



# Solvent polarity effect on quality of n-octadecanethiol self-assembled monolayers on copper and oxidized copper



Yaozhong Zhang<sup>a</sup>, Jun Zhou<sup>b</sup>, Xiaoli Zhang<sup>a,\*</sup>, Jun Hu<sup>a</sup>, Han Gao<sup>a</sup>

<sup>a</sup> School of Chemical Engineering, Northwest University, Xi'an, 710069, China

<sup>b</sup> Xi'an Chuanglian Huate Surface Treatment Tech. Co. Ltd, Xi'an, 710065, China

## ARTICLE INFO

### Article history:

Received 10 June 2014

Received in revised form

12 September 2014

Accepted 12 September 2014

Available online 20 September 2014

### Keywords:

Solvent polarity

Alkanethiols

SAMs

Oxidized copper

Reduction reaction

## ABSTRACT

This article reports the effect of solvent polarity on the formation of n-octadecanethiol self-assembled monolayers (C<sub>18</sub>SH-SAMs) on pure copper surface and oxidized copper surface. The quality of SAMs prepared in different solvents (n-hexane, toluene, trichloroethylene, chloroform, acetone, acetonitrile, ethanol) was monitored by EIS, RAIRS and XPS. The results indicated that C<sub>18</sub>SH-SAMs formed in these solvents were in good barrier properties on pure copper surface and the structures of monolayers formed in high polarity solvents were more compact and orderly than that formed in low polarity solvents. For comparison, C<sub>18</sub>SH adsorbed on the surface of oxidized copper in these solvents were studied and the results indicated that C<sub>18</sub>SH could be adsorbed on oxidized copper surface after the reduction of copper oxide layer by thiols. Compared with high polarity solvents, a limited reduction process of oxidized copper by thiols led to the incompletely formation of monolayers in low polarity solvents. This can be interpreted that the generated water on solid–liquid interface and a smaller reaction force restrict the continuous reduction reaction in low polarity solvents

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Self-assembled monolayers (SAMs) can not only improve surface properties of solid such as friction, wetting and adhesion, but also provide outstanding potential applications in the fields of biomimetics, chemical sensing and protection of metals against corrosion [1–7]. In particular, SAMs formed by chemisorption of thiols onto gold surface are a very extensive research system because of its high chemical inertness [8]. As an active metal, copper is widely used in chemical and microelectronics industries due to its excellent thermal and electrical conductivity [9–11]. However, copper is easily oxidized in air, which limits its further application. The densely packed monolayers are formed though the chemisorption onto copper surface, which is an effective method to be applicable on copper against the oxidization [12].

The most common method for preparing alkanethiols SAMs is immersion of the metal substrate into an assembly solution containing thiols at room temperature. Since the properties of solvent affect the formation and the assembly mechanism of SAMs, the qualities of SAMs formed in different solvents show striking

differences. Many researchers have studied the thiol SAMs formed on gold surface in different solvents; however, the influence mechanism for thiol SAMs was uncertain. Bain et al. [13] evaluated the effect of various solvents (DMF, THF, ethanol, CCl<sub>4</sub>, acetonitrile, hexadecane, cyclooctane and toluene) on the formation of SAMs on gold. It was found that the hexadecanethiol monolayers adsorbed on gold in hexadecane exhibited low contact angles when reached the expected thickness, which possibly attributed to the incorporation of hexadecane into the monolayer. Danenberger et al. [14] reported the preparation of n-alkanethiol SAMs onto polycrystalline gold in hexane, dodecane, hexadecane and ethanol, the results showed that the rate constant of thiols adsorption in ethanol equaled to that in dodecane and solvent molecules adsorbed on the surface played a crucial role in the process of thiols adsorption. Hamoudi et al. [15] prepared the self-assembly of nonane-alkanedithiol monolayers on gold in n-hexane and ethanol. The results showed that nicely organized HSC<sub>9</sub>SH SAMs could be obtained in n-hexane under N<sub>2</sub>-degassed solutions and all preparation steps were performed in the absence of ambient light. Bensebaa et al. [16] studied the formation kinetics of C<sub>22</sub>SH-SAMs on gold by RAIRS. The results showed that an ordered film was rapidly obtained in ethanol and the SAMs formed in CCl<sub>4</sub> were more disordered. Kumar Sur and Lakshminarayanan reported that the interfacial capacitance of alkanethiol SAMs on gold was

\* Corresponding author. Tel.: +86 29 88373052; fax: +86 29 88373052.

E-mail address: [xlzhang@nwu.edu.cn](mailto:xlzhang@nwu.edu.cn) (X. Zhang).

**Table 1**  
Solvent polarity ( $E_T(30)$  and  $E_T^N$ ).

Solvent	$E_T(30)$ (kcal mol <sup>-1</sup> )	Solvent polarity ( $E_T^N$ )
n-Hexane	31.0	0.009
Toluene	33.9	0.099
Trichloroethylene	35.9	0.160
Chloroform	39.1	0.259
Acetone	42.2	0.355
Acetonitrile	45.6	0.460
Ethanol	51.9	0.654

measured by EIS and CV in different non-aqueous solvents (n-hexane, chloroform, toluene ethanol, DMF, acetonitrile and hexadecane). The results showed that the thiol-SAMs in hexane and chloroform were highly impermeable [17].

The above researches have mainly focused on solvent effect on the formation of thiol monolayers on gold. However, the effect of solvent for easy oxidized metal, such as copper, is a more complicated process in different solvents because oxides layer may occur on the metal surface during the formation of thiol-SAMs. Ron et al. [18] reported the formation of long-chain alkanethiol SAMs on copper with ethanol and toluene as solvents. It was found that ethanol had a negative effect on SAMs on copper because of its chemical interactions to copper. Better oriented and crystalline alkanethiol monolayers were obtained in toluene.

In the previous study, we found that the influence of solvent polarity ( $E_T^N$ ) on the quality of SAMs on copper was very significant.  $E_T^N$  is defined as the overall solvation capability of solvent, which depends on the summation of all molecular properties (interaction between solvent molecules and solute molecules).  $E_T^N = [E_T(30) (\text{solvent}) - 30.7]/32.4$ , where  $E_T(30)$  is the absorption energy of the Reichardt's dye. It is a simple, practical and semi quantitative method to express solvent polarity by the value of  $E_T^N$  [19].

In this paper, we focus on the effect of solvent polarity ( $E_T^N$ ) on the preparation of SAMs of n-octadecanethiol ( $C_{18}SH$ ) on pure copper surface and oxidized copper surface. The selected solvents for the preparation of SAMs are n-hexane, toluene, trichloroethylene, chloroform, acetone, acetonitrile, ethanol and their polarity ( $E_T^N$ ) is arranged from low to high (Table 1). The properties of  $C_{18}SH$ -SAMs on pure copper and oxidized copper were investigated by EIS, FTIR and XPS. The correlations between the value of  $E_T^N$  and the quality of  $C_{18}SH$ -SAMs were discussed. The experimental results provide a better understanding to the effects of solvent polarity on the structure and formation of SAMs on pure copper and surface oxidized copper.

## 2. Experimental

### 2.1. Materials and reagents

Copper slice ( $\geq 99.95\%$ ) was used as substrates (thickness was 1 mm). Octadecanethiol ( $C_{18}SH$ ,  $\geq 98\%$ ) was purchased from Aldrich. Ethanol, n-hexane, toluene, trichloroethylene, chloroform, acetone, acetonitrile (A.R., Sinopharm Chemical Reagent Co. Ltd.) were employed as solvents for thiols. Sulfuric acid and potassium chloride (A.R.) were purchased from Sigma. Deionized water (18 M $\Omega$  cm) was purified with an ion exchange system. All solvents and deionized water were removed oxygen by bubbling  $N_2$  (99.99%) for 1 h before use.

### 2.2. Sample and monolayer preparation

The copper sample was mechanically polished by a semi-automatic polishing system (Tegramin-20, Struers, Denmark) using

emery paste of 9, 3 and 1  $\mu\text{m}$  (surface roughness of  $1 \pm 0.05 \mu\text{m}$ ), then it was washed by deionized water and ethanol in the ultrasonic cleaner, respectively. The polished specimens were chemically etched in a mixed solution of  $H_2SO_4$  (3 M) and ethanol (3:1, v:v) to remove surface oxides. Then it was washed by deionized water and ethanol and immediately dried with a high-purity  $N_2$ .

The pure copper samples were transferred in the airtight PMMA glovebox which filled with  $N_2$  and were immersed in 1  $\mu\text{M}$  solution of  $C_{18}SH$  dissolved in various solvents (n-hexane, toluene, trichloroethylene, chloroform, acetone, acetonitrile, ethanol) for 24 h at the temperature of 25 °C. Then, all modified samples were rinsed by the corresponding pure solvents in the ultrasonically cleaner for 10 min to remove redundant thiol molecules and dried in  $N_2$ .

The oxidized copper samples were prepared by above the treated pure copper in a hydrogen peroxide ( $H_2O_2$ ) solution at 60 °C for 30 min. The thickness of the oxide layer was about 43 nm as measured by ellipsometry. Then oxidized copper samples were also immersed in a 1  $\mu\text{M}$  solution of  $C_{18}SH$  in various solvents for 24 h without  $N_2$  protection and temperature was also 25 °C. Then, all modified samples were rinsed by the corresponding pure solvents and dried in  $N_2$ .

### 2.3. Measurement method.

Electrochemical impedance measurements of  $C_{18}SH$ -SAMs on copper samples were performed by the electrochemical workstation (Ametek, US) including a conventional three electrode system. The working electrode was modified copper electrode (10 mm  $\times$  10 mm). The reference electrode and the auxiliary electrode were a saturated calomel electrode (SCE) and platinum foils, respectively. Test condition was an ac signal of 5 mV amplitudes using frequency range of 100 kHz to 0.1 Hz. Electrolyte solutions (0.1 M KCl) were deoxygenated by purified  $N_2$ . Film resistance and capacitance values were obtained by equivalent circuit fitting analysis using least square method.

IR spectra were recorded using a Vertex70v RAIRS spectrometer (Bruker, Germany), equipped with a grazing incidence reflection attachment using Ge as reflective crystal with an incident angle of 80° from the surface normal. A liquid-nitrogen cooled mercury cadmium telluride (MCT) detector was used. The spectra were taken at 2  $\text{cm}^{-1}$  resolution with the accumulation of 1024 scans over 4000–660  $\text{cm}^{-1}$  spectral range.

XPS analysis (Thermo Scientific, US.) of  $C_{18}SH$  adsorbed on oxidized copper were recorded using a focused monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ). The analyzer was operated with pass energy of 20 eV and the pressure was kept below  $1 \times 10^{-9}$  Torr. The peaks were calibrated with respect to the binding energy of the C1s line set at 284.6 eV. Core peaks were analyzed using a nonlinear Shirley-type background subtraction.

## 3. Results and discussion

### 3.1. Effect of solvent polarity on structure of $C_{18}SH$ -SAMs on pure copper

The structural integrity of the thiols modified pure copper is evaluated by the electrochemical impedance (EIS) [20]. Fig. 1 shows the EIS spectra (Nyquist plots) of  $C_{18}SH$  adsorbed on pure copper in different organic solvents (n-hexane, toluene, trichloroethylene, chloroform, acetone, acetonitrile and ethanol) for 24 h immersion. All the plots of  $C_{18}SH$  modified copper electrode exhibit semicircles in the entire range of frequency, implying the films have an excellent blocking behavior and a complete charge transfer control

Download English Version:

<https://daneshyari.com/en/article/5349615>

Download Persian Version:

<https://daneshyari.com/article/5349615>

[Daneshyari.com](https://daneshyari.com)