

Silver Hierarchical Bowl-Like Array: Synthesis, Superhydrophobicity, and Optical Properties

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We present a facile synthetic route to a silver bowl-like array film with hierarchical structures on glass substrate using the colloidal monolayer as a template. In these special hierarchical structures, microstructures were provided by a colloidal template of polystyrene latex spheres and nanostructures resulting from the thermal decomposition of silver acetate. These structures were chemically modified with 1-hexadecanethiol, and a corresponding self-assembled monolayer (SAM) was formed on their surfaces. Due to the lotus leaf-like morphology with hierarchical micro/nanostructures, the film displayed an extraordinary superhydrophobicity after chemical modification. Water contact angle and sliding angle were 169° and 3° (the weight of water droplets: 3 mg), respectively. Additionally, its optical property has also been investigated. This structure could be used in microfluidic devices, optical devices, and biological science.

Introduction

Hierarchical micro/nanostructures have attracted much attention owing to their unique properties and applications in optoelectronic devices, microfluidic devices, biomedical science, field emission, etc.^{1–3} Generally, hierarchical structures could be synthesized by the replication induced by an electric field,^{1a} chemical vapor deposition,^{1b–e} template technique,² electron irradiation,³ etc.

Recently, the superhydrophobicity with self-cleaning also has received much interests because of their applications in preventing the adhesion of water and snow to windows or antennas as well as for self-cleaning utensils, antioxidation coating, and microfluidic devices.⁴ As we know, superhydrophobicity belongs to wettability phenomena that are governed by the chemical composition and geometrical microstructures of surfaces. Biomimetic research has recently revealed the self-cleaning effect of a lotus leaf (lotus effect) that removes contamination and dirt on their surfaces due to strong superhydrophobicity with a water contact angle (CA) larger than 150° and a sliding angle (SA) less than 10° on their leaf surface.⁴ The unique functionalities (lotus effect) of the natural organism were attributed to the combination

of special hierarchical micro/nano surface structures and low surface-free energy materials covering the surfaces.⁴ Inspired by this, various techniques to synthesize superhydrophobic surfaces have been developed, including a rough polymer surface by argon plasma etching,⁵ a hierarchical micro/nano film by the wet chemical method,⁶ an aligned carbon nanotube (CNT) film or ZnO film by chemical vapor deposition,⁷ a binary structure by colloidal assembly,⁸ a transparent boehmite/silica film by sublimation,⁹ superhydrophobic rough surfaces by electrochemical methods,¹⁰ polymer patterns by the polymerization on the etched silicon substrate,¹¹ stable bionic superhydrophobic surfaces by solution-immersion process,¹² and porous films by electron-irradiation or template techniques.¹³

A colloidal monolayer, as a very useful template or mask, has proved to be a successful and promising technique to fabricate periodical arrays including periodic nanoparticle arrays, pore arrays, nanoring arrays, nanopillar arrays, etc.¹⁴

Here, we present a facile route to fabricate a silver hierarchical bowl-like ordered array film on glass substrate based on the

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colloidal monolayer. In this method, using the polystyrene (PS) colloidal monolayer as a template and silver acetate solution as the precursor, the hierarchical silver bowl-like array was fabricated by solution-dipping method and subsequent heating decomposition. The morphology of the as-prepared film bears much resemblance to lotus leaves that consists of hierarchical micro/nanostructured roughness.⁴ As a result, the synthesized surface shows strong superhydrophobicity and a self-cleaning effect after surface modification with thiol. The as-prepared hierarchical structures could be used in microfluidic devices, optical devices, and biosensors of organic molecule detection.

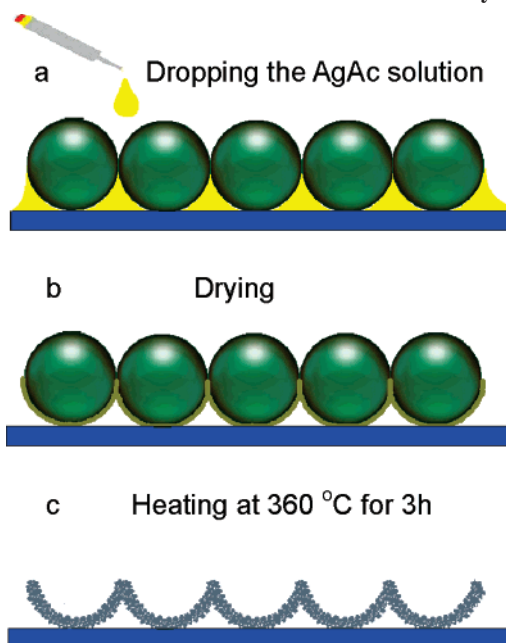
Experimental Section

Material Preparation. Ordinary glass substrates with sizes of 25 mm × 25 mm × 1.2 mm were obtained from the Shanghai Xinhua Glass Factory. Commercialized powders of monodispersed polystyrene (PS) spheres with particle sizes of 5.0 μm in diameter were purchased from Soken Co. (Chemisnow SX-130H). They were well-dispersed in deionized water and prepared as a suspension with concentration of 2.5 wt % before fabricating colloidal monolayers. The chemical-grade silver (I) acetate (Kojima Chemicals Co. Ltd) and 1-hexadecanethiol (CH₃(CH₂)₁₅SH, Alfa Aesar Co.) were used without further purification. The 0.5 M silver acetate (AgAc) aqueous solution was prepared from silver acetate powders dissolved in distilled water. Several small droplets (less than 0.5 mL) of nitric acid were added into them to facilitate solubilization. Glass substrates were ultrasonically cleaned in acetone and then in ethanol for 1 h.

Synthesis of a Hierarchical Silver Bowl-Like Array Film. The PS colloidal monolayer were first prepared on cleaned substrates by spin coating.¹⁵ Briefly, a droplet of 20 μL of PS sphere suspension was added onto a cleaned substrate fixed on the spin coater, the rotating speed was kept at 100 round/min for 5 min, and a colloidal monolayer with area of about 2 cm² was formed on the substrate by the self-assembling process. Subsequently, 10 μL of AgAc solution with concentration of 0.5 M was dripped onto the colloidal monolayer with a quantitative pipet. The solution quickly infiltrated into spaces between the substrate and the colloidal monolayer. A thin AgAc coating on under half part of the PS colloidal monolayer was formed after drying at room temperature. Finally, the sample was heated for 3 h at 360 °C in an oven. The temperature was increased by 1 °C/min in order to obtain a homogeneous sintering and nitrogen was used in the process of temperature decreasing. The silver hierarchical bowl-like ordered array film was thus synthesized. The fabrication process is illustrated in Scheme 1.

Preparation of Silver Films with Different Morphologies. Other silver films with different morphologies including a flat film, a nanoparticle film, and pore array film with smooth inner walls were synthesized in order to systematically investigate the wettability of the hierarchical bowl-like array. A flat silver film was prepared by thermal evaporation deposition under a base pressure of 10⁻⁶ Pa and at a deposition rate of 0.2 nm/min. The thickness of deposited film was monitored by a quartz crystal microbalance. A silver nanoparticle film was prepared by thermal decomposition of the AgAc coating on the glass substrate at 360 °C for 3 h. A silver pore array film was synthesized on the ITO glass by the electrodeposition method using the colloidal monolayer with PS sphere size of 5 μm as the template. In the electrodeposition process, a mixed solution of AgNO₃ (45 g/L), (NH₄)₂S₂O₃ (250 g/L), NH₄Ac (20 g/L), and Na₂SO₃ (80 g/L)

Scheme 1. Schematic Illustration of Fabrication Process of the Hierarchical Silver Bowl-Like Ordered Array Film



was used as the electrolyte and the pH was kept to 5.0. PS colloidal monolayer was heated at 120 °C for 30 min in order to tightly adhere to the conduct substrate. The deposition voltage was controlled to 1.5 V, and the deposition time was 30 min. After electrodeposition, the PS colloidal monolayer was removed by ultrasonically washing in CH₂Cl₂ solution, and silver pore arrays film was finally prepared.

Chemical Modification. Before chemical modification, silver films with different morphologies were ultrasonically cleaned in both acetone and ethanol for 30 min, respectively. An ethanol solution of 2 mM 1-hexadecanethiol was prepared, and it was bubbled under argon in order to eliminate all traces of oxygen in the solution. Then, the samples were soaped 1 h in the solution. After modification, they were copiously rinsed with ethanol and finally dried at room temperature.

Characterization. The morphologies of the samples were characterized with a field emission scanning electron microscope (FEI XL30 FEG). The X-ray diffraction (XRD) measurement was performed to identify the crystal structure of the as-prepared sample on a Rigaku D/MAX-RC XRD machine using Cu Kα radiation. The X-ray photoelectron spectra (XPS) were characterized by an Escalabmk2 spectrophotometer at a take off angle of 35° relative to the surface normal for the different silver surfaces. Static water CAs were measured on a home-built contact angle meter at room temperature. The weight of individual water droplets used for the static CA measurements was 3 mg. CA values were obtained by averaging five measurement results on different areas of the sample surface. The measurement of sliding angle (SA) is as follows: a droplet of 3 mg of water was added on the sample surface, and it began to slide down when the sample was tilted. The angle that the sample tilted was the SA. The optical absorption of hierarchical structures was measured on a Cary-5E UV-Vis-NIR spectrophotometer at room temperature.

Results and Discussion

Hierarchical Silver Bowl-Like Array Film. Figure 1 displays the field-emission scanning electron microscope (FESEM) images of the as-prepared sample by using a colloidal monolayer as the template and silver acetate as the precursor after heating at 360 °C for 3 h. The synthetic film has the periodicity of 5 μm, and the ordered array exhibits a hexagonal arrangement, which corresponds well to the colloidal monolayer. Interestingly, each unit takes on a bowl-like structure (Figure 1a,b) in the array, and

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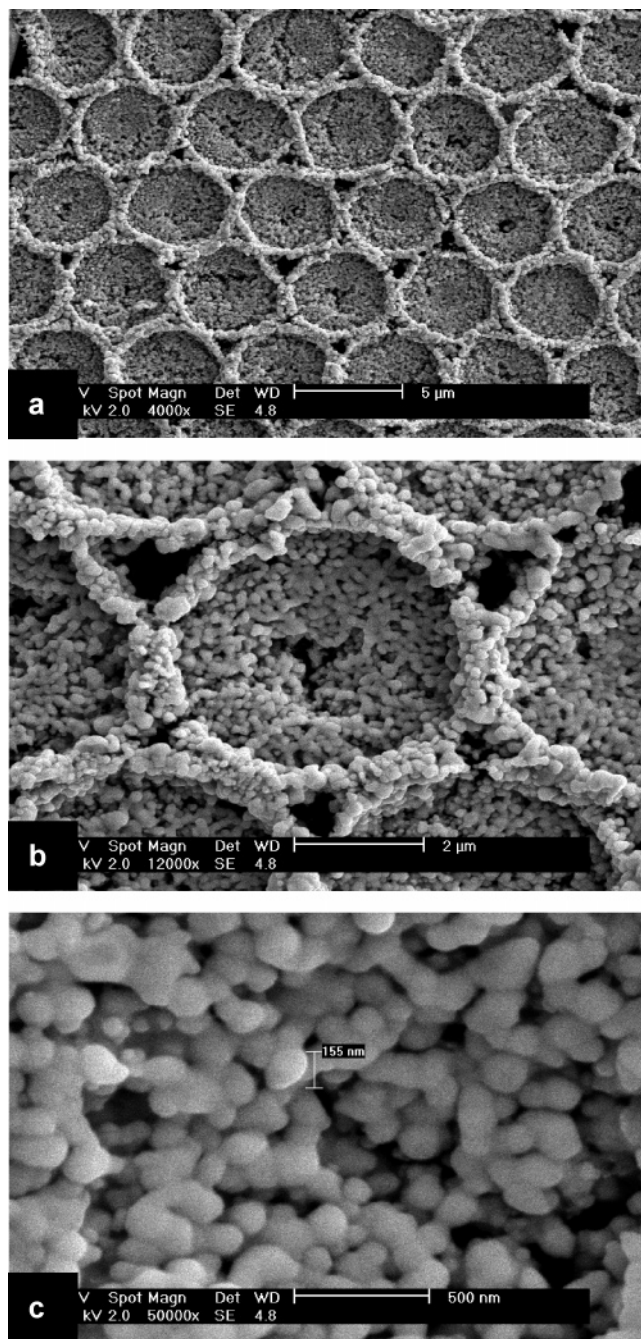


Figure 1. FE-SEM images with different magnifications of hierarchical bowl-like array film. (a) A typical FE-SEM image of hierarchical bowl-like array film obtained using the PS colloidal monolayer with sphere size of the $5\ \mu\text{m}$. (b) An image of a feature bowl-like unit. (c) An image of bowl bottom with larger magnification.

the whole bowl-like array has rough inner walls composed of nanoparticles with average size of ca. 135 nm, as shown in Figure 1c and Figure S1 (in the Supporting Information). The X-ray diffraction pattern indicated that these nanoparticles were silver crystals, as shown in Figure 2, which resulted from thermal decomposition of AgAc.¹⁶ Moreover, the X-ray photoelectron spectra (XPS) were further applied to verify for the surface composition, as displayed in Figure 3. The XPS survey spectrum indicated that, besides silver, the oxygen and carbon were also detected (Figure 3a). Usually, Ag $3d_{5/2}$ in level for metallic Ag

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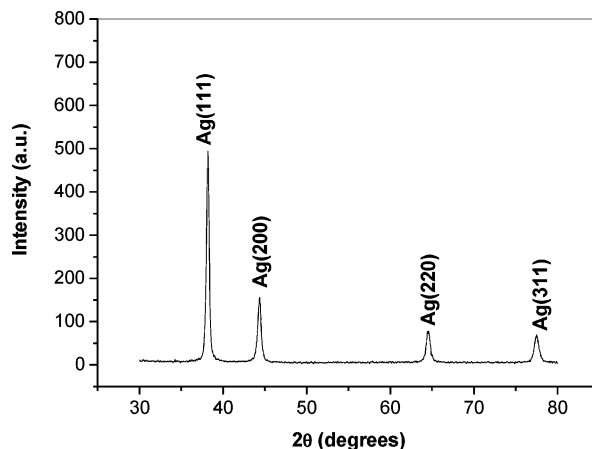


Figure 2. XRD spectrum of the hierarchical bowl-like structures synthesized after heated at $360\ \text{°C}$ for 3 h using AgAc as precursor and the colloidal monolayer as a template.

and AgO locates at 368.2 and 368.0 eV, respectively, so it is difficult to differentiate between the two species according to the silver line of XPS. However, the O 1s core level in AgO occurs at 530.2 eV, which could evidently distinguish from the O 1s position in oxidized carbon (532.0–533.5 eV).¹⁷ The O 1s level in our results (Figure 3b) shows that the peak arose at 532.7 eV, which reflects the presence of the hydrocarbon contaminants or carbon oxidized species on the sample surface. The C 1s level (Figure 3c) indicates that a complex composition of carbons comes from alkyl-type carbons (285.0 eV), C–OH and C–O–C groups (286.4 eV), carbonyl functions or C=O (287.9 eV), and oxidized carbons (289.1 eV).¹⁸ Above analyses indicated that no silver oxide was produced on the sample surface.

From Figure 1c, one can clearly see that most silver nanoparticles are welded with neighbors because of the surface melt during the heating process. The heating process leads to the formation of highly durable micro/nanostructured arrays: these structures were not destroyed and the whole hierarchical arrays were not detached from a substrate even when the substrate was ultrasonically washed in water for 30 min.

The formation of silver nanoparticles is closely related to the heating temperature. For the AgAc, an organic salt, it can be decomposed into silver at a low temperature of $360\ \text{°C}$.¹⁶ In this decomposition process, silver nucleation is formed, and subsequently silver particles grow up. If the temperature increases much, the as-produced silver nanoparticles will be melted again and larger particles or films will incline to be generated. In our experiments, if the heating temperature is higher than $400\ \text{°C}$, the silver hierarchical bowl-like array will not be prepared as a result of the particle melt. For instance, a silver microplate array and a silver microparticle array were obtained at higher temperatures of 450 and $500\ \text{°C}$, respectively, for 3 h, as shown in Figure S2a,b (in the Supporting Information). These results suggest that a suitable temperature is very important for the formation of the silver nanoparticle. Additionally, if the temperature is lowered (to say, $260\ \text{°C}$ for 3 h), although the silver nanoparticles are formed, the hierarchical bowl-like structures cannot be obtained because of incomplete decomposition of PS spheres, as displayed in Figure S3 (in the Supporting Information).

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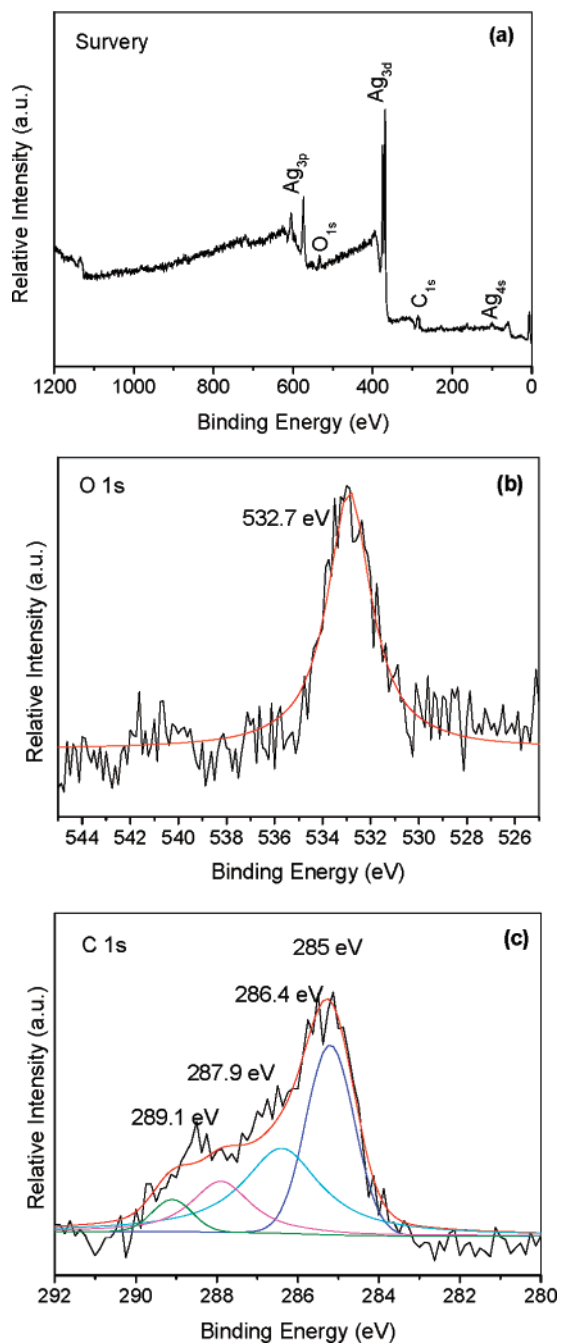


Figure 3. XPS spectra of the hierarchical structures. (a) XPS survey spectrum. Panels b and c are O 1s and C 1s core level, respectively.

In our method, heating at 360 °C for 3 h has two roles: one is to make the AgAc decompose into silver nanoparticles and the other is to remove the PS colloidal monolayer template by burning it out at this temperature.

Our results indicated the synthesized ordered array was hierarchical micro/nano structure, microstructure was supported by ordered bowl-like array caused by colloidal monolayer template, and nanostructure was resulted from the decomposition of silver acetate.

Wettability. The wettability of the as-prepared sample was evaluated by the water CA measurement. Before chemical modification with thiol, when the water droplet was added on the hierarchical micro/nanostructured array, it spread out rapidly and the surface exhibited the hydrophilicity with water CA of $23 \pm 0.4^\circ$. However, after modification, the shape of water droplet was nearly close to spherical and the sample took on the

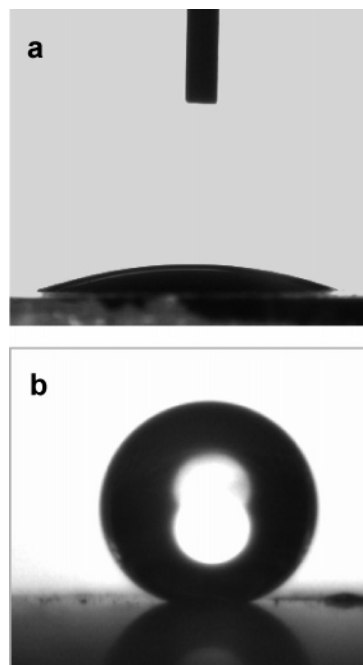


Figure 4. Water droplet shapes of hierarchical bowl-like structured film: (a) before chemical modification with thiol, CA: 23° , (b) after modification, CA: 169° .

superhydrophobicity with water CA of $169 \pm 0.5^\circ$, as shown in Figure 4; moreover, the sliding angle was as small as 3° , which was a typical self-cleaning effect.¹⁹

After modification, the C 1s level increased greatly compared with that before modification, as shown in Figure 5a. The enlarged portion of the C 1s level (Figure 5b) displayed that two components exist for the sample, a main peak at 285.0 eV is attributed to alkyl moieties of carbon species (1-hexadecanethiol and possibly residual contaminants) and a small one at 286.3 eV is ascribed to oxidized carbon contaminants. The S 2p level displays a doublet structure, as shown in Figure 5c; the S 2p_{3/2} component in S 2p level at 161.9 eV demonstrates that the formation of thiolate bonds with silver is produced. Additionally, the S 2p_{3/2} component with weak intensity at 163.0 eV is associated with a small amount of free thiols, which always caused by modification in ethanol, as reported by Mekhalif's group.¹⁸ XPS spectra indicated that the self-assembled monolayer with a good quality was formed on the silver hierarchical structure.

In order to investigate the origin of the superhydrophobic property of the synthesized structures, we fabricated a relative flat silver film (Figure 6a), a silver nanoparticle film (Figure 6b), and a pore array film with smooth inner walls²⁰ (Figure 6c) and then systematically investigated the CAs of the films before and after the modification of surfaces with thiol (Figure 6). The results are shown in Table 1 (the standard errors of the water CAs were less than 1°). XPS spectra indicates that self-assembled monolayers of thiol have been formed on different silver films after surface modification, as demonstrated in Figure S4 in the Supporting Information. The water CA of the flat silver film was 69° , and the film was transformed into a hydrophobic film with a water CA of 108° after the surface modification (Figure. 6a). For the silver nanoparticle film, the water CA was 35° and 134° before and after modification, respectively. The above experimental data indicate that the silver flat film and nanoparticle film

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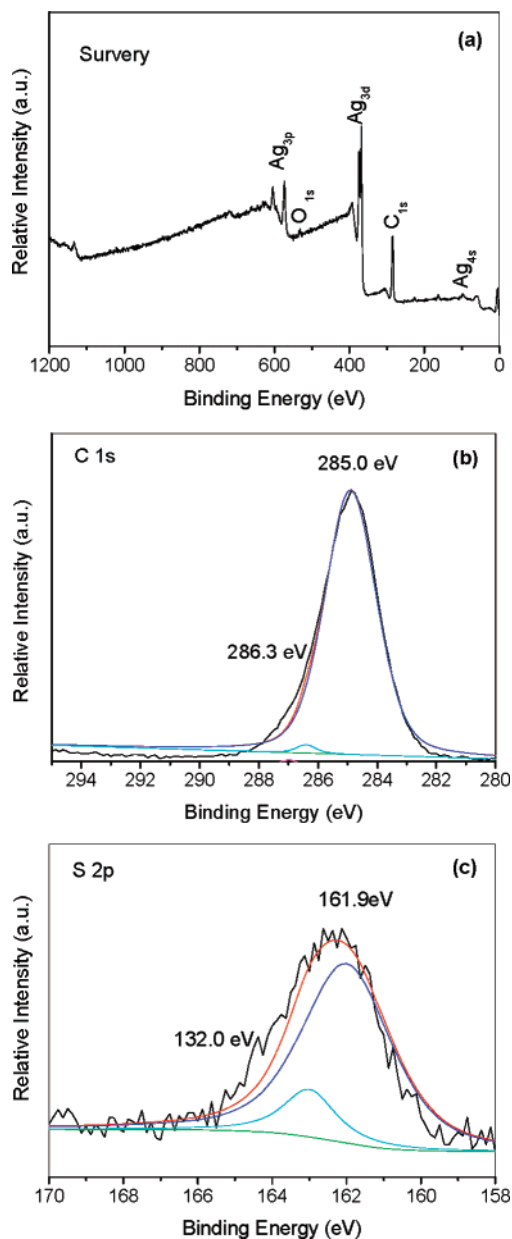


Figure 5. XPS spectra of the hierarchical structures after chemical modification with 1-hexadecanethiol. (a) XPS survey spectrum. Panels b and c are C 1s and S 2p core level, respectively.

cannot induce superhydrophobicity. The silver pore array film had a water CA of 33° , which was lower than the flat silver film. The CA of the film was enhanced to 151° after the surface modification (Figure 6b). Although the silver pore array film exhibited the superhydrophobicity after surface modification, it was far away from the requirement of the self-cleaning effect. In addition, the water droplet of 3 mg cannot roll off on its surface when the film was tilted to any angle, even upside down, which is mainly due to the stable, continuous three phase contact line (air–liquid–solid) formed on such a netlike pore array structure when the water drop is added on the surface.¹³ Therefore, our results demonstrated that the self-cleaning effect of the as prepared ordered bowl-like array film resulted from the special combination of micro and nano structures of hierarchical array, like lotus leaves.

As the lotus effect revealed, the wettability is generally related to the surface roughness of a certain material. Two well-established models are generally used for describing the wettability of a rough surface. When a water droplet can dip into

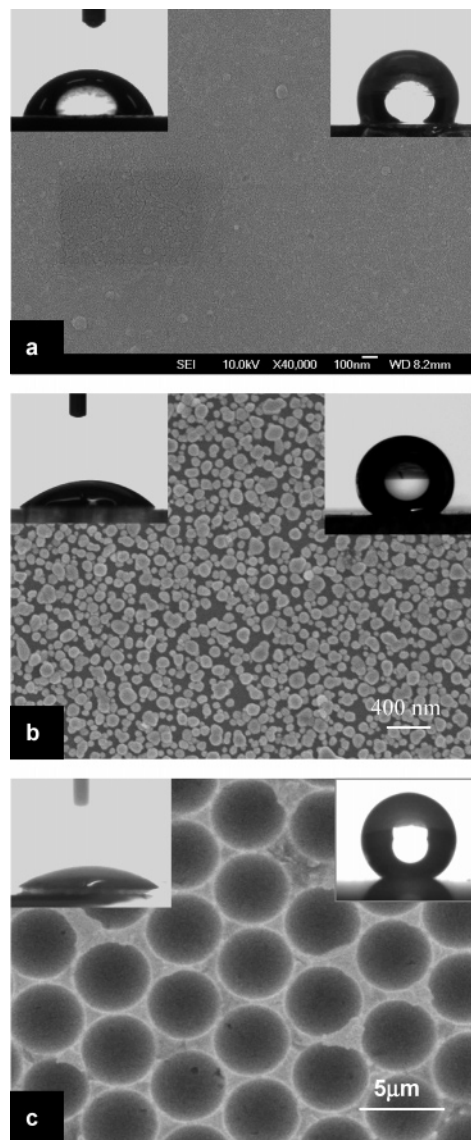


Figure 6. (a) A relative flat silver film on the glass substrate obtained by the thermal evaporation deposition. (b) A silver particle film on the glass substrate synthesized by the decomposition of AgAc coating at 360°C for 3 h. (c) A silver pore array film with smooth pore walls synthesized by the electrodeposition using colloidal monolayer with sphere size of $5\ \mu\text{m}$. The insets on left top and on the right top are water droplet shapes before and after modification with thiol, respectively.

Table 1. Water CAs of Different Silver Films

	flat film	particle film	pore array film	hierarchical bowl-like array film
CA ($^\circ$) before modification	69	35	33	23
CA ($^\circ$) after modification	108	134	151	169

the groove on the surface of material, Wenzel gave a wettability description by²¹

$$\cos \theta_r = r \cos \theta \quad (1)$$

where r is the roughness factor (the ratio of total surface area to the projected area on the horizontal plane) and θ_r and θ are the CAs of a rough surface and a native flat surface, respectively. Equation 1 describes the fact that the surface roughness enhances

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the hydrophilicity of a hydrophilic surface ($\theta < 90^\circ$) and hydrophobicity of a hydrophobic surface ($\theta > 90^\circ$). Here θ is 69° and 108° before and after modification. Because of the nanoparticle film, the pore array film with smooth inner walls and a hierarchical bowl-like array belong to the rough surface; therefore, the Wenzel mode can well explain why these surfaces are more hydrophilic and more hydrophobic before and after modification. In the above cases, the hierarchical bowl-like array has the smallest water CA and the biggest CA before and after modification, respectively, which indicates that this hierarchical structure has the largest roughness.

Particularly, when a water droplet is added on the chemically modified ordered bowl-like array film with the hierarchical structure, air can be trapped in interstices or corrugations that are produced between the microstructure and the nanostructure.²² In this case, another model for the wettability, presented by Cassie and Baxter, can be used²³

$$\cos \theta_r = f_1 \cos \theta - f_2 \quad (2)$$

where f_1 and $f_2 (=1 - f_1)$ are the area fractions of a water droplet in contact with the surface and with air on the surface, respectively. Since the measured water CAs of the flat silver surface and the bowl-like array film modified with thiol are 108° and 169° , respectively, f_2 for the as prepared surface is calculated to be 0.98. For the pore array film obtained by electrodeposition, its water CA after modification is 151° and corresponding f_2 is only 0.90.

This reveals that the synthesized hierarchical structured surface produces large amount of air trapped between the microstructure and the nanostructure and that the strong superhydrophobicity of the bionic surface is mainly caused by the unique hierarchical micro/nanostructures and the subsequent surface chemical treatment.

For both the silver microplate array and microparticle array (Figure S2) synthesized at higher temperatures, after surface modification with thiol, they only exhibited water CAs of 129° and 133° , respectively, owing to their lower roughness as a result of the absence of hierarchical micro/nanostructures. These two cases also prove that the hierarchical micro/nanostructures are very important to induce the superhydrophobicity with self-cleaning effect.

Optical Property. The optical absorption property of the hierarchical silver bowl-like ordered array was presented in Figure 7. The absorption peak of this Ag nanostructures is located at about 410 nm, which is a unique "fingerprint" for quasispherical Ag nanoparticles and originates from the well-known surface plasmon resonance (SPR) of Ag nanoparticles.²⁴ This suggested that the as-prepared hierarchical bowl-like silver pore array film is constructed by quasispherical silver nanoparticles. As we know, nanostructured silver has attracted considerable attention mainly due to its remarkable optical properties which including surface

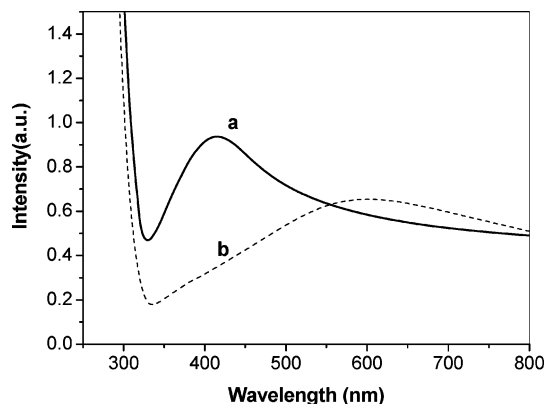


Figure 7. Optical absorption spectra of hierarchical silver bowl-like array film (a) and a relative flat silver film (b) on the glass substrate.

plasmonics, surface-enhanced Raman scattering (SERS), and chemical and biological sensing. Compared with silver films, the hierarchical bowl-like silver pore array film is composed of the silver nanoparticles and hence possesses a higher specific surface area, which could lead to an enhancement of its activity and sensitivity in the above fields. Therefore, besides the superhydrophobicity, the hierarchical structures also have attractive applications in nonlinear optics and optical devices²⁵ and in biological fields.²⁶

Conclusion

In conclusion, we present a facile synthetic route to an ordered hierarchical micro/nanostructured array film with superhydrophobic and self-cleaning properties. Just by the simple solution dipping method and subsequent heating decomposition, the silver hierarchical bowl-like structured film could be prepared. The surface with a silver bowl-like ordered array is fabricated by thermal decomposition of AgAc using the monolayer colloidal crystal as a template. Since such a surface is composed of regularly ordered rough structures resulting from the colloidal monolayer, the surface has uniform superhydrophobicity on the whole surface. This surface has potential applications in interesting scientific fields such as microfluidic devices and optical device.

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Supporting Information Available: Particle size distribution of silver nanoparticles in hierarchical structures, FE-SEM images of silver ordered arrays obtained by the decomposition of AgAc coating at different temperatures (450, 500, and 260 °C) for 3 h using the PS colloidal monolayers as templates and XPS S2p core level of other different modified silver surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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