

## Highly durable non-sticky silver film with a microball-nanosheet hierarchical structure prepared by chemical deposition†

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**Non-sticky and highly adhesive superhydrophobic microball-nanosheet hierarchically structured silver films were obtained after surface modification and storage respectively.**

Super-hydrophobic surfaces have attracted people's attention for many years due to their excellent properties, such as water repellency, anti-corrosion,<sup>1</sup> self-cleaning and antifouling properties.<sup>2</sup> Inspired by natural phenomena, including the lotus leaf,<sup>3</sup> petals,<sup>4</sup> gecko's feet,<sup>5</sup> and insect wings,<sup>6</sup> various surface structures with the super-hydrophobic properties have been fabricated *via* different methods, including plasma etching,<sup>7</sup> chemical vapor deposition,<sup>8</sup> and so on.<sup>9</sup> But most of these structures are difficult to produce on a large-scale due to the severe conditions, complex process control and special equipment needed, and their poor durability. Compared with many methods, chemical deposition is environmentally friendly and energy saving and is therefore more likely to be widely used. More and more efforts have been made to investigate this area.<sup>10</sup> Due to the excellent corrosion resistance of silver, surface replacement deposition of silver on different metals has attracted many researchers.<sup>11</sup> However, most reports about chemical deposition concern replacement reactions, which are strictly selective for the substrate and show poor mechanical behaviour. With respect to the mechanism, researchers have examined a synergistic effect between electrochemical deposition and chemical deposition,<sup>12</sup> but no effort has been made to investigate the relationship between reductant-free chemical deposition and chemical deposition in the presence of a reductant. On the other hand, micro-nano hierarchical structures have proven to have excellent superhydrophobic properties based on both theoretical and experimental research.<sup>13</sup> Materials with long alkyl or CF<sub>x</sub> groups are used to modify a structured surface to gain superhydrophobic films.<sup>14</sup> Due to the stability of the Ag-S bond,

researchers have employed alkylthiols to modify silver films to gain superhydrophobic surfaces.<sup>10b</sup> In recent years, highly adhesive superhydrophobic surfaces have attracted many researchers for their application in valuable liquid transportation.<sup>15</sup> Different explanations of this highly adhesive superhydrophobic property have given by researchers.<sup>4,5</sup>

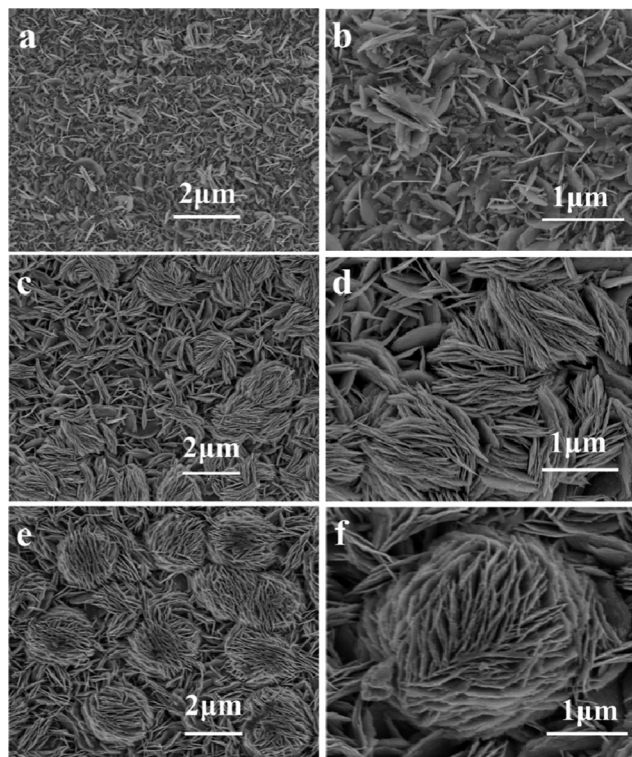
Most of the reported highly adhesive surfaces are composed of polymer materials, which could be easily decomposed in high temperature environments and corroded in acid or alkaline solutions. Their poor mechanical properties also limit the application of polymeric highly adhesive superhydrophobic surfaces. The method reported here employs a simple deposition process to gain highly adhesive superhydrophobic silver films on copper substrates without modification, these are easily obtained and have highly durable properties.

In this communication, we report a microball-nanosheet hierarchically structured silver film prepared by chemical deposition. By immersing the copper plate into a solution composed of silver nitrate and ammonium citrate, a disordered nanosheet structured silver film (Fig. 1a and b) was deposited *via* a surface galvanic exchange reaction. When 0.15 mol L<sup>-1</sup> reductant NaH<sub>2</sub>PO<sub>2</sub> (SHP)<sup>16</sup> was added to the reaction bath, extremely thin nanosheet aggregates appeared on the surface of the copper plate (Fig. 1c and d). While the amount of SHP was 0.30 mol L<sup>-1</sup>, the thin nanosheets grew taller and formed ball-like shapes (Fig. 1e and f). Immersion of copper in the plating solution initiates the metal reduction process on the copper surface, which acts as a catalyst.<sup>17</sup> SHP migrated towards the surface *via* diffusion to give electrons to Ag<sup>+</sup>.<sup>18</sup> Due to the non-uniformity of SHP scattered on the copper surface, some areas gained larger amounts of electrons and had a larger growth velocity. Thus, high density nanosheets aggregated into microballs (illustrated in SI 1, ESI†).

The crystallinity and composition of the products were analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The XRD pattern (shown in SI 2, ESI†) of an as-deposited silver film exhibits peaks for Ag and Cu after deposition. TEM and high-resolution TEM (HRTEM) analysis provide more information about the nanostructure and the growth mechanism of

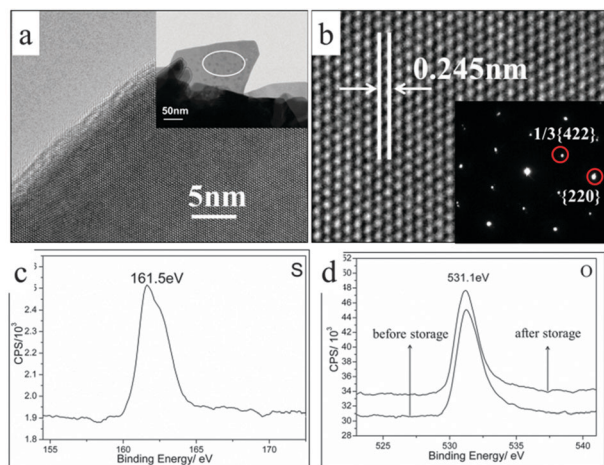
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**Fig. 1** SEM images of the silver film deposited by (a) surface galvanic exchange reaction without SHP, (b) magnification of (a), (c) chemical deposition with  $0.15 \text{ mol L}^{-1}$  SHP, (d) magnification of (c), (e) chemical deposition with  $0.30 \text{ mol L}^{-1}$  SHP, (f) magnification of (e).

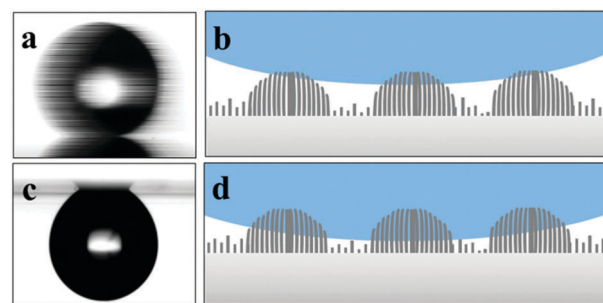
the silver film on the copper alloy substrate. The TEM image (inset of Fig. 2a) shows the layer-by-layer morphology of the microball-nanosheet structure in detail. In the HRTEM image (Fig. 2a), a perfect single-crystal of silver can be observed clearly. The selected-area electron diffraction (SAED) pattern (Fig. 2b inset) from the area indicated in Fig. 2a shows the  $[111]$  zone diffraction. From the magnified HRTEM image (Fig. 2b), the crystalline plane spacing was measured. The spacing is  $0.245 \text{ nm}$ ,



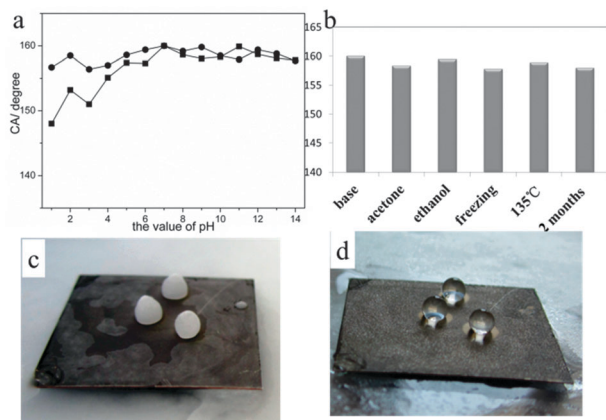
**Fig. 2** (a) HRTEM image of Ag nanosheet. Inset is the TEM image of the silver structure. (b) Magnified image of (a). Inset is the SAED pattern of the selected area in the inset of (a). (c) XPS spectra of S after modification. (d) XPS spectra of O before and after storage for one month.

which is believed to originate from the  $(1/3)\{422\}$  reflection which is normally forbidden in a fcc lattice.<sup>19</sup> This may be caused by an incomplete ABC stacking sequence, which breaks the regular fcc interference pattern and gives rise to the  $(1/3)\{422\}$  reflections.<sup>20</sup> Comparing the TEM image of the hierarchical structure with the nanosheet structure (shown in SI 3, ESI<sup>†</sup>), fewer defects can be observed on the surface of the nanosheet.

A number of chemical surface treatments which use silane-based, fluorinated and synthetic polymers to form a low energy surface have been investigated in recent studies.<sup>9–11</sup> In our study, the perfect non-sticky property was gained by modification with environmentally friendly *n*-hexadecanethiol. Robust Ag-S bonds<sup>10b</sup> formed on the copper substrate with the long alkane chains oriented outwards. After modification, the non-sticky superhydrophobic surface showed a contact angle of  $160^\circ$  (shown in SI 4, ESI<sup>†</sup>) and a sliding angle of  $6^\circ$  (Fig. 3a) (supported by SI 5, ESI<sup>†</sup>). In the X-ray photoelectron spectroscopy (XPS) spectrum (Fig. 2c), the peak located at  $161.5 \text{ eV}$  is attributed to the S in the *n*-hexadecanethiol. The S atom concentration was  $3.33 \text{ at\%}$ . When the specimen was left without modification for one month a highly adhesive superhydrophobic surface was obtained. The contact angle of the surface changed dramatically from  $19^\circ$  to  $158.4^\circ$  (shown in SI 6, ESI<sup>†</sup>). The water droplet adhered to the plate even when turned upside down (Fig. 3c). From XPS analysis of the specimens, before and after one month's storage (Fig. 2d), an increase of  $3.34 \text{ at\%}$  in the oxygen atom concentration was observed, which corresponded to the S atom concentration after modification. The difference in the superhydrophobic behaviour is ascribed to the different contact states between water and the surface. Cassie's state was established because the long alkyl chains kept the water from immersing the nanosheets (Fig. 3b) due to the steric-hindrance effect. The air pockets between the microballs and the air sheets between the nanosheets together keep the water droplet from penetrating further. However, when the surface material was silver oxide, the water impregnated the microballs to some extent. This contact mode between the water and surface could be called Cassie's impregnating state (Fig. 3d). The high density of the nanosheets caused a large contact area between the water and silver oxide. Therefore, it can be deduced that the adhesion is mainly caused by the intimate contact



**Fig. 3** (a) Sliding moment of a  $4 \mu\text{L}$  water drop on a non-sticky superhydrophobic surface. (b) Schematic diagram of the contact state of (a). (c) The behaviour of a water droplet on a highly adhesive surface. (d) Schematic diagram of the contact state of (c).



**Fig. 4** (a) Contact angles on non-sticky surface. Circles represent the contact angle of different liquid droplets with varied pH values. Squares represent the contact angle of water after immersion in acidic or alkaline conditions for one day. (b) Contact angles on non-sticky silver film after immersion in different conditions for one day. (c) The water droplets on the non-sticky surface after freezing. (d) The water droplets on the non-sticky surface after melting.

between the silver nanosheets and water, leading to a large van der Waal's force between water and silver film.<sup>5a</sup>

The non-sticky silver film and the highly adhesive silver film can be used in valuable liquid transportation (demonstrated in SI 7, ESI†). The hierarchically structured silver film, without modification, has excellent anti-corrosion properties because of the inert nature of the silver. Experiments have demonstrated that the silver film, after modification with *n*-hexadecanethiol, has anti-corrosion and liquid-repulsion properties, as well as adaptation to various conditions. In order to evaluate the effect of various corrosive solutions on the wettability of the non-sticky silver film, the water contact angles of a water droplet on the modified silver film after immersion in solutions with different pH values for one day have been measured (Fig. 4a). The contact angle is larger than 150° when the pH is in the range between 2 and 14. Acid and alkaline droplets with different pH values, varying from 1 to 14, were shown to be non-sticky on the silver surface after modification (Fig. 4a). Other conditions, like acetone, ethanol, freezing and high temperature were also shown to have little influence on the superhydrophobicity.

In conclusion, a microball-nanosheet hierarchically structured non-sticky superhydrophobic silver film with high durability and liquid repellence was prepared by chemical deposition and modification. In addition, the hierarchically structured silver film, without any modification, also showed superhydrophobicity after one month's storage. The different properties exhibited by the two superhydrophobic surfaces revealed two different contact states between water and the surface. Since these surfaces can be prepared by one simple chemical deposition, they have brilliant prospects in the application of valuable water transportation.

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