研究简报

# 具有米状纳微阶层结构的仿生超疏水十二硫醇铅表面的简单制备

黄 旭 胡春晖 蔡晓晶 陈 莉 陈 苏*
(材料化学工程国家重点实验室,南京工业大学化学化工学院,南京 210009)

**关键词**：超疏水表面；十二硫醇铅；一步法反应
**中图分类号**：TB383；O614.43+3 **文献标识码**：A **文章编号**：1001-4861(2009)01-0184-05

# Simple Fabrication of Biomimetic Superhydrophobic Lead Dodecanethiolate Surface with Rice-like Hierarchical Micro/Nanostructure

HUANG Xu HU Chun-Hui CAI Xiao-Jing CHEN Li CHEN Su*
(*The State Key Laboratory of Material-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing* 210009)

**Abstract:** A superhydrophobic surface of lead dodecanethiolate with the water contact angle(CA) of 152.2°±1.2° and the sliding angle(SA) of 3.8°±1.0° was fabricated using a simple and relative inexpensive route based on our previous reported method. The procedure employed a one-pot reaction between lead salt and alkanethiolate to form a thermal stable superhydrophobic coating under mild conditions. SEM images revealed the lead dodecanethiolate surface morphology with packed aggregate "rice-like" particles of micrometer scale in length and nanometer scale in thickness. Also, Lead dodecanethiolate powder was investigated by TGA and XRD.

**Key words:** superhydrophobic surface; lead dodecanethiolate; one-pot reaction

Over the past decade, considerable efforts have been devoted to the development of biomimetic superhydrophobic surfaces, describing a surface with a water contact angle(CA) larger than 150° based on lotus-effect because the wet ability of solid surfaces is one of the most important aspects in both theoretical research and industrial applications[1~8]. The superhydrophobic surface exhibits water repellency and self-cleaning properties, which is governed by both the chemical composition of the surface material and the cooperative effect of a hierarchical structure with micro- and nanostructures. Until now, a number of approaches, such as etching etching[9~11], chemical vapor deposition(CVD)[12,13], nanotubes[14,15], sol-gel processing[16,17] and others[18,19], have been developed for creating superhydrophobic surfaces with specific surface topography. However, the reported methods used either expensive materials or complicated methods, hindering the application of superhydrophobic surfaces. In our previous work, we fabricated a durable superhydrophobic organic-inorganic (PS/$SiO_2$) hybrid coating by the sol-gel process[20]. Also, "flower-like" cadmium dodecanethiolate films and "leaf-like" zinc

收稿日期：2008-09-15。收修改稿日期：2008-11-06。
国家自然科学基金(No.20576053,20606016,10676013 NSAF),国家 863 重大科技专项(No.2007AA06A402),江苏省教育厅高校重点自然科学基金(No.07KJA53009)项目。
*通讯联系人。E-mail:chensu@njut.edu.cn; Fax:(86) 25-83587194
第一作者：黄 旭,男,24 岁,硕士研究生;研究方向：超疏水表面的构筑。

dodecanethiolate films were successfully prepared by a one-pot reaction[21]. Herein, we follow the one-pot procedure to fabricate an artificial "rice-like" superhydrophobic surfaces via the reaction of lead(Pb) salt and alkanethiols, containing long-chain alkyl groups with lower surface free energy. Through this procedure, a stable superhydrophobic surface with a water contact angle of 152.2°±1.2° and sliding angle of 3.8°±1.0° was obtained. In addition, alkanethiols themselves can be readily chemisorbed onto the surfaces of metal clusters to generate a self-assembled monolayer[22]. Significantly, the advantage of this synthetic method is simple and feasible as well as the materials used are relatively inexpensive.

## 1 Experimental

### 1.1 Materials

Lead acetate ($Pb(Ac)_2 \cdot 3H_2O$) was purchased from Shanghai No.4 Reagent & H.V Chemical Co., Ltd, n-dodecanethiol and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received.

### 1.2 Preparation of lead dodecanethiolate based film

Lead dodecanethiolate based film was prepared following the procedure we developed before[21]. Lead acetate($Pb(Ac)_2 \cdot 3H_2O$, 5 mmol) was dissolved in a solution containing distilled water (5 mL) with the addition of ethanol (15 mL). Then an n-dodecanethiol (10 mmol) ethanol solution(15 mL) was added drop-wise after stirring at ambient temperature. The reaction mixture was kept stirring for 4 h in a lucifugal reactor and the resultant precipitation was removed and washed with ethanol and acetone for several times and then dispersed in ethanol (90wt%) under sonication. The resultant suspension was poured on a glass wafer and dried overnight at about 25℃ to form the uniform lead dodecanethiolate thin film. The thickness of dried film was approximately 50 μm.

### 1.3 Characterization

Contact angles were measured on a Drop Shape Analysis System DSA 100 (KRÜSS, Germany) contact-angle system at room temperature. A distilled water droplet (5 μL) was used as the indicator in the experiment to characterize the wetting property of the as-prepared surfaces. The microscopic features of the prepared films were characterized using an environmental scanning electron microscopy (ESEM, QUATA-2000) at a voltage of 40 kV. The weight-loss of the Lead Dodecanethiolate ($Pb(SC_{12}H_{25})_2$) on heating was studied by thermogravimetric analysis (TGA) using a thermogravimetric apparatus Shimadzu-TGA 50 under a nitrogen atmosphere. Measurements were taken with a heating rate of 10 ℃·min$^{-1}$ from 38 to 600 ℃. The sample was prepared by drying in a vacuum oven at 60 ℃ for 2 days at a pressure of 70 kPa for solvent removal. The powder X-ray diffraction (XRD) patterns were recorded on a Bruker-AXS D8 ADVANCE X-ray diffractometer at a scanning rate of 6°·min$^{-1}$ in $2\theta$ ranging from 10° to 80° with Cu $K\alpha$ radiation ($\lambda$ =0.154 18 nm) at a generator voltage of 40 kV and a current of 30 mA, and a nickel filter is employed for removing the $K\beta$ radiation and scintillation counter is used for X-ray recording.

## 2 Results and discussion

Fig.1 shows scanning electron microscope(SEM) images of the lead dodecanethiolate film at different magnifications. As shown in Fig. 1b, the packed aggregate "rice-like" particles have regular sizes ranging from 200~300 nm. The lead dodecanethiolate particles are in microscale aggregation (Fig.1a), minimizing the surface energy while the solution evaporates at room temperature. In addition, these particles overlap to form hierarchical structure, therefore, a rough lead dodecanetiolate based film with a micro/nanostructure has been prepared by one pot method. Air can be trapped in the interspace among the hierarchical structure. Meanwhile, with the low-surface-energy long alkyl chain outside, the apparent contact angle(CA) of this special surface is about 152.2°±1.2°(Fig.2a). Further evidence for the superhydrophobicity of the surface is given by the low sliding angle (SA) that reflects the difference between advancing and receding contact angle. The SA of a 5 μL water droplet on the surface in this case is about 3.8°±1.0°, as shown in Fig.2b, indicating that water droplets are unstable on the surface and roll off easily.

Therefore, the fabricated lead didodecanethiolate films possess novel alkyl-chain tethered micro/nanostructures and exhibit superhydrophobic properties.

The superhydrophobicity of the as-prepared lead dodecanethiolate is governed by both the roughness and the low-free energy long alkyl chain outside the particles. We believe that the lead dithiloate possesses a pseudo-tetrahedral environment where four sulphur atoms surround the lead atom (Scheme 1), which is consistent with that proposed for the metal dithiolates generated from smaller thiols[23].

To confirm the composition of the thiolate compounds, stoichiometric information concerning the thermolysis products was obtained by TGA. Thermal decomposition of lead thiolate usually occurs according to

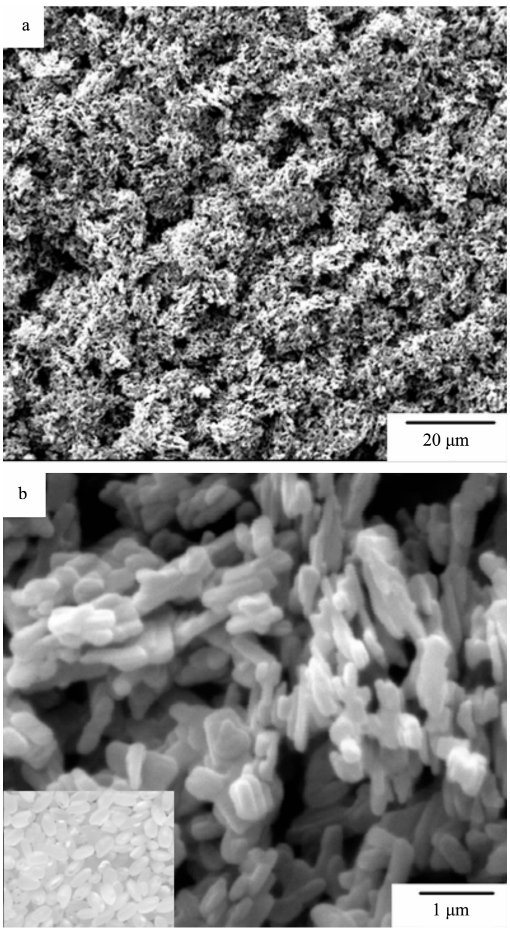



Fig.1 (a, b) SEM images of the as-prepared lead dodecanethiolate "rice-like" films at low and high magnifications. (inset: a photograph of rice) The morphologies were characterized by QUANTA 200(Philips-FEI, Holland) at 30.0 kV

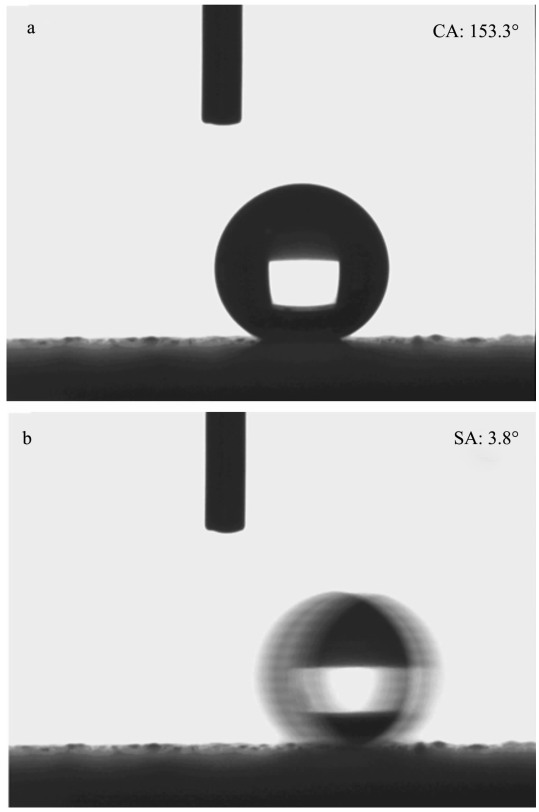
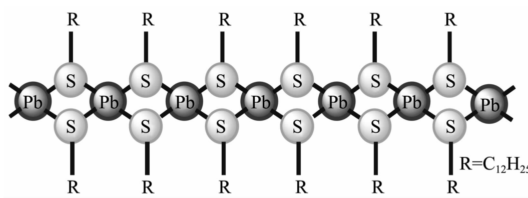



Fig.2 (a) Contact angle(CA) and (b) tilt angle(TA) measurements on the surfaces of lead dodecanethiolate based films. $n_{Pb(Ac)_2}/n_{CH_3(CH_2)_{11}SH}=$ 1:2 in ethanol. The values were acquired at room temperature using DSA 100 (KRÜSS, Germany) by sessile drop and tilting plate measuring method(water drop size: 5 μL)




Scheme 1 Proposed formulation of lead dodecanethiolate

the following reaction scheme[24]:

$$Pb(SR)_2 \rightarrow PbS + RSR$$

As shown in Fig.3, mass loss of Pb dodecanetiolate occurs in a single step ranging from 220 to 360 ℃. On the basis of the weight of lead didodecanethiolate ($Pb(SR)_2$, $R=C_{12}H_{25}$), the final residual mass is 39.16% of the parent compounds, indicating that the actual remnant is attributed to PbS compound since the value coincides with the theoretical one (39.23%) exactly. These results confirm that the product prepared by the reac-

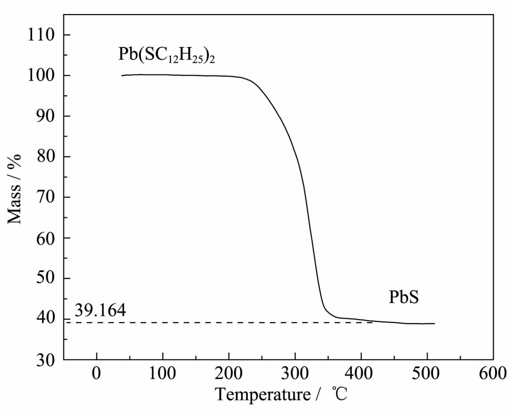



Fig.3 TGA-thermogram of lead dodecanetiolate compounds

tion between Pb salt and *n*-dodecanethiol is $Pb(SC_{11}H_{25})_2$ and the final remnant of the thermal decomposition is PbS.

XRD pattern of the as-prepared lead dodecanethiolate is shown in Fig.4a. As seen in Fig.4a, a well-developed progression of intense reflections indicates successive orders of diffraction from a layer structure with the same d spacing, *i.e.*, the as-prepared $Pb(SC_{11}H_{25})_2$ possesses a highly ordered crystalline structure. According to the computational method of other published silver thiolate compounds (AgSR) system [25,26], the average $d$ spacing calculated for lead dodecanethiolate ($Pb(S(CH_2)_nCH_3)_2$, $n=11$) is 3.79 nm. Therefore, we believe that the layer structure of lead dodecanethiolate, shown in Fig.4b, is similar to that we proposed in our previous work [21], and the intralayer structure provides the characterization of the uniformity and the layer thicknesses. We also believe that the special structure of bi-molecular assembly in a self-consistent series of pillared, layered long-alkyl-chain lead thiolate contributes to the superhydrophobic behavior.

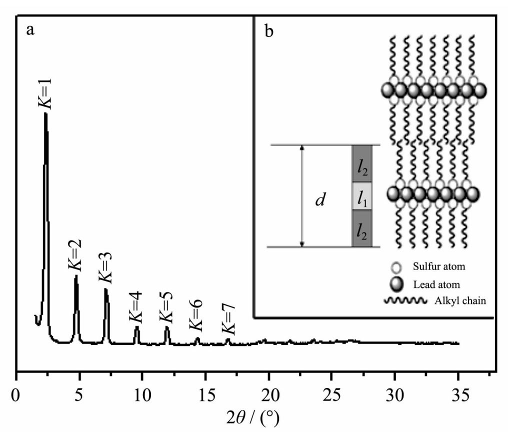



Fig.4 (a) XRD pattern of lead dodecanethiolate. Lines indexed to the interlayer spacing (0$k$0) are labeled, (b) Cross-sectional view of the layer structure of lead dodecanethiolate. Lead atoms: shaded circles; sulfur atoms: open circles; alkyl chains: wavy lines

## 3 Conclusions

A simple and relatively inexpensive method to fabricate superhydrophobic surfaces in one step procedure was carried out by casting micro/nanostructure lead dodecylthiolates based films under ambient temperature. The morphology of lead didodecanethiolate shows a rice-like structure with the size of about 200 nm and the XRD parttern of lead didodecanethiolate demonstrates that the compounds process parallel slabs of connected lead and sulfur atoms with the stacking of layers between the distal atoms of the thiolate substituents. Hydrophobicity test reveals that these materials are very efficient in repelling water and practical applications, for instance, in the self-cleaning field, may follow.

**Acknowledgement:** This work was supported by Natural Science Foundations (NSFs) of China (Grant No. 20576053, 20606016), NSF (NASA) of China (Grant No. 10676013), 863 Important National Science & Technology Specific Project(Grant No. 2007AA06A402), and the NSF of the Jiangsu Higher Education Commision of China (Grant No. 07KJA53009).

## References:

[1] Wenzel R N. *Ind. Eng. Chem.*, **1936**,**28**:988~994

[2] Cassie A B D, Baxter S. *Trans. Faraday Soc.*, **1944**,**40**:546~551

[3] Blossey R. *Nat. Mater.*, **2003**,**2**:301~306

[4] Nakajima A, Hashimoto K, Watanabe T. *Monatsh. Chem.*, **2001**, **132**:31~41

[5] Neinhuis C, Barthlott W. *Ann. Bot.*, **1997**,**79**:667~677

[6] Barthlott W, Neinhuis C. *Planta*, **1997**,**202**:1~8

[7] Richard D, Clanet C, Quéré D. *Nature*, **2002**,**417**:811

[8] Erbil H Y, Demirel A L, Avci Y, et al. *Science*, **2003**,**299**: 1377~1380

[9] Olde Riekerink M B, Terlingen J G A, Feijen J, et al. *Langmuir*, **1999**,**15**:4847~4856

[10]Öner D, McCarthy T J. *Langmuir*, **2000**,**16**:7777~7782

[11]Shirtcliffe N J, McHale G, Newton M I, et al. *Langmuir*, **2005**,**21**:937~943
[12]Liu H, Feng L, Jiang L, et al. *Langmuir*, **2004**,**20**:5659~5661
[13]Huang L, Lau S P, Yang H Y, et al. *J. Phys. Chem. B*, **2005**, **109**:7746~7748
[14]Li H, Wang X, Jiang L, et al. *Angew. Chem. Int. Ed.*, **2001**, **40**:1743~1746
[15]Jin M, Feng X, Jiang L, et al. *Adv. Mater.*, **2005**,17:1977~1981
[16]Tadanaga K, Kitamuro K, Minami T, et al. *J. Sol-Gel Sci. Technol.*, **2003**,**26**:705~708
[17]Han J T, Lee D H, Cho K, et al. *J. Am. Chem. Soc.*, **2004**,**126**: 4796~4797
[18]Nakajima A, Abe K, Hashimoto K, et al. *Thin Solid Films*, **2000**,**376**:140~143
[19]Genzer J, Efimenko K. *Science*, **2000**,**290**:2130~2133
[20]Yang S Y, Chen S, Chen L, et al. *Chem. Mater.*, **2008**,**20**: 1233~1235
[21]Chen S, Hu C H, Xu N P, et al. *Chem. Commun.*, **2007**,**19**: 1919~1921
[22]Zhang X, Shi F, Yu X, et al. *J. Am. Chem. Soc.*, **2004**,**126**: 3064~3065
[23]Black S J, Einstein F W B, Tuck D G, et al. *Inorg. Chem.*, **1986**,**25**:4181~4184
[24]Carotenuto G, Martorana B, Perlo P, et al. *J. Mater. Chem.*, **2003**,**13**:2927~2930
[25]Dance I G, Fisher K J, Banda R M H, et al. *Inorg. Chem.*, **1991**,**30**:183~187
[26]Parikh A N, Gillmor S D, Swanson B I, et al. *J. Phys. Chem. B*, **1999**,**103**:2850~2861