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Short Communications

Nanocomposite Monolayer of Copper and Lead on Gold and Its Effect on Nitrate Electroreduction

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The nanocomposite surface layer of copper and lead on Au was produced by solution-phase electrochemical methods called dipping technique. Submonolayer of Cu and Pb on Au was deposited electrochemically in series. Copper was deposited under semi-infinite linear diffusion controlled condition where thickness of copper can be controlled by deposition time. In the same solution, underpotential deposition (upd) of lead on the Cu modified Au(111) was performed with and without nitrate. The composite surface showed a top-on-top layer of Pb-Cu thin film on Au and alloying was not observed. The composite surface demonstrated catalytic nitrate reduction by copper adatom. Pb adatom on Cu modified Au showed a blocking effect on catalytic nitrate reduction so that catalytic reduction disappeared by the blocking active sites of Cu by Pb.

Keywords: Underpotential deposition, Nanocomposite, Nitrate reduction, Electrocatalyst, Adlayer

1. INTRODUCTION

Physicochemical properties of nanocomposite metallic surfaces differ from those of bulk materials due to quantum size effects. Goodman et al. reported that the unusual catalytic activity of gold clusters depends on the thickness of clusters and the unique catalytic property can be achieved as one dimension of the metal becomes smaller than several monolayers [1]. Composition, as well as dimension, can affect the performance of catalysts. Multimetallic clusters have drawn interest due to a combination of both effects.

Thin composite films are the alternative targets to study effects of composition and local structure as a catalyst [2]. While most of composite surfaces are manufactured by UHV techniques under high temperatures and low pressures, underpotential deposition (upd) can be an economic procedure that forms highly ordered surface structures from the liquid phase under ambient conditions. In addition, the structure, coverage and other phenomenon of upd are well known [3,4], so a precise and deliberate control of surface coverage and structure is possible. However, only a limited number of the surface composite layers using upd have been reported [5-9]. Jüttner et al. deposited Ag and Pb on Au(111) using the dipping technique [7]. In this technique, Ag was deposited under semi-infinite linear diffusion controlled conditions concurrently with the upd of Pb in the same solution. Abruña and co-worker showed the co-adsorption of upd copper and irreversibly adsorbed bismuth on Pt(111) and Pt(100) [8]. After bismuth was deposited irreversibly, the electrolyte was replaced with copper solution. Laibinis et al. demonstrated composite monolayer of Ag and Cu on Au(111) by sequential underpotential deposition [9]. Ag (the more noble metal) was underpotentially deposited and the modified electrode was removed from the silver electrolyte and replaced with copper solution. Then, Cu (the less noble metal) was deposited underpotentially. They suggested that the less noble metal must not underpotentially deposit onto the more noble adlayer to prepare a laterally mixed single monolayer. Recently, Hwang et al. reported the cooperative catalytic activity of composite surfaces of Ag-Pb/Au by sequential underpotential deposition on nitrate reduction [10]. Nanocomposite monolayer of silver and lead by sequential upd process showed the enhanced catalytic effect on nitrate electroreduction.

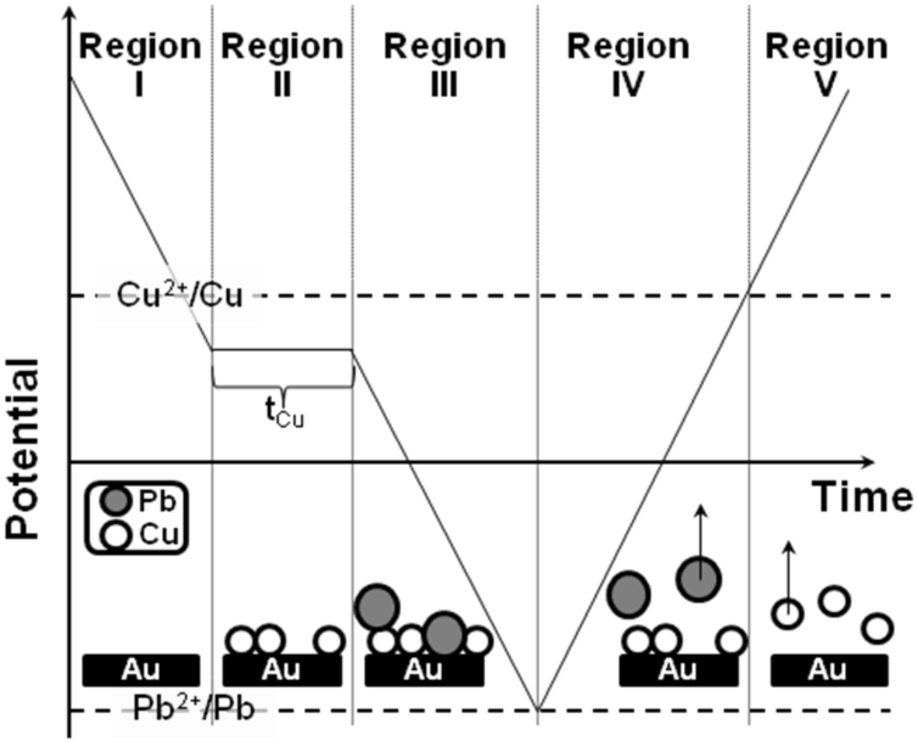
Herein we report the electrochemical formation of two-component metal thin films (copper and lead) on Au and its effect on nitrate electroreduction. Using dipping method, copper was deposited under semi-infinite linear diffusion controlled condition where thickness of copper can be controlled by deposition time. In the same solution, Pb upd process on the Cu modified Au(111) was characterized by cyclic voltammetry (CV) with and without nitrate. The composite surface showed a top-on-top layer of Pb-Cu thin film on Au and alloying was not observed. The composite surface demonstrated catalytic nitrate reduction by copper. Pb upd on Cu blocked the active sites so that catalytic reduction disappeared.

2. EXPERIMENTAL SECTION

Voltammetric data were collected using a Pt wire counter electrode and a saturated Hg/Hg_2SO_4 reference electrode (MSE) connected to the electrochemical cell via a capillary salt bridge to minimize contamination from the reference electrode. The solution was purged with Ar prior to use, and an atmosphere of Ar was maintained in the cell during all electrochemical measurements. Potential control and sweeps were established using an Autolab potentiostat (Eco Chemie, Netherlands).

The solution for electrochemical deposition was composed of 0.1 M H_2SO_4, 5 mM PbO, and 10 μM $CuSO_4$. The polarization routines employed to investigate the sequential deposition of copper and lead are shown in Scheme 1. Cu was deposited at -0.5 V vs MSE where Cu is under extremely diffusion controlled condition caused by low concentration. Therefore, the coverage of Cu can be easily controlled by variation in deposition time. Pb is underpotentially deposited on Cu modified Au(111) with a negligible additional deposition of Cu at these potential. Gold working electrodes, with the electroactive area of 0.283 cm^2, were prepared by electron beam evaporation to produce a titanium layer 40 nm thick and a gold layer 150 nm thick on the silicon (100) wafer surfaces. The electrodes were cleaned in piranha solution (1:3 [v/v] H_2O_2/H_2SO_4), rinsed with water, and dried under N_2 gas.

(WARNING: piranha reacts violently with organics). Copper substrate is deposited electrochemically on gold substrate by defect-mediated growth [11,12].



Scheme 1. Schematic potential program for dipping technique. In region II, the deposition of copper takes place under extremely diffusion controlled condition, so that the coverage of copper can be controlled by variation of t_{cu}. Subsequent potential scan in region III and region IV enables adsorption and desorption of Pb upd on Cu modified Au substrate, respectively. Continued potential scan desorbs copper adatoms indicating the coverage from charge.

3. RESULT AND DISCUSSION

3.1 Formation of Composite Layer of Copper and Lead by Dipping Technique

To deposit composite monolayer of copper and lead, Au substrate was subjected to the sequence of potential scans and steps as shown in Scheme 1 in the electrolyte containing 0.1 M H_2SO_4, 5 mM PbO, and 10 μM $CuSO_4$. Caused by very low concentration of Cu^{2+}, the bulk deposition of Cu in region II (at -500 mV vs MSE) takes place under strictly diffusion-controlled condition so that the coverage could be determined by variation of t_{cu}, the Cu deposition time. The subsequent underpotential deposition and corresponding desorption of Pb takes place in region III and region IV, respectively. Finally, Cu was desorbed in region V and the coverage of Cu was calculated from the charge of copper stripping.

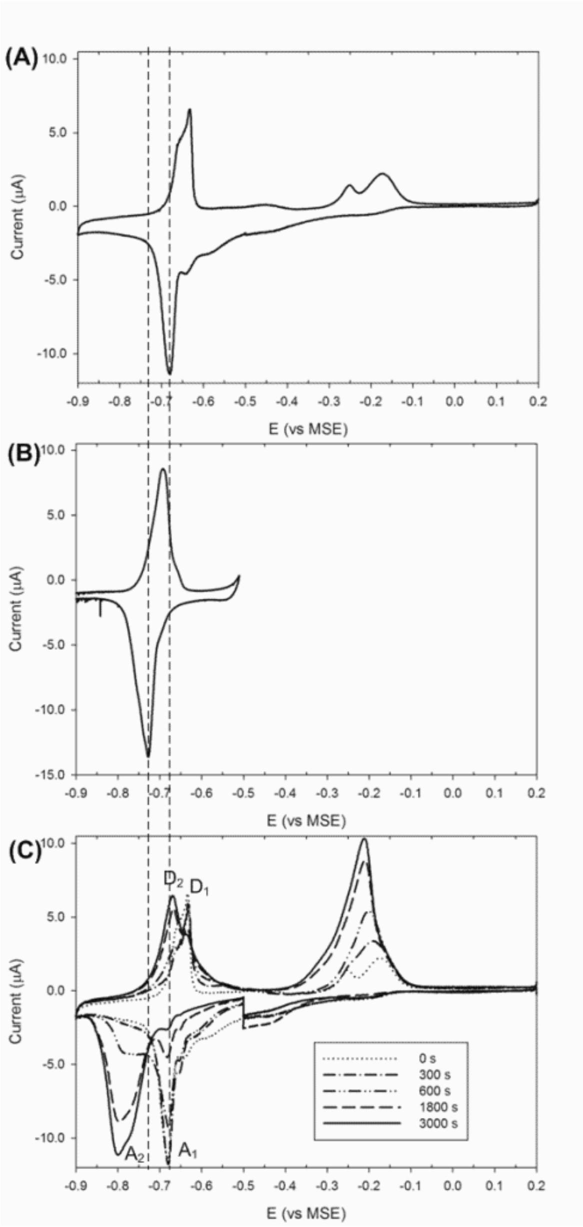


Figure 1. CVs for Pb upd in 10 μM $CuSO_4$, 5 mM PbO, and 0.1 M H_2SO_4: (a) on Au substrate (b) on Cu substrate (c) on Cu modified Au with various coverage of Cu by variation of t_{cu}. Scan rate = 0.01 V/s.

Figure 1 shows cyclic voltammograms (CVs) of Pb upd. Pb upd on Au substrate in the absence of copper ion in Figure 1(A) exhibited the typical CV of the Pb upd on Au, which was consistent with the ones previously rerpoted [13]. The CV of Pb upd on Cu substrate shown in Figure 1(B) is also in good agreement with the previously reported studies on the Pb upd on Cu(111) electrode [14]. Figure 1(C) is CVs of Pb upd on copper modified Au with various coverage. At t_{cu}=0, CV was similar to Figure 1(A) demonstrating that the deposition of copper during potential scan is negligible due the extremely diffusion controlled condition. As coverage of copper increase by elongated t_{cu}, the Pb upd peak around -680 mV and corresponding desorption peak (A_1/D_1) decrease while adsorption peak at -800 mV and corresponding desorption peak at -670 mV (A_2/D_2) appears. Comparing CVs of the Pb upd on Au substrate and on Cu substrate in Figure 1(A) and Figure 1(B), respectively, with CVs in Figure 1(C), it is obvious that A_1/D_1 can be attributed to the Pb upd on Au and the peaks A_2/D_2 to Pb upd on Cu. Both gold and copper contributed to the Pb upd, indicating that formation of copper layer was insufficient to completely screen the properties of gold substrate. Assuming 445 $\mu C/cm^2$ for the epitaxial deposition of copper monolayer on Au(111) [9], the coverage of copper at t_{cu}=3000 s was ca. 0.67 ML from stripping charge of copper at -200 mV. Another interesting phenomenon in the Pb upd on Cu-modified Au is the peak shift of the Pb upd on Cu. While the peaks corresponding to the Pb upd on Au (A_1/D_1) was observed at the same potential as that on the bare Au (Figure 1(A)), the peaks corresponding to Pb upd on Cu (A_2/D_2) showed a slight negative shift. The explanation for this phenomenon might be electronic interaction between thin copper adatoms and the gold substrate so that the properties of the submonolayer copper may differ from thick copper layer. Overall, the Pb upd on the copper-modified Au by variation of t_{cu} showed that the Pb upd on the open Au site decreased as more Cu adatoms cover the Au substrate. On the other hand, the Pb upd on the Cu adatoms increased and the electronic interaction between the Cu adatoms and the gold substrate slightly changed the characteristics of the Pb upd.

3.2 Electrocatalytic Nitrate Reduction on Cu-Pb/Au

The catalytic effect of the Cu-Pb/Au for nitrate reduction was investigated in the presence of nitrate. Figure 2 exhibits CVs for Pb upd in the presence of 5 mM $NaNO_3$ on a Cu modified Au electrode. The catalytic current from nitrate reduction on the Cu modified Au rises abruptly at ca. -500 mV. The peak of the current was observed at -740 mV and dropped to a small value at ~ –900 mV because the completed Pb upd on both the Cu and the Au sites at this potential region inhibited the catalytic effect. Previous study reported a similar inhibition of hydrogen evolution or oxygen reduction system [13]. As the coverage of copper increased by elongated t_{cu}, the catalytic current also increased indicating that copper sites are active toward nitrate reduction. Compared with CV for nitrate reduction on Cu modified Au in the absence of Pb^{2+}, the catalytic current decreased while the onset potential for nitrate reduction kept constant. In previous studies, a number of Pb islands grew at potentials positive of peak A_1 on gold surface [15]. Assuming that Pb islands are formed on Cu at the positive potential similarly, the diminished catalytic effect in the presence of Pb ions is caused by the blocked area of copper by these Pb islands on Cu. The catalytic current started decreasing at -740 mV, where the Pb upd completely covers the open Au site but not the Cu site. Therefore, the Pb upd layer on the Au site does not affect the catalytic effect for nitrate reduction. In addition, the current dropped to a small value at -900 mV where the Pb upd covers both the Au and the Cu sites indicating that Pb upd layer on Cu inhibited the catalytic nitrate reduction. These imply that catalytic reduction of nitrate occurs only at the Cu site and that the Pb layer on Cu inhibits the catalytic effects. The overall results are summarized in Scheme 2. In previous reports on nanocomposite monolayer of Ag-Pb/Au, trimetallic composition (Ag, Pb, Au) was crucial for nitrate electroreduction [10]. In contrast to Ag, Cu does not show any enhanced catalytic effect in the presence of thin Pb upd. The catalytic effect of Cu for nitrate reduction may be originated from copper surface, or Cu/Au interface. Our results demonstrate that only the Cu site is the active site for nitrate reduction because catalytic activity is high even when the Pb upd layer covers the whole Au site as shown in Scheme 2.

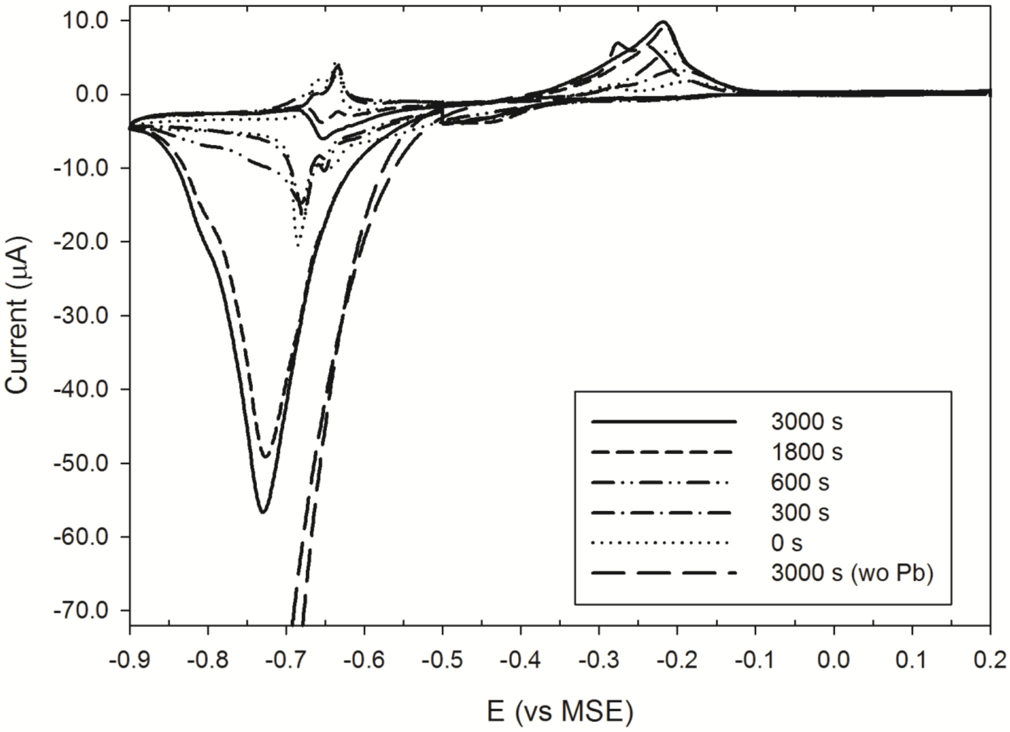
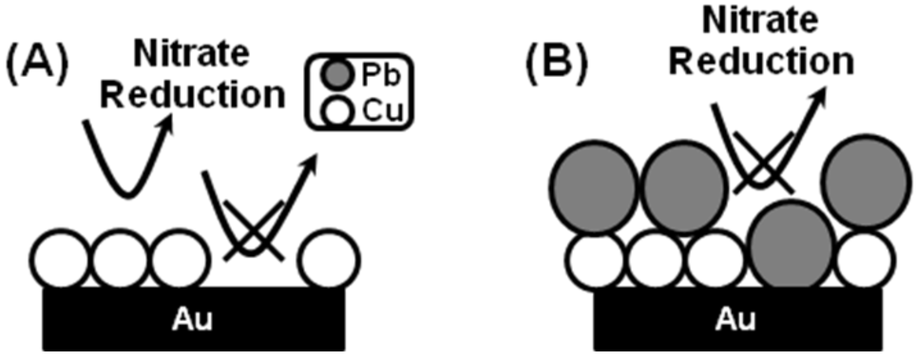


Figure 2. CVs for Pb upd in 10 μM $CuSO_4$, 5 mM PbO, 5 mM $NaNO_3$ and 0.1 M H_2SO_4 on Cu modified Au with various coverage of Cu by variation of t_{cu}. As a control, CV without Pb in 10 μM $CuSO_4$, 5 mM $NaNO_3$ and 0.1 M H_2SO_4 was shown. Scan rate = 0.01 V/s.



Scheme 2. Schematic diagram of nitrate reduction (A) on copper modified Au and (B) Pb upd layer on Cu modified Au.

4. CONCLUSION

A composite surface layer of Cu and Pb on Au could be produced by solution-phase electrochemical methods called dipping technique. Submonolayer of Cu and Pb on Au was deposited electrochemically in series. The voltammograms of Pb upd on Cu-covered Au exhibited contributions of both the Au and the Cu sites while the Pb upd on the Cu thin layer showed a slight change in potential probably due to electronic interaction of the Cu adatoms and the Au substrate. The Cu-Pb/Au composite monolayer system showed a blocking effect on catalytic nitrate reduction which is an intriguing subject of fundamental interest in nitrogen cycle [16]. The dipping technique is expected to be useful as a new synthetic route for novel bimetallic adlayer on substrate with possible electrocatalytic capabilities and atomically tailored interfacial properties.

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