Supplementary Material (ESI) for Chemical Communications


# Supporting Information

## Facile Fabrication of Superhydrophobic Surface from Micro/Nanostructure Metal Alkanethiolates Based Films

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### Experimental Details

*Preparation of Cadmium Dodecanethiolate Based Films*

Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$, 5 mmol) was dissolved in a solution containing distilled water (5 mL) and ethanol (15 mL). Then an n-dodecanethiol (10 mmol) ethanol solution (15 mL) was added drop-wise under stirring at ambient temperature. A slurry was generated immediately due to the formation of the thiolate, and the reaction mixture was kept stirring for 4 h in a lucifugal reactor. The resultant precipitation was removed and washed with ethanol and acetone. The solid was dispersed in ethanol (90 % wt) under sonication, and the resultant suspension was poured on a glass wafer. The uniform cadmium dodecanethiolate thin film was dried overnight after ethanol was completely evaporated at about 25 $^{o}$C. The thickness of dried film was about 50 μm. The similar superhydrophobic surfaces of cadmium dodecanethiolate can also be obtained by cadmium acetate and cadmium nitrate.

| Element | Found (wt %) | Calcd (wt %) |
|---|---|---|
| Cd | 42.57 | 42.80 |
| S | 24.57 | 24.41 |
| C | 27.37 | 27.72 |
| H | 5.49 | 5.37 |

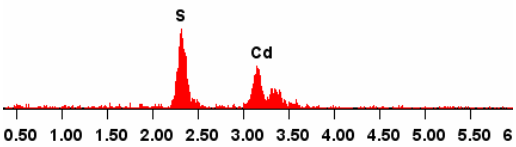


Figure S1. EDAX spectrum of cadmium propylthiolate. ($[CdCl_2]/[CH_3(CH_2)_2SH]$ = 1 : 2 mol/mol from ethanol). Note: The EDAX spectrum and the mass fractions of cadmium and sulfur were recorded on QUANTA 200 (Philips, Holland) and the mass fractions of carbon and hydrogen were recorded on Elementa Vario EL III (Vario, America). The calculated values: Cd, 42.80; S, 24.41; C, 27.72; H, 5.37. (wt %)

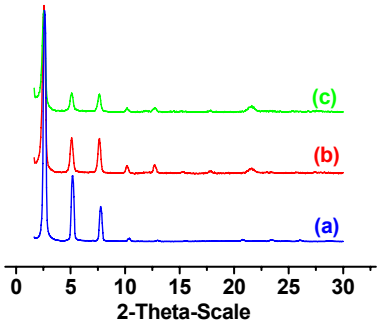


Figure S2. XRD patterns of cadmium dodecanethiolate from different cadmium salts. (a, $[CdCl_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol; b, Cd $[Cd(NO_3)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol; c, $[Cd(OAc)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol) The XRD patterns were recorded on a Bruker-AXS D8 ADVANCE (Bruker, Germany) X-ray diffractometer at a scanning rate of 6° /min in 2θ ranging from 1° to 75° with CuKα radiation (λ = 0.1542 nm).

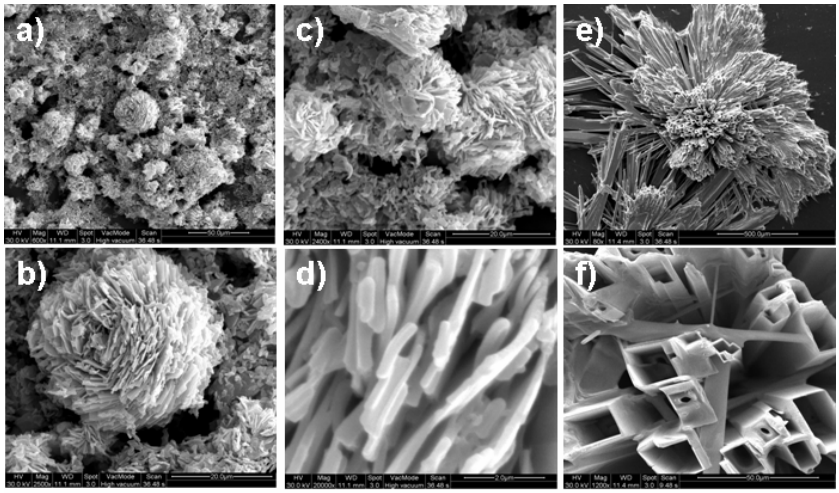


Figure S3. SEM images of cadmium dodecanethiolate obtained from $CdCl_2$. (a, ×500) the flower-like film surface,; (b, ×2500) and (c, ×2400) bigger and smaller "flower" spheres; (d, ×20000) the rods on the "flowers". (e) and (f) SEM images of cadmium chloride crystal clusters (×50 and ×1200, respectively). The morphologies were characterized by QUANTA 200 (Philips-FEI, Holland) at 30.0 kV.

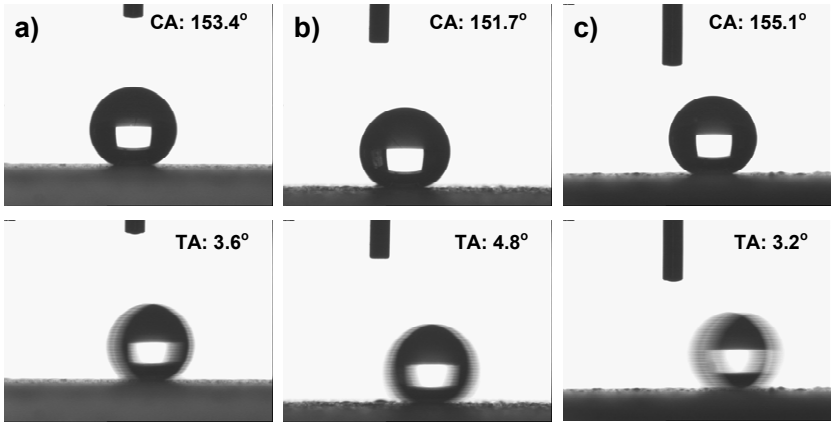


Figure S4. Contact angle (CA) and tilt angle (TA) measurements on the surfaces of cadmium dodecanethiolate based films. a, $[CdCl_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol; b, $[Cd(NO_3)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol; c, $[Cd(Ac)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2 mol/mol from ethanol. The values were acquired at room temperature using DSA 100 (KRÜSS, Germany) by sessile drop and tilting plate measuring method (water drop size: 5 µL).

## *Preparation of Zinc Dodecanethiolate Based Films*

Zinc acrylate (10 mmol) was dispersed in toluene (20 mL) in a lucifugal reactor equipped with a stirrer. Then, a n-dodecanthiol (10 mmol) toluene solution (20 mL) was added drop-wise. The reaction was performed at ambient temperature for 12 h. The resultant solid was removed and washed with toluene and acetone. Then, it was dispersed in toluene (90% wt) under sonication. The uniform zinc dodecanethiolate thin film was obtained in the same way as used with cadmium dodecanethiolate. The similar superhydrophobic surfaces of zinc dodecanethiolate can also be obtained by zinc acetate in ethanol.

| Element | Found (wt %) | Calcd (wt %) |
|---|---|---|
| Zn | 31.61 | 30.33 |
| S | 28.71 | 29.73 |
| C | 33.39 | 33.40 |
| H | 6.29 | 6.54 |

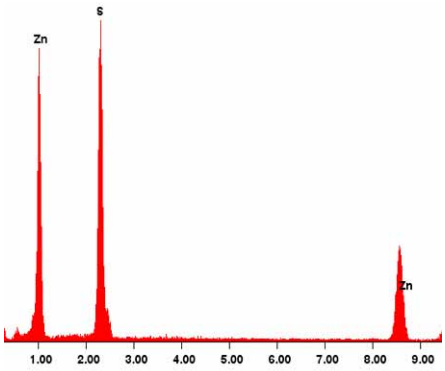


Figure S5. EDAX spectrum of zinc propylthiolate. ([Zinc acrylate]/$[CH_3(CH_2)_2SH]$ = 1 : 2 from ethanol). The EDAX spectrum and the mass fractions of zinc and sulfur were recorded on QUANTA 200 and the mass fractions of carbon and hydrogen were recorded on Elementa Vario EL III. The calculated values: Zn, 30.33; S, 29.73; C, 33.40; H, 6.54. (wt %)

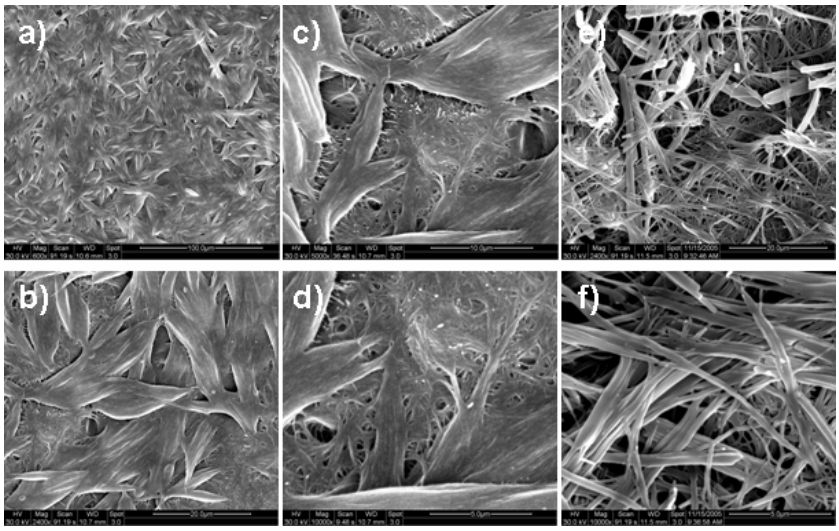


Figure S6. SEM images of the zinc dodecanethiolate "leaf-like" films obtained from zinc acrylate (a, the "leaf-like" film surface; b-d the images in bigger magnifications (a, ×600; b, ×2400; c, ×5000; d, ×10000) and of zinc acrylate (e, ×2400; f, ×10000). The morphologies were characterized by QUANTA 200 at 30.0 kV.

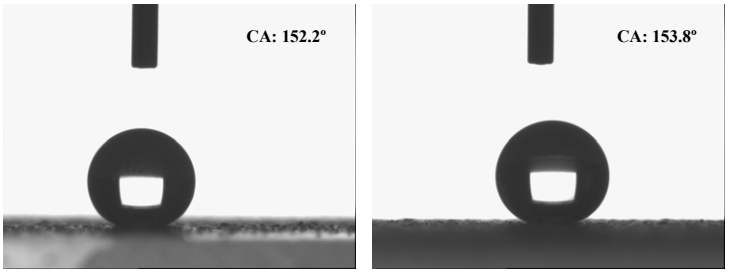


Figure S7. CA and TA measurements on the surfaces of zinc dodecanylthiolate based films. (a, [Zinc acrylate]/[$CH_3(CH_2)_{11}SH$] = 1 : 1 from toluene; b, [$Zn(OAc)_2$]/[$CH_3(CH_2)_{11}SH$] = 1 : 1 from ethanol). The CA and TA values were acquired at room temperature using DSA 100 by sessile drop and tilting plate measuring method. (Water drop size: 5 μL)

Table S1. FT-IR absorptions of $M(S(CH_2)_nCH_3)_2$ (M = Cd, Zn; n = 2, 11). ($cm^{-1}$)

| | a | b | c | d | e | f | g | h |
|---|---|---|---|---|---|---|---|---|
| $CH_3$ asymmetric stretching | 2956.03 | 2956.02 | 2956.60 | 2957.00 | 2956.14 | 2956.14 | 2960.80 | 2963.29 |
| $CH_2$ asymmetric stretching | 2919.70 | 2919.50 | 2918.91 | 2922.10 | 2921.76 | 2920.66 | 2929.28 | 2929.95 |
| $CH_2$ symmetric stretching | 2850.31 | 2850.16 | 2848.96 | 2851.76 | 2851.64 | 2851.02 | 2870.92 | 2871.34 |
| $CH_2$ asymmetric bending | 1466.81 | 1467.08 | 1464.44 | 1466.14 | 1466.01 | 1465.01 | 1458.94 | 1460.29 |
| $(CH_2) \geq 6$ in-plane deformations rocking | 722.49 | 722.46 | 721.56 | 721.82 | 721.06 | 721.61 | | |

a) $[Cd(OAc)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2, solvent: ethanol; b) $[Cd(NO_3)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2, solvent: ethanol; c) $[CdCl_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2, solvent: ethanol; d) [Zinc acrylate]/$[CH_3(CH_2)_{11}SH]$ = 1 : 2, solvent: DMF; e) $[Zn(OAc)_2]/[CH_3(CH_2)_{11}SH]$ = 1 : 2, solvent: ethanol; f) [Zinc acrylate]/$[CH_3(CH_2)_{11}SH]$ = 1 : 2, solvent: ethanol; g) [Zinc acrylate]/$[CH_3(CH_2)_2SH]$ = 1 : 2, solvent: ethanol; h) $[CdCl_2]/[CH_3(CH_2)_2SH]$ = 1 : 2, solvent: ethanol.