Facile fabrication of superhydrophobic surface from micro/nanostructure metal alkanethiolate based films†

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A series of superhydrophobic surfaces with micro/nanostructure have been successfully achieved by a simple process *via* the reaction between metal (such as Cd and Zn) salts and alkanethiolates.

In nature, lotus and rice leaves exhibit an unusual superhydrophobicity and self-cleaning property resulting from the cooperative effect of micro/nanostructures and low-surface energy materials on their surfaces. To mimic this "lotus-effect",[1] considerable efforts have been devoted to the design and controlled fabrication of superhydrophobic surfaces. An artificial superhydrophobic surface is defined as one with a water contact angle (CA) larger than 150°. Many approaches for preparing superhydrophobic surfaces involve roughening a surface and lowering surface energy.[2,3] Until now, a large number of techniques, such as etching (chemical etching[4] and plasma etching[5]), post treating,[6] chemical vapor deposition (CVD),[7] densely packed aligned carbon or polymer nanotubes,[8] sol–gel processing[9] and others,[10] have been applied to tailor surface topography and to enhance hydrophobicity *via* coating a fabricated rough surface with a hydrophobic thin- or mono-layer. To date the materials that have been used to prepare superhydrophobic surfaces include inorganics (such as ZnO and SiO_2), organic polymers (such as polypropylene) and their hybrids. However, in many cases the reported methods employed either high cost materials, such as carbon nanotubes and semi- or perfluorinated materials, or harsh preparative conditions, thereby limiting the applications of superhydrophobic surfaces.

In this communication we present a simple procedure for fabrication of a series of artificial superhydrophobic surfaces *via* the reaction of metal salts and alkanethiols. Alkanethiols contain long-chain alkyl groups that have lower surface free energy. Also, under certain conditions the mercapto group in an alkanethiol can coordinate to some metal ions to yield controlled rough surfaces and, hence, allows the tethered alkyl groups to create superhydrophobic surfaces *in situ*. On the other hand, alkanethiols themselves can be readily chemisorbed onto the surfaces of metal clusters to generate a self-assembled monolayer. Zhang and his coworkers used this approach to form a monolayer on a smooth gold surface and a dendritic gold cluster surface generated by electro-chemistry to give a water contact angle of 95° and 156°, respectively.[4a] Carotenuto and his coworkers utilized metal *n*-alkanethiolates to prepare polymer-embedded metal and metal sulfide clusters.[11] However, the utilization of metal alkanethiolates to generate and fabricate superhydrophobic surfaces has not been described.

The successful synthesis of metal alkanethiolates demonstrates that we can rationally design lotus-like morphology by using a class of inorganic compounds. It is very exciting that such a metal alkanethiolate exhibits a superhydrophobic property. Significantly, we can produce the stable superhydrophobic surfaces under ambient atmosphere using cheap metal salts and thiols. In our work, cadmium and zinc salts are directly reacted with *n*-dodecanethiol (1 : 2 in molar ratio) to give new metal dithiolates in yields of $> 95\%$ (see Supporting Information). The uniform cadmium dodecanethiolate thin film was dried overnight after ethanol was evaporated at about 25 °C. The thickness of the dried film is about 50 µm. When the reaction is complete, the hydrophilicity of the reagents disappears and the products exhibit hydrophobic properties. Fig. 1 shows scanning electron microscopy (SEM) images of the cadmium dodecanethiolate film at different magnifications and the pure cadmium chloride crystal cluster for comparison. Fig. 1a illustrates the surface morphology with packed aggregate "flower-like" spheres ranging from 5 µm to 37 µm in diameter. The magnified image in Fig. 1b shows a single "flower-like" sphere that is composed of a number of microrods. The average diameter of the microrods is about 200 nm. Fig. 1b also shows that the microrods grow separately on the substrate, thereby enabling the growth of the micro/nanostructures. In addition, these microrods can self-aggregate to contribute to the rough hierarchical surfaces in this case, and air can be trapped in

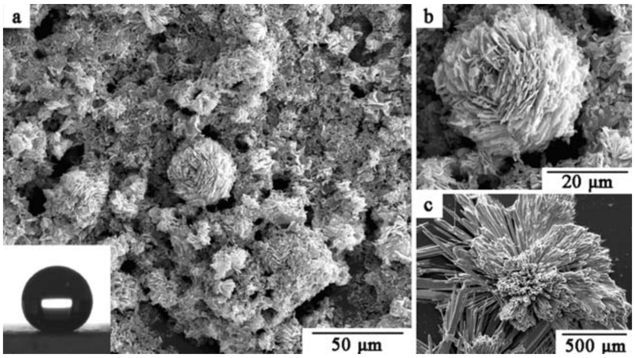

Fig. 1 (a, b) SEM images of the as-prepared cadmium dodecanethiolate "flower-like" films at low and high magnifications. (c) SEM image of pure cadmium chloride crystal clusters. The morphologies were characterized by QUANTA 200 (Philips-FEI, Holland) at 30.0 kV. Insert: A 5 µL water drop profile in CA measurement by using DSA 100 (KRÜSS, Germany) at ambient temperature.

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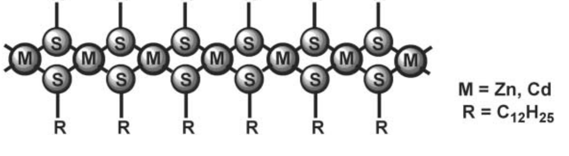
the troughs between individual microrods. On the other hand, the result also indicates that the surface of cadmium dodecanethiolate film possesses natural lotus-like micro- and nano-hierarchical structure. Fig. 1c is a SEM image of pure cadmium chloride crystal clusters. As seen in Fig. 1c, the morphology of cadmium chloride is similar to that of the product as prepared, indicating that the structure of cadmium dodecanethiolate is related to the original structure of cadmium chloride. As a matter of fact, a wetting experiment shows the water contact angle (CA) of this special surface is about 154.0 ± 2.0° (Fig. 1a insert). Further evidence for the superhydrophobicity of the surface is given by the low tilt angle that reflects the difference between advancing and receding contact angle. The tilt angle on the surface is 3.8 ± 1.3°, indicating that water droplets roll off easily (see Supporting Information). In this case, the fabricated cadmium dodecanethiolate films possess novel alkyl-chain tethered micro/nanostructures and exhibit superhydrophobic properties. Similar superhydrophobic surfaces of cadmium dodecanethiolate can also be successfully obtained. These are prepared by reaction between cadmium acetate and *n*-dodecanethiol and cadmium nitrate and *n*-dodecanethiol, respectively (see Supporting Information).

To gain a better understanding of the unique morphology of cadmium dodecanethiolate film requires definition of the fine structure of metal thiolates. The results of elemental analysis and X-ray diffraction (XRD) show that microrods are composed of $Cd(SR)_2$ ($R = C_{12}H_{25}$) and demonstrate good crystallinity (see Supporting Information). Metal dodecanethiolates with small organic R groups have been synthesized by electrochemistry,[12] but further investigations are inhibited by the insolubility of most such species in common organic solvents. The compounds are air-stable solids and the insolubility of these species presents the same problem in characterization. However, we found that cadmium dodecanethiolates and zinc dodecanethiolates have superhydrophobic properties. The composition as formulated $[M(SC_{12}H_{25})_2]$ (M = Zn, Cd) is supported by microanalysis. In addition, infrared and far infrared spectroscopies indicate the presence of the organic group, C–S and M–S bonds. The insolubility of the two metal dithiolates with a longer *n*-dodecyl chain is compatible with a polymeric structure where each metal atom is surrounded by four sulfur atoms in a pseudo-tetrahedral environment (Scheme 1). This is consistent with that proposed for the metal dithiolates generated from smaller thiols.[12]



Scheme 1 Proposed formulation of zinc or cadmium dodecanethiolate.

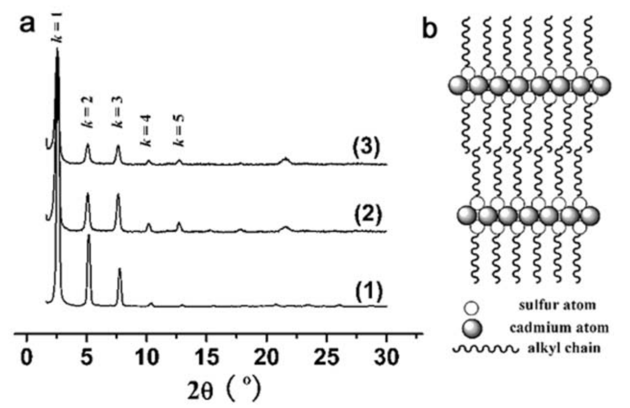


Fig. 2 (a) XRD patterns of cadmium dodecanethiolate from different cadmium salts. ((1), $[CdCl_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol; (2), $[Cd(NO_3)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol; (3), $[Cd(OAc)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol). Lines indexed to the interlayer spacing (0*k*0) are labeled. The XRD patterns were recorded on a Bruker-AXS D8 ADVANCE (Bruker, Germany) X-ray diffractometer at a scanning rate of 6° min^{-1} in 2θ ranging from 1° to 75° with CuKα radiation (λ = 0.1542 nm). (b) Cross-sectional view of the layer structure of cadmium dodecanethiolate. Cadmium atoms: shaded circles; sulfur atoms: open circles; alkyl chains: wavy lines.

Fig. 2a shows X-ray powder diffraction (XRD) patterns of cadmium dodecanethiolates prepared with three kinds of different cadmium salts. As seen in Fig. 2a, all these patterns present almost the same patterns and good crystallinity. Also a well-developed progression of intense reflections is seen, showing successive orders of diffraction from a layer structure with the same *d* spacing. In agreement with published data for silver thiolate compounds (AgSR),[13] the *d* spacing evaluated for cadmium dodecanethiolate ($Cd(S(CH_2)_nCH_3)_2$, $n = 11$) is 34.83 Å. Therefore, we believe that the model in terms of the layer structure of Fig. 2b is relative to the observed interlayer separations and then we consider possible bonding patterns for the Cd and S slab in relation to the additional reflections of the diffraction patterns. As seen in Fig. 2b, the model is comprised of parallel slabs of connected Cd and S atoms and there is stacking of layers between the distal atoms of the thiolate substituents. Each layer of cadmium dodecanethiolate is separated from the neighboring layer by twice the length of the dodecyl chain. The intralayer structure provides the packing characteristics of the organic as well as the inorganic slabs while the interlayer structural attributes provide characterization of the uniformity and the layer thicknesses. In particular, it leads to films with preferential orientation, which is favorable for the subsequent growth of cadmium dodecanethiolate microrods. This result also reveals that the cadmium dodecanethiolate particles stack together, thus forming a hierarchical structure, along with higher surface roughness.

Zinc dodecanethiolate is synthesized by the reaction between zinc acrylate and *n*-dodecanethiol with toluene as the solvent. Figs. 3a and 3b are the SEM images of the resulting zinc dodecanethiolate films at different magnifications, which may be compared to a SEM image of zinc acrylate in Fig. 3c. Figs. 3a and 3b reveal a surface morphology composed of a packed aggregate “leaf-like” pattern with the diameter ranging from 2.5 μm to 5 μm. A similar structure can be seen from a SEM image of zinc acrylate (around 270 nm) as shown in Fig. 3c. These observations suggest that the overlapped “leaf-like” pattern of zinc dodecanethiolate arises from zinc acrylate, which forms a rough hierarchical surface. Moreover, on the surface of the microscale aggregate “leaves”, nanoscale multimolecular “leaves” are observed. Air can be trapped among the hierarchical “leaves”. The hydrophobicity of a rough surface can be further enhanced by increasing the proportion of air/water interface *via* evaporation of the selective solvent. As a result, the apparent water contact angle (CA) of this special surface is

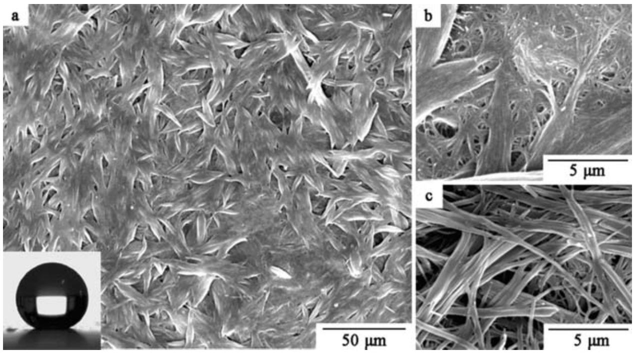


Fig. 3 (a, b) SEM images of the as-prepared zinc dodecanethiolate "leaf-like" films at low and high magnifications. (c) SEM image of pure zinc acrylate. Insert: Water drop profile in CA measurement (5 µL droplet size).

153.2 ± 2.0° (Fig. 3a insert). The tilt angle on the surface is 12.2 ± 1.3°. Hence, the superhydrophobic surface of zinc dodecanethiolate has been achieved in a packed "leaf-like" pattern. Similar superhydrophobic surfaces of zinc dodecanethiolate can be obtained *via* the reaction between zinc acetate and *n*-dodecanethiol.

In conclusion, a convenient and inexpensive approach to fabricate superhydrophobic surfaces through metal alkanethiolates has been described. The rough hierarchical micro/nanostructures that contribute to superhydrophobic properties are controlled in the preparation of this type of materials. A parallel approach to that of this investigation constitutes a promising way to fabricate superhydrophobic surfaces. Practical applications, for instance, in the self-cleaning field, may follow. Hence, systematic research on metal alkanethiolate surfaces continues.

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