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Rapid formation of well-ordered self-assembled monolayers of dodecanethiol on polycrystalline gold by microwave irradiation

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Abstract

This article reports a rapid method of preparing self-assembled monolayers of dodecanethiol (C_{12}SH-SAMs) on polycrystalline gold by microwave irradiation (MWI, 650 W, duty cycle is 10%). The qualities of C_{12}SH-SAMs were characterized by both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results show that the C_{12}SH-SAMs formed by MWI in 120 s (C_{12}SH-SAMs$_{\mathrm{MWI,120\,s}}$) have low ionic permeability (the differential capacitance C_d values are independent of the scan rate and phase angle at 1 Hz $\Phi_{1\,\mathrm{Hz}} = 89 \pm 0.9°$), excellent electrochemical blocking ability towards the redox probe (the current $i_{\mathrm{MWI,120\,s}}$ obtained from CV is lowest when compared to other SAMs and charge transfer resistance $R_{ct} = (1.15 \pm 0.19) \times 10^6\ \Omega\,\mathrm{cm}^2$), and high surface coverage ($99.996 \pm 0.001\%$).

Keywords: Rapid formation; Self-assembled monolayer; Dodecanethiol; Microwave irradiation; Cyclic voltammetry; Electrochemical impedance spectroscopy

1. Introduction

During the course of chemical reactions, heat, light, pressure, electric field and mechanical force can provide energy for reactant molecules to overcome the thermodynamic reaction barrier and accelerate reaction rate [1]. Compared to conventional heating methods, microwave irradiation (MWI) can dramatically facilitate chemical reactions, increase product yields, and enhance product purities [2]. Recently, MWI has been applied to electrochemical processes such as adsorption, metal deposition, ECE-type electrochemical dehalogenation reactions, and electron transfer reactions [3–5]. Self-assembled monolayers (SAMs) of organothiols disulfides on metal surfaces, especially monolayers of alkanethiols on gold, have been the subject of considerable interest [6–10]. High-quality alkanethiolate SAMs are most often formed by immersing the metal into a solution containing the alkanethiol for one day to several days. The application of direct current potential and ultrasonic during the self-assembly process has shown to accelerate the assembly rate [10–12]. In this paper, we prepare dodecanethiol SAMs (C_{12}SH-SAMs) on polycrystalline gold by MWI for different time. Since the C_{12}SH-SAMs have been extensively studied and its chemical behavior is well understood, we select it as the model SAMs to inspect the MWI's effect by comparing with the common immersing method. The results of CV and EIS showed that highly dense and well-ordered SAMs can be formed in quite a short time (120 s) by MWI (650 W, duty cycle is 10%).

2. Experimental

2.1. Chemicals and apparatus

1-Dodecanethiol (C_{12}SH; 98+%, Aldrich), ethanol (⩾99.9%, Merck). All chemical reagents were of analytical

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grades (AR) and used as received. Double-distilled water was used to prepare the aqueous solutions. $C_{12}SH$-SAMs were prepared in a modified multimode microwave oven (Sanle WP650, 2.45 GHz, Nanjing, China) with pulsed MWI (650 W, duty cycle is 10%). CV and EIS measurements were performed using a CHI-660B electrochemical workstation (CH Instruments, USA). A conventional three-electrode cell was employed, with a SAM modified gold electrode as working electrode, a large-area platinum foil as counter electrode, and a saturated calomel reference electrode (SCE).

2.2. Fabrication of SAMs on gold

Polycrystalline gold electrode (2.0 mm diameter, CH Instruments) was hand-polished on microcloth pads (CH Instruments) with alumina slurries of decreasing particle size (1.0, 0.3 and 0.05 μm) and then sonicated in double-distilled water for 15 min. The gold surface was then cleaned with freshly prepared *aqua regia* solution (60% v/v H_2O, 30% HCl, and 10% HNO_3). The electrode was then rinsed with double-distilled water and cycled from –0.4 to +1.5 V in 0.5 M H_2SO_4 at 0.1 V s^{-1} until a stable baseline was obtained. According to the previously reports with the similar pretreatment method [13–16], we assume that the roughness factor of gold electrode is 1.1.

$C_{12}SH$-SAMs were prepared by keeping the gold electrodes in 10 mM ethanol solution of $C_{12}SH$ in microwave oven (650 W, duty cycle is 10%, namely the microwave oven work at 650 W for 3 s and keep silence for 27 s) for 30 s, 60 s, 120 s, 300 s and 600 s, respectively. *Special care is required when metal objects are placed into a microwave cavity.* Based on the microwave power (650 W), actual microwaving time (3 s) and electrode surface area (3.14×10^{-2} cm^2), the power density value (defined as the ratio of microwave power to electrode surface area) and irradiation dose value (defined as the product of power density and actual microwaving time) [17] were calculated to be 0.21×10^5 W cm^{-2} and 0.63×10^5 W s cm^{-2}, respectively. There is no explosion of the vapour phase caused by sparking during the SAMs preparation under microwave irradiation with these power density value and irradiation dose value. In order to avoid explosion of the vapour phase caused by sparking during the SAMs preparation under microwave irradiation, some additional safety advices and precautions are emphasized as follows: (1) the geometric gold electrode surface area (A_g) should be small, e.g. $A_g = 3.14 \times 10^{-2}$ cm^2 in this case; (2) the distance (d) between the gold electrode and the bottom of microwave oven should not be too close, e.g. $d = 2$ cm in this case; (3) the volume (V) of the ethanol should be appropriate and not be too large, e.g. $V \approx 10$ mL in this case; (4) the bottle containing ethanol and gold electrode should not be sealed; (5) the ethanol should not be boiled. In addition, the microwave leakage should be avoided. Readers are advised to take appropriate precautions. Prior to electrochemical characterization, the SAM-coated electrode was rinsed with a copious amount of absolute ethanol followed by double-distilled water.

2.3. Electrochemical characterization

Supporting electrolyte, 0.1 M Na_2SO_4, was purged with highly pure nitrogen gas for 10 min prior to measurements, and kept under an nitrogen atmosphere during the course of the experiments. All experiments were carried out at 25 ± 1 °C. CV measurements: (a) C_d was calculated from CV performed from –0.2 to 0.2 V at different scan rate in 0.1 M Na_2SO_4 [13]; (b) the current i was obtained from CV performed in 0.1 M Na_2SO_4 containing 2 mM $K_3Fe(CN)_6$ at 0.1 V s^{-1}. EIS measurements: (a) phase angle at 1 Hz $\Phi_{1\ Hz}$ and C_d were obtained by EIS performed in 0.1 M Na_2SO_4 with frequency ranging from 1 Hz to 100 kHz and 5 mV amplitude at 0 V [13,18,19]. (b) R_{ct} was measured using EIS performed in 0.1 M Na_2SO_4 containing 2 mM $K_3Fe(CN)_6$-2 mM $K_4Fe(CN)_6$ with frequency ranging from 0.1 Hz to 100 kHz and 5 mV amplitude at the formal potential of the redox couple (0.18 V).

3. Results and discussion

3.1. Cyclic voltammetry

(a) CV performed in 0.1 M Na_2SO_4 without any redox species.

C_d values were determined by $C_d = i_c/2vA$ (Table 1) [13], where i_c is the sum of the cathodic and anodic capacitive current measured at 0 V, v is the scan rate, and A is the real electrode area. The C_d value of the $C_{12}SH$-$SAMs_{MWI,120\ s}$ is independent of the scan rate and is in agreement with previous reports (1.1–1.2 μF cm^{-2}) [9,13], therefore, SAMs can be considered to resist ionic permeation [20]. The thickness d value of the monolayer can be calculated using $d = \varepsilon\varepsilon_0/C_d$ [20], where ε is the dielectric constant, ε_0 is the permittivity of vacuum, C_d value was measured at 20 V s^{-1}. The d value of the $C_{12}SH$-$SAMs_{MWI,120s}$ was calculated to be 17.8 ± 0.6 Å. The tilt angle φ value of the molecules in this monolayer was calculated to be 28.3 ± 4.3° from the gold surface normal using $\varphi =$ across$(d/l) \times 180/3.14$, where l is the length from gold surface to the chain end of $C_{12}SH$ (20.3 Å) [20–21]. These values are similar to previous reports (17 ± 1 Å and 25–30°) [21–22]. These results indicate that highly dense and organized $C_{12}SH$-SAMs can be formed by MWI at 650 W (duty cycle is 10%) in 120 s.

(b) CV performed in 0.1 M Na_2SO_4 containing 2 mM $K_3Fe(CN)_6$.

$C_{12}SH$-SAMs prepared by MWI do not show any peak formation (Fig. 1b), as the redox reaction is completely blocked by the monolayer [18]. The magnitude of the current order is as follow: $i_{MWI,120\ s} < i_{RT,24\ h} < i_{MWI,300\ s} < i_{MWI,600\ s} < i_{MWI,60\ s} < i_{MWI,30\ s} \approx i_{67°C,120\ s} < i_{RT,120\ s}$ (MWI, RT and 67 °C mean that the SAMs were formed by MWI,