In situ STM imaging of polyethylene glycol adsorbed on an Au(111) electrode in pH 3

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ABSTRACT

In situ scanning tunneling microscopy (STM) is used to examine the electrified interface of Au(111) immersed in a pH 3 sulfate medium containing polyethylene glycol (PEG) with an average molecular weight of 6000. The cyclic voltammograms thus obtained show two sharp peaks at -0.35 and -0.38 V (vs. reversible hydrogen electrode), which correlates with the STM observation of a highly ordered $(2 \times 2\sqrt{3})$rect structure and the adsorption of PEGs. X-ray photoelectron spectroscopy is used to examine the film formed at -0.4 V, revealing prominent C–C and C–O–C structures, thereby supporting the view of adsorption and reduction PEGs on the Au(111) electrode. STM imaging at the initial stage of PEG's adsorption reveals winding linear segments 0.6 nm wide and 20–40 nm long, implying helical conformations of PEGs. The PEG film dissolves and yields a high density of nanoclusters, as the potential is switched stepwise from -0.4 to 0.9 V.

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1. Introduction

Polyethylene glycol (PEG) together with chloride is known to suppress copper electrodeposition, which is of critical importance in the current process of Cu electroplating. The adsorption of PEG at electrified interfaces of Cu, Ag, and Au has been studied with a variety of techniques, including Raman spectroscopy [1], quartz microbalance [2], ellipsometry [3], and scanning tunneling microscopy (STM) [4]. It is known that the aforementioned suppressing can arise from the formation of a stable PEG-Cu$^+$-chloride complex during Cu deposition [1], which holds back the reduction reaction of Cu$^+$ [1]. Moreover, the adsorption of PEGs depends greatly on the presence of chloride and electrode potential [2].

In situ STM has been used to study the adsorption of molecules at electrified interfaces [5], and not only have small molecules been reported for this, but also polymeric species, such as polyaniline anodically deposited on Au(111) and Au(100) electrodes [6,7]. The difficulty in achieving high-quality STM images of adsorbate is inversely proportional to the strength of adsorption. PEG is notorious for its weak interaction with metal electrodes, which makes it difficult to be imaged by STM. An STM study of PEG's adsorption on Au(111) electrodes was first reported in 2004, but this only yielded images of the reconstructed Au(111) substrate, and not the PEG admolecules [8]. However, in 2012 a small PEG

molecule (MW 200) was imaged, which was possible due to its strong interaction with a Pt(111) substrate [9]. Since then, we have continued to investigate the adsorption of large PEG molecules on a metal electrode. In this report, we show clear STM images obtained with PEG (with an average molecular weight of 6000) adsorbed on Au(111) in pH 3 sulfate media.

2. Experimental

The Au(111) electrode was a single bead made of gold wire. The preparation and pretreatment of the electrode followed the conventional procedure. The potentiostat used for the CV experiments was a CHI 627 (Austin, TX). The electrochemical cell was equipped with a Pt counter and a reversible hydrogen electrode (RHE). The STM is a DI machine (formerly Veeco, Santa Barbara, CA) equipped with a high-resolution scanner A (maximal scan size of 500 nm). The tip was made out of a tungsten wire by etching in 1 M KOH. Apeazon wax was applied to coat the whole tip for insulating purposes. All STM images presented in this report were acquired with the constant-current mode. Suprapure sulfuric acid and potassium sulfate were purchased from Merck (Darmstadt, DFG), and triple-distilled water (Milli-Q, Billerica, MA) was used to prepare all electrolytes. Guaranteed reagent and analytical grade PEG6000 was obtained from Sigma-Aldrich (St. Louis, MO), and this actually contains polymers with molecular weights ranging between 6170 and 6690. X-ray photoelectron spectroscopy (XPS) was carried out with a Sigma Probe (Thermo Scientific) with a microfocused and monochromatic Al Kα X-ray source (1486.6 eV, 400 μm) at a takeoff

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angle of 45° from the surface normal. The system was pumped down to below 10^{-10} Pa. Spectra were collected with a pass energy set to 58.7 eV. The Au 4f peaks at 84 and 88 eV are used as internal standards for the binding energy.

3. Results and discussion

3.1. Characterization with cyclic voltammetry

Fig. 1a shows the *steady-state* CV (dotted line) recorded at a potential scan rate of 500 mV/s with an Au(111) electrode in 0.1 M K_2SO_4 + 1 mM H_2SO_4 (pH 3). The morphology of the CV is similar to that obtained in 0.1 M H_2SO_4 [10], where two pairs of peaks due to the adsorption of (bi)sulfate anions and a coupled structural transition of the Au(111) substrate are seen at 0.55 and 0.73 V. In 0.1 M H_2SO_4 more (bi)sulfate anions are adsorbed with more positive potential, leading to a disorder-to-order transition of the adsorbed bisulfate at 1.05 V. This is not seen in the present pH 3 sulfate media. At E < −0.2 V hydrogen evolution causes a rapid increase in current. According to the reported results, the point of zero charge (pzc) of an Au(111) electrode is about 0.5 V [11], the onset of (bi)sulfate adsorption.

The CV obtained in 0.1 M K_2SO_4 + 1 mM H_2SO_4 (pH 3) + 0.1 mM PEG6000 features two sharp reduction peaks at −0.35 and −0.38 V (C2 and C3) before hydrogen evolves at E < −0.45 V, and only one oxidative peak A2 is seen at −0.35 V in the reversed scan, as revealed by the solid trace in Fig. 1a. The sharp peak shapes of C2 and C3 imply that they originate in the adsorption and desorption of species present in the PEG sample, which causes a negative shift of the H_2 evolution reaction by about 0.2 V. At E > 0.6 V the adsorption of bisulfate anions gains importance, as manifested in a pair of symmetric peaks at 0.72 V, with this value being 0.1 V more positive than that seen in the absence of PEG. These CV results are also observed PEGs that have molecular weights of 2000 and 8000 (not shown).

Voltammetric experiments in pH 7 K_2SO_4 solution containing 0.1 mM PEG6000 were performed to compare the results with those obtained in pH 7 Na_2SO_4 [4]. The resultant CV is shown in Fig. 1b, revealing a pair of broad peaks at 0.74 V (B1/D1) at the positive end and two pairs

of peaks at −0.34 (B2/D2) and −0.42 V (B3/D3) before hydrogen evolution. These features are similar to those seen in the pH 3 medium, as described above. More importantly, these features are essentially the same as those reported by others [4], except B3/D3 is overlooked by the previous study, as the negative end of the potential window was set at −0.40 V in the former work.

3.2. In situ STM and XPS characterization

Fig. 2a–b show STM images acquired with an Au(111) electrode potentiostated at −0.36 V in 0.1 M K_2SO_4 + 1 mM H_2SO_4 + 0.1 mM PEG6000. Distinct ordered structures are seen on the reconstructed Au(111) – ($\sqrt{3} \times 22$) structure characterized by a parallel linear pattern. Based on the dimensions of the unit vectors (marked as I and II in Fig. 2b), this ordered structure is designated as $(2 \times 2\sqrt{3})$rect. This STM result corresponds to the sharp peak of C2 in the CV (Fig. 1a). It is difficult to envision that a soft linear molecule such as PEG6000 could be adsorbed in such a well-ordered pattern seen in Fig. 2a–b. Because this ordered $(2 \times 2\sqrt{3})$rect structure was imaged shortly (<5 min) after the PEG sample was admitted into the STM cell, it is unlikely this structure is due to some small organic molecules derived from the decomposition of PEG6000 molecules, if this ever happened. It seems that the PEG used in this study is contaminated with some unknown organics.

The nature of the C3 peak in the CV was examined by changing the potential abruptly from −0.36 to −0.4 V in an upward STM scan (indicated in Fig. 2c), followed by an immediate scan, as shown Fig. 2d, revealing notable changes at the electrode within 1.5 min. A number of corrugated patches emerge on terraces and at step defects, and then grow within 1 min into prominent islands with crooked perimeters. These results indicate a random, not defect-oriented nucleation of adsorbates. Islands grow with time and eventually (~30 min) coalesce into a uniform thin film, residing on the reconstructed Au(111) substrate, as revealed by the inset of Fig. 2e. This film is stable against protracted STM scanning under an appropriate tunneling current and bias voltage of 0.2 nA and 500 mV. It is 0.12 ± 0.02 nm higher than the gold substrate, and does not thicken with time. It is possible to obtain molecular-resolution STM imaging of the PEG deposit only at the initial stage. Winding linear protrusions are 0.6 nm wide and 20 ~ 40 nm long, which can match the dimensions of PEG6000 admolecules, depending on their conformations. Ideally, PEG6000 are ca. 44 and 33 nm long in the fully extended and the 7/2 helix conformations [12,13] (seven monomeric units turn two times per fiber period). The operating conditions greatly affect the imaging quality of STM, as the tip comes into physical contact with the sample.

The potential was then switched stepwise from −0.4 to 0.9 V to see its effect on a compact PEG film formed after prolonged (~30 min) STM imaging at −0.4 V. The results showed it hardly changed at E < 0.7 V, but dissolved slowly at 0.7 V (Fig. 3a) and rapidly at 0.9 V (Fig. 3b), leaving spots statistically dispersed on the surface. These features measure 1 ~ 2 nm wide and 0.16 nm high, and are stable at 0.7 V or more positive potentials. It is possible that the adsorbed PEGs could decompose at some point during the STM imaging of the PEG film at −0.4 V. The dissolution at E > 0.7 V likely results from the adsorption of (bi)sulfate, which competes with and displaces the adsorbed PEGs. In order to confirm the adsorption of PEG, we used X-ray photoelectron spectroscopy (XPS) to analyze the film deposited on Au(111) potentiostated at −0.4 V. The spectra of C1s shown in Fig. 3c have a prominent peak at 284.7 eV and a shoulder at 286.5 eV, which are ascribed to C–C and C–O structures. The former is unexpected for adsorbed PEGs, which suggests that some adsorbed PEGs are reduced at −0.4 V, producing C–C structure in the film. In line with these results, an O1s emission yields a major peak at 532 eV (Fig. 3d), indicating an organic C–O functional group. These XPS results support the existence of PEGs on the gold electrode.
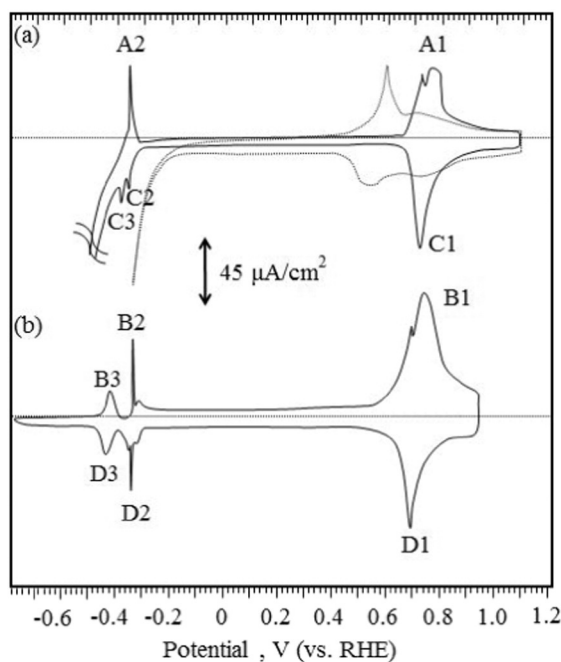

Fig. 1. CVs recorded at 500 mV/s with an Au(111) electrode in pH 3 (a) and pH 7 (b) 0.1 M K_2SO_4 + H_2SO_4 (dotted lines) + 0.1 mM PEG6000 (solid line).