid shapes, and the tips became much smaller (Figure 5b). From the corresponding TEM image and SAED pattern (Figure 5c), we know that the crystallization of deposited aligned nanorods on the PS sphere becomes worse than that obtained at lower oxygen pressure, although hierarchical micro-/nanostructures were still observed at such high oxygen pressure. When the ambient gas pressure increased to as high as 79.8 Pa,

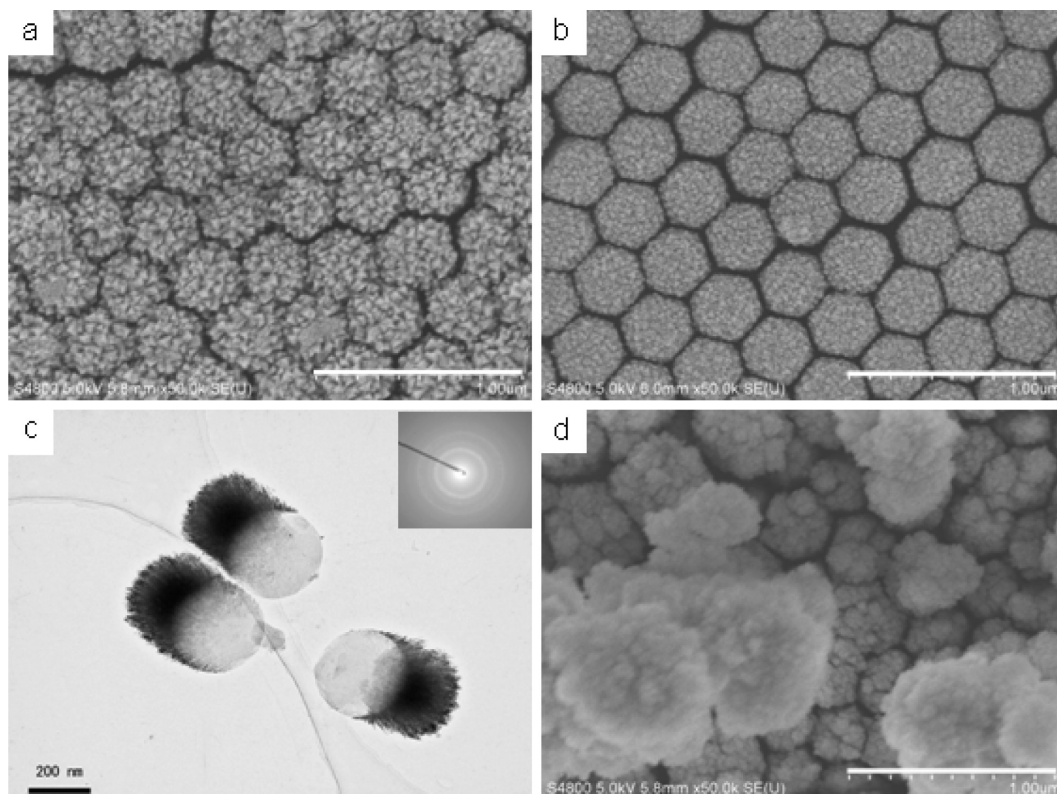


FIGURE 5. Images obtained by increasing the ambient oxygen pressures: (a, b, d) FE-SEM images of the samples obtained under ambient oxygen pressure of 26.7, 53.3, and 79.8 Pa, respectively; (c) TEM image of the sample obtained at 53.3 Pa and the corresponding SAED pattern of several units. Scale bars in (a), (b), and (d) indicate 1 μm .

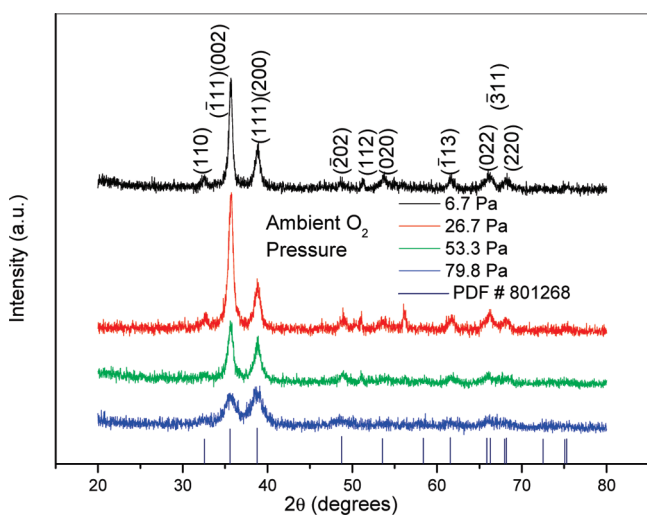


FIGURE 6. XRD patterns of the samples obtained under different oxygen pressures.

no similar hierarchical micro-/nanostructured array was obtained, and many aggregates of small particles were produced on the colloidal monolayer (Figure 5d). The XRD patterns of the samples obtained under different oxygen pressures are presented in Figure 6. Strong preferential orientation growth along (002) was observed when the pressure increased to 26.7 Pa. Further increase of oxygen pressure resulted in weakening of this preferential orientation as well as broadening of X-ray diffraction peaks. This result indicates that deposited materials gradually changed to small nanoparticles from aligned nanorod arrays and the

particles became much smaller with an increase of oxygen pressure during deposition, in accordance with FE-SEM results. When the oxygen pressure was increased to 79.8 Pa, the deposited material was completely composed of small nanoparticles or the aggregates of small particles, and no preferential orientation growth was found.

A CuO hierarchical micro-/nanostructured array is formed as follows. Once the ions (Cu^{2+} , O^{2-} , and so on) or atoms from the plasma created by laser beam irradiation by ambient gas reach the substrate, they will condense and nucleate on it at room temperature. The CuO nanorods then grow on the nucleation along with the preferable crystallized facet of high interface energy with further deposition. In this case, the nanorods tend to grow along the normal direction of the substrate (Figure S1a, Supporting Information). When the substrate is changed from a flat silicon wafer to a colloidal monolayer, the nanorods grow along the normal direction of the PS microsphere surface, further leading to the well-aligned nanostructure of the CuO nanorod with a radially aligned shape on the PS sphere. When the oxygen pressure increases to a high value, the plume is compressed further into a smaller space, and the possibility of collision among ions or atoms is greatly enhanced, further resulting in a kinetic energy decrease of ions or atoms, which leads to less crystallization and smaller nanoparticle formation (16).

In addition to CuO, similar hierarchical micro-/nanostructured arrays of Fe_2O_3 and ZnO can be fabricated by the proposed strategy. The deposited Fe_2O_3 and ZnO also exhibited

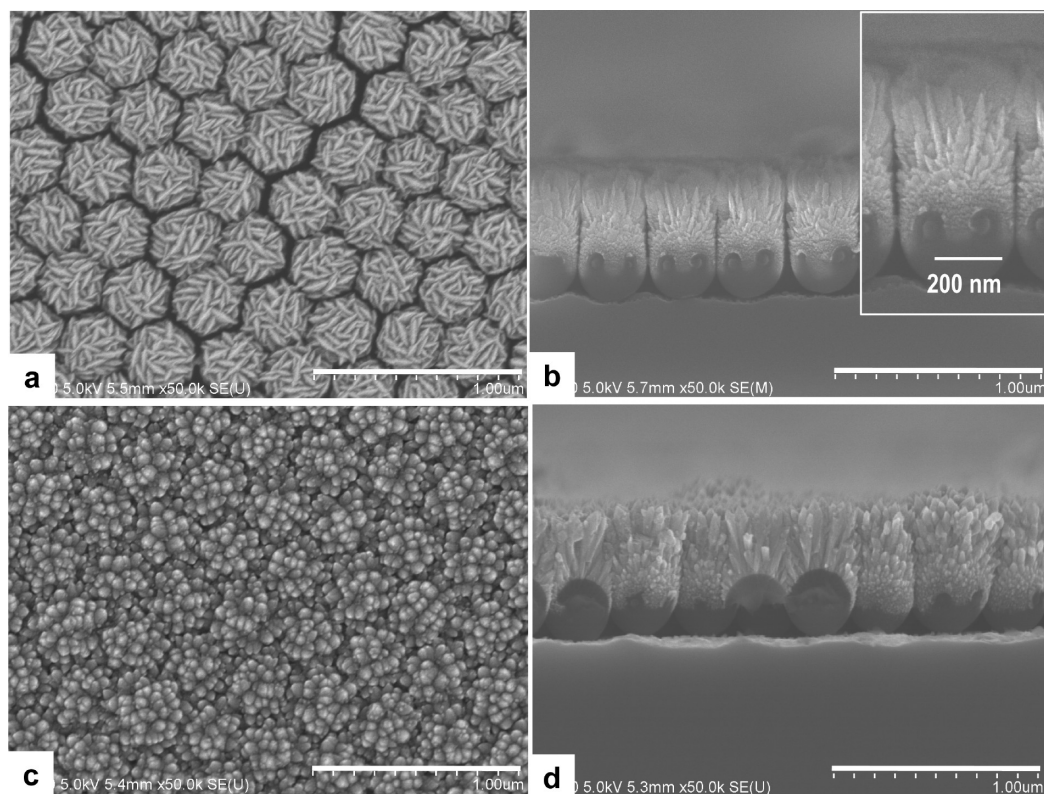


FIGURE 7. FE-SEM images of hierarchical micro-/nanostructured arrays of Fe_2O_3 and ZnO produced by the proposed strategy: (a, b) Fe_2O_3 ; (c, d) ZnO. Parts a and c give top views, and parts b and d give side views. The inset in (b) is the magnified image of a single Fe_2O_3 hierarchical micro-/nanostructure.

polycrystalline structures. Parts a and b of Figure 7 depict Fe_2O_3 micro-/nanostructured arrays obtained by PLD on a colloidal monolayer using Fe_2O_3 as a target (oxygen pressure 6.7 Pa, deposition time 1.5 h). We observed that Fe_2O_3 nanobelts were well aligned on the PS spheres, like those of CuO. Similarly, the ZnO hierarchical structured array was synthesized at an oxygen pressure of 6.7 Pa and 40 min deposition time, using ZnO as a target (Figure 7c,d). The deposited ZnO also exhibited an aligned nanorod array on the PS sphere, but the nanorod tops were not like those of CuO. The slight differences among CuO, Fe_2O_3 , and ZnO fine nanostructures could be determined mainly by their various chemical and physical properties: for example, a crystal facet of the interface with different energies, etc.

3. CONCLUSION

In summary, a strategy for designing and fabricating hierarchical micro-/nanostructured arrays is presented on the basis of the combination of a colloidal monolayer substrate and the PLD process. Our results confirm that the proposed method is efficient and successful. In this approach, microstructures are provided by the colloidal monolayer and can be tuned by changing colloidal monolayer periodicities, while nanostructures are supplied by PLD and can be controlled by PLD experiment parameters (e.g., ambient gas pressure). In comparison with the traditional lithography techniques, the proposed method obviously has the advantage of low cost. However, more importantly, the complicated hierarchical micro-/nanostructure arrays obtained by the presented strategy cannot easily be designed and synthesized by traditional lithography

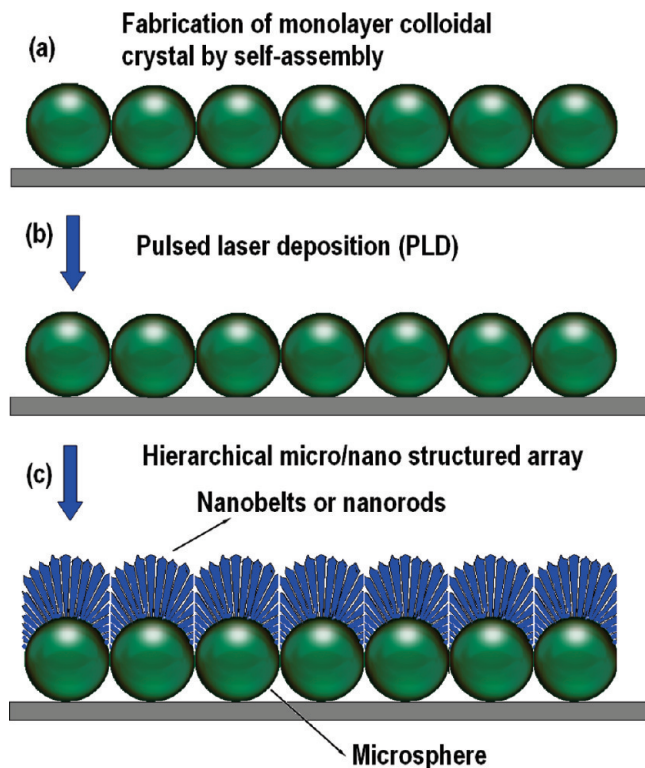
techniques. This fact suggests that the proposed method can be a quite powerful alternative to fabricate the complicated hierarchical arrays by complementing the weakness of traditional lithographic routes. Additionally, the route also features uniform surface morphology, room-temperature reaction, and pure sample surfaces that are highly valuable to build a new generation of microdevices or nanodevices in nanophotonics, energy storage, etc.

4. MATERIALS AND METHODS

Suspensions of monodispersed PS spheres (concentration, 2.5 wt %; size deviation, less than 5%) with different diameters (350 nm, 750 nm, and 1 μm) were purchased from Alfa Aesar Co. PS monolayer colloidal crystals were fabricated on the cleaned Si substrates by spin coating (17). Briefly, a droplet of a PS microsphere suspension was dropped onto a cleaned substrate fixed on a spin coater. Rotation speeds were maintained at different values for the different PS sphere suspensions (350 nm PS sphere, 1500 rpm; 750 nm PS sphere, 800 rpm; 1 μm PS sphere, 500 rpm) for 5 min, and 2 cm^2 monolayer colloidal crystals with different PS sphere sizes formed on the substrates by a self-assembling process.

The substrate with a colloidal monolayer was placed in a chamber for PLD in an off-axis configuration to the target (18). A laser beam with a wavelength of 355 nm from a Q-switched Nd:YAG laser (Continuum, Precision 8000), operated at 10 Hz with 100 mJ/pulse and a pulse width of 7 ns, was applied and focused onto a target surface within a spot 2 mm in diameter. Densely sintered pellets of Fe_2O_3 , ZnO, and CuO were used as a target for PLD. The substrate was rotated at 40 rpm and the target at 30 rpm. PLD was performed in a chamber (base pressure of 2.66×10^{-4} Pa) with different oxygen pressures. After deposition, a hierarchical micro-/nanostructured array will be obtained; the whole process is schematically illustrated in Scheme 1.

Scheme 1. Schematic Illustration of Fabrication Process for Micro-/Nanostructured Array Based on Colloidal Monolayer and PLD Process



The morphologies of the prepared samples were observed by FE-SEM (Hitachi S-4800) and TEM (JEOL JEM-2000FX). The TEM samples were prepared by removing the prepared periodic structures from the substrate by a scalpel and then transferring onto a copper grid for transmission electron microscope (TEM) observation. The crystal structure and chemical states of the samples were examined by X-ray diffraction (Ultima IV/PSK X-ray diffraction meter with Cu K α radiation with a wavelength of 0.154 056 nm) and XPS (PHI 5600ci).

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Supporting Information Available: FE-SEM images of 1D nanostructured arrays on a flat substrate prepared by PLD without using PS template and a CuO hierarchical micro-/nanostructured array produced by PLD using the colloidal monolayer with a PS sphere size of 750 nm. This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- Morariu, M.; Voicu, N.; Schäffer, E.; Lin, Z.; Russell, T. P.; Steiner, U. *Nat. Mater.* **2003**, *2*, 48.
- (a) Ye, C. H.; Zhang, L. D.; Fang, X. S.; Wang, Y. H.; Yan, P.; Zhao, J. W. *Adv. Mater.* **2004**, *16*, 1019. (b) Dorozhkin, S. V. *J. Mater. Sci.: Mater. Med.* **2007**, *18*, 363. (c) Lao, J. Y.; Wen, J. G.; Wang, D. Z.; Ren, Z. F. *Nano Lett.* **2002**, *2*, 1287. (d) Gao, P. X.; Ding, Y.; Wang, Z. L. *Nano Lett.* **2003**, *3*, 1315.
- Meng, G. W.; Jung, Y. J.; Cao, A. Y.; Vajtai, R.; Ajayan, P. M. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 7074.
- Ye, L.; Guo, W.; Yang, Y.; Du, Y.; Xie, Y. *Chem. Mater.* **2007**, *19*, 6331.
- (a) Wallraff, G. M.; Hinsberg, W. D. *Chem. Rev.* **1999**, *99*, 1801. (b) Smith, H. I.; Schattenburg, M. L. *IBM J. Res. Dev.* **1993**, *37*, 319. (c) Stroschio, J. A.; Eigler, D. M. *Science* **1991**, *254*, 1319. (d) Liu, G.-Y.; Xu, S.; Qian, Y. *Acc. Chem. Res.* **2000**, *33*, 457. (e) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661.
- (a) Cavallini, M.; Albonetti, C.; Biscarini, F. *Adv. Mater.* **2009**, *21*, 1043. (b) Cavallini, M. *J. Mater. Chem.* **2009**, *19*, 6085.
- (a) Antony, S.; Dimitrov, A. S.; Nagayama, K. *Langmuir* **1996**, *12*, 1303. (b) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132. (c) Kralchevsky, P. A.; Denkov, N. D. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 383. (d) Im, S. H.; Kim, M. H.; Park, O. O. *Chem. Mater.* **2003**, *15*, 1797. (e) Kitaev, V.; Ozin, G. A. *Adv. Mater.* **2003**, *15*, 75. (f) Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* **1992**, *8*, 3185. (g) Wang, X. D.; Summers, C. J.; Wang, Z. L. *Nano Lett.* **2004**, *4*, 423.
- (a) Ozin, G. A.; Yang, S. M. *Adv. Funct. Mater.* **2001**, *11*, 95. (b) Jiang, P.; McFarland, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 13778. (c) Wang, D.; Möhwald, H. *Adv. Mater.* **2004**, *16*, 244. (d) Sun, F. Q.; Yu, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 773. (e) Li, Y.; Cai, W. P.; Duan, G. T. *Chem. Mater.* **2008**, *20*, 615. (f) Hultheen, J. C.; Van Duyne, R. P. *J. Vac. Sci. Technol., A* **1995**, *13*, 1553. (g) Li, Y.; Huang, X. J.; Heo, S. H.; Li, C. C.; Choi, Y. K.; Cai, W. P.; Cho, S. O. *Langmuir* **2007**, *23*, 2169. (h) Li, Y.; Li, C.; Cho, S. O.; Duan, G.; Cai, W. *Langmuir* **2007**, *23*, 9802.
- (a) Rybczynski, J.; Ebels, U.; Giersig, M. *Colloids Surf., A* **2003**, *219*, 1. (b) Ctistis, G.; Patoka, P.; Wang, X.; Kempa, K.; Giersig, M. *Nano Lett.* **2007**, *7*, 2926. (c) Ctistis, G.; Papaioannou, E.; Patoka, P.; Gutek, J.; Fumagalli, P.; Giersig, M. *Nano Lett.* **2009**, *9*, 1.
- (a) Yang, S.-M.; Jang, S. G.; Choi, D.-G.; Kim, S.; Yu, H. K. *Small* **2006**, *2*, 458. (b) Yan, X.; Yao, J.; Lu, G.; Li, X.; Zhang, J.; Han, K.; Yang, B. *J. Am. Chem. Soc.* **2005**, *127*, 7688. (c) Wang, L.; Li, G.; Xia, L. H.; Wan, Y.; Li, H. L.; Zhao, X. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4725. (d) Yan, F.; Goedel, W. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2084.
- (a) Duan, G.; Cai, W.; Luo, Y.; Li, Y.; Lei, Y. *Appl. Phys. Lett.* **2006**, *89*, 181918. (b) Mihi, A.; Ocaña, M.; Mígguez, H. *Adv. Mater.* **2006**, *18*, 2244. (c) Zhang, T.; Tuo, X.; Yuan, J. *Langmuir* **2009**, *25*, 820.
- Li, Y.; Sasaki, T.; Shimizu, Y.; Koshizaki, N. *J. Am. Chem. Soc.* **2008**, *130*, 14755.
- (a) Sun, Y.; Addison, K. E.; Ashfold, M. N. R. *Nanotechnology* **2007**, *18*, 495601. (b) Solanki, R.; Huo, J.; Freeouf, J. L.; Miner, B. *Appl. Phys. Lett.* **2002**, *81*, 3864. (c) Nam, H. J.; Sasaki, T.; Koshizaki, N. *Mater. Res. Soc. Symp. Proc.* **2006**, *900E*, 009–17.1. (d) Yoon, J. W.; Sasaki, T.; Roh, C. H.; Shim, S. H.; Shim, K. B.; Koshizaki, N. *Thin Solid Films* **2005**, *471*, 273.
- Chang, Y.; Zeng, H. C. *Cryst. Growth Des.* **2004**, *4*, 397.
- (a) Cavallini, M.; Stoliar, P.; Moulin, J. F.; Surin, M.; Leclère, P.; Lazzaroni, R.; Breiby, D. W.; Andreasen, J. W.; Nielsen, M. M.; Sonar, P.; Grimsdale, A. C.; Müllen, K.; Biscarini, F. *Nano Lett.* **2005**, *5*, 2422. (b) Cavallini, M.; Bergenti, I.; Milita, S.; Ruani, G.; Salitros, I.; Qu, Z. R.; Chandrasekar, R.; Ruben, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8596. (c) Greco, P.; Cavallini, M.; Stoliar, P.; Quiroga, D.; Dutta, S.; Zacchini, S.; Lapalucci, C.; Morandi, V.; Milita, S.; Merli, P. G.; Biscarini, F. *J. Am. Chem. Soc.* **2008**, *130*, 1177.
- Nam, H. J.; Sasaki, T.; Koshizaki, N. *J. Phys. Chem. B* **2006**, *110*, 23081.
- (a) Kosiorek, A.; Kandulski, W.; Glaczynska, H.; Giersig, M. *Small* **2005**, *1*, 439. (b) Marczewski, D.; Goedel, W. A. *Nano Lett.* **2005**, *5*, 295. (c) Tessier, P. M.; Velev, O. D.; Kalambur, A. T.; Lenhoff, A. M.; Rabolt, J. F.; Kaler, E. W. *Adv. Mater.* **2001**, *13*, 396. (d) Li, Y.; Lee, E. J.; Cai, W. P.; Kim, K. Y.; Cho, S. O. *ACS Nano* **2008**, *2*, 1108. (e) Li, Y.; Cai, W.; Cao, B.; Duan, G.; Sun, F.; Li, C.; Jia, L. *Nanotechnology* **2006**, *17*, 238. (f) Li, Y.; Cai, W.; Duan, G.; Cao, B.; Sun, F.; Lu, F. *J. Colloid Interface Sci.* **2005**, *287*, 634.
- (a) Li, Y.; Sasaki, T.; Shimizu, Y.; Koshizaki, N. *Small* **2008**, *4*, 2286. (b) Li, Y.; Fang, X.; Koshizaki, N.; Sasaki, T.; Li, L.; Gao, S.; Shimizu, Y.; Bando, Y.; Golberg, D. *Adv. Funct. Mater.* **2009**, *19*, 2467.

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