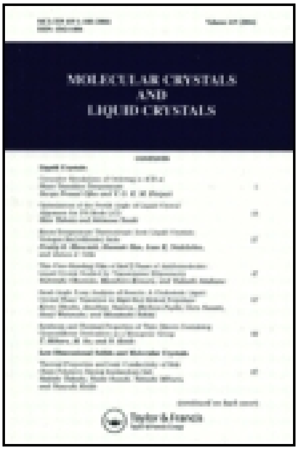

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Technique for Determination of Gold Electrode Area and its Application of Characterization in Self-Assembling Process

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Technique for Determination of Gold Electrode Area and its Application of Characterization in Self-Assembling Process

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Underpotential deposition(UPD) of copper at polycrystal gold surface under different concentrations has been studied, and its reversibility and stability in high concentration (0.2M $CuSO_4$+0.1M H_2SO_4) have been demonstrated by cyclic voltermmetry and EQCM. A valid approach to determine the gold electrode area in presence of adsorbed species has been provided by using Cu UPD method. Further, the growth kinetics of decane thiol on gold has also been investigated based on such a Cu UPD technique.

Keywords: underpotential deposition(UPD); self-assembled monolayers

INTRODUCTION

In the studies of real-time characterization of surface process, the knowledge of the active or effective surface area of the given substrate is of fundamental importance. Although many methods[1-3] have been used for estimation of the electrode surface area, maybe they are unavailable to calculate the surface area with adsorbed molecules.

The underpotential deposition (UPD) of copper on gold electrode plays a significant role, and has been widely studied[4-6]. Previous work showed that the adlayer copper atom of UPD has well-defined structure on single crystal gold, and such an adsorbed structure is proportional to surface area[4]. Here we provide an easy-to-used method for determining the gold surface area based on Cu UPD. Further, the assembling process of decane thiol($C_{10}SH$) SAMs was investigated using this method.

EXPERIMENTAL

Decane thiol($C_{10}SH$) was purchased from Aldrich Chemical Company. $CuSO_4$(A.R) purchased from Beijing Chemical Co. was used in this work. All other chemicals were used without further purification.

The electrochemical experiment was described in previous work[7], and the UPD of copper was taken in 0.2M $CuSO_4$+0.1M H_2SO_4 solution. The variation of mass involved in UPD process was monitored by the time-resolved EQCM system (made in Wuhan University, China). The nominal oscillation frequency of the AT-cut quartz crystal was 9 MHz. Self-assembled monolayers were formed by conventional self-assembling technique. 0.05 mM of $C_{10}SH/C_2H_5OH$ was used as assembling solution.

RESULTS AND DISCUSSION

UPD BEHAVIOR OF COPPER ON NAKED GOLD ELECTRODE

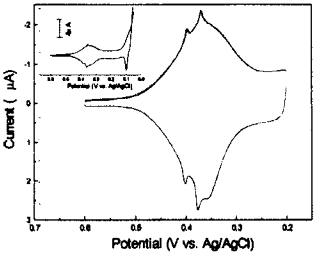

FIGURE 1 Cyclic voltammograms of naked Au electrode in 0.2 $CuSO_4$+0.1M H_2SO_4 Scan rate: 0.1 V/s

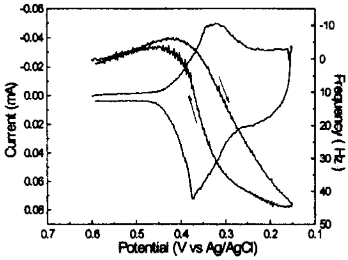

FIGURE 2 In-situ EQCM of naked Au electrode in 0.2M $CuSO_4$+0.1M H_2SO_4. Scan rate: 0.1 V/s

Figure 1 shows a typical Cu UPD behavior on naked Au electrode. The cyclic voltammograms (CVs) show one pair of symmetrical broad waves with two pairs of small and sharp peaks. Here these small and sharp peaks do not emerge on the single crystal surface[4], so they seem to be corresponded to Cu UPD on different gold facets. When the potential scan expands negatively more than 0.05V, the normal bulk deposition and stripping peaks of 3D Cu cluster will possibly occur (see insert). Therefore, it is considered that the Cu UPD appears in the potential scan range from 0.6V to 0.1V.

The UPD behavior of copper under high concentration was also investigated by in-situ EQCM at scan rate 0.005~0.5V/s. Fig.2 shows both the changes of current and frequency while potential scan proceeds. From the difference of frequency at 0.25V and 0.5V, we can obtain the change of mass in UPD process as 57ng, and the corresponding change of faraday's coulomb as 0.048mC, implying that a copper atom plus two sulfates coadsorbs in this process. The number of sulfates was larger than that under low concentration of $CuSO_4$[5].

The Cu UPD behavior was also studied in different concentrations of $CuSO_4$ with 0.1M H_2SO_4 at 0.1V/s. The symmetric wide peaks were not observed in lower concentration(less than 0.02 M, Fig.3a and Fig.3b), and the CV behaviors are so alterable that the integration of current waves can hardly be carried out. This behavior is very similar to Yoneyama's work[6]. On the contrary, the Cu UPD behavior has high stability and reversibility in 0.2M $CuSO_4$+0.1M H_2SO_4 (Fig3c). So it was taken as the optimum condition for measurement of electrode area.

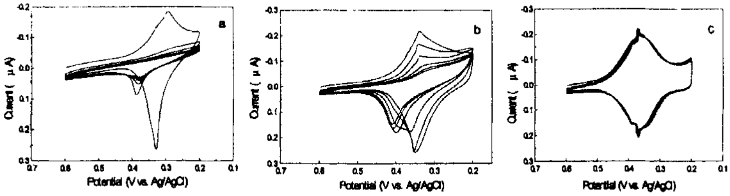

FIGURE 3 Effect of concentration of $CuSO_4$ on UPD behavior a) 0.002M; b)0.02M; c)0.2M

DETERMINATION OF SURFACE AREA AND SURFACE COVERAGE OF SAM

Assuming that the Au (111) surface is predominant at polycrystal gold electrode surface, the measurement of Cu-adlayer-occupied area could be extended into estimating the real area of polycrystal gold electrodes similar to Soriaga et al. method[1] by the following equation:

$$A = Q / Q_{calc} \qquad (1)$$

Where Q is the integrated coulomb derived from cathodic or anodic waves in Fig.1 for naked gold area, Q_{calc} the calculated integrated coulomb per unit area. The number of atoms of an ideal Au (111)-(1×1) surface is $1.39\times10^{15}/cm^2$. Therefore, a charge of $Q_{calc}=0.44\ mC/cm^2$ is expected to be required for the desorption of a UPD monolayer of Cu atoms which occupy each Au atom, corresponding to two electrons per Cu atom[4]. The calculated electrode area is equal to $0.40\pm0.04mm^2$. This value is less than those calculated by another method, such as integration of Au-oxide reduced peak ($A=0.59\pm0.05$), because Cu atom acts as a small probe in the measurement.

Using this method, the self-assembling process of $C_{10}SH$ on gold electrode was also investigated. Fig. 4a shows the typical CV of Cu UPD in the presence of $C_{10}SH$ SAM. The Cu deposition/stripping peaks can be observed with a considerable peak separation, because the presence of $C_{10}SH$ SAM leads to inhibiting of both deposition and stripping. The stripping peak has a well-defined shape which could be used to determine the free gold area using the above treatment.

Self-assembling process corresponds to the decrease of active surface area. Previous studies demonstrate that the growth is in agreement with the simple first-order Langmuir adsorption kinetics

$$d\theta / dt = k_{ad} c\,(1-\theta) \quad \text{i.e.} \quad \ln(1-\theta) = -k_{ad} C\, t \qquad (2)$$

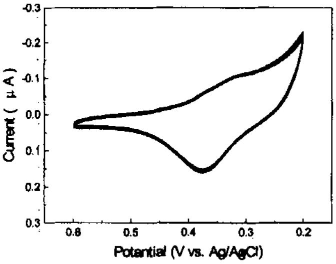

FIGURE 4a The typical UPD behavior of copper on SAM modified electrode

Assembling time: 9s

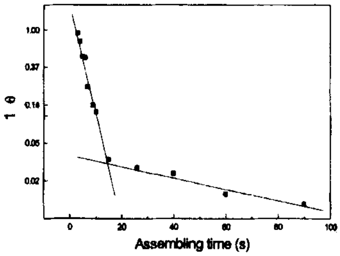

FIGURE 4b Plot of 1-θ against assembling time

where θ is the fraction of occupied sites. Here θ was replaced by $\theta = 1-Q_t/Q_0$. Q_0 is the integrated coulomb of Cu UPD at naked gold electrode. Fig.4b shows the relationship of 1-θ with t. Two steps of growth were observed in our experiment. Using equation (2), the k_{ad1} and k_{ad2} were obtained to be $5.76\times10^3 mol^{-1}dm^3s^{-1}$ and $3.23\times10^2 mol^{-1}dm^3s^{-1}$, respectively. We consider that the self-assembled molecules on gold surface undergoes a transition from disorder to order arrangement in the self-assembling process.

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