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Pt Nano-Layer Formation by Redox Replacement of Cu Adlayer on Au(111) Surface

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Platinum is one of the most important catalysts for many chemical and electrochemical reactions.[1] Deposition of small amount of platinum on metal surfaces has been shown to improve the electrocatalytic properties of the metal electrodes.[2] Platinum does not exhibit underpotential deposition (UPD) behavior and studies showed that electrochemical deposition of platinum on Au(111) surface from platinum complex solutions proceeded with a layer by layer growth mode to form a multilayer of Pt,[3] or produced 3D clusters and a cauliflower-like Pt appearance[4] or Pt nanoparticles.[5,6] Recently a new method, which is now recognized as surface limited redox replacement reaction (SLR^3), was presented to prepare a Pt submonolayer/monolayer on gold surface.[7,8] This method has been widely used to form a Pt adlayer on golds for different purposes.[8,9]

Since controversy exists on the platinum film electrochemically deposited by using $PtCl_6^{2-}$ versus $PtCl_4^{2-}$,[3,4] and a single UPD Cu replacement with Pt(II) ions can yield a full monolayer but the previous elaboration was limited to $PtCl_6^{2-}$ case only,[7] we investigated the redox replacement of UPD Cu adlayer on Au(111) in $PtCl_4^{2-}$ solutions as a function of time by using X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and scanning tunneling microscopy (STM).

All chemicals were of the best quality available commercially and used as received. A Au (111) single crystal was prepared as before.[10] XP spectra were obtained using a Rigakudenki model XPS-7000 X-ray photoelectron spectrometer with an Mg Kα radiation. STM measurements were carried out as before.[11]

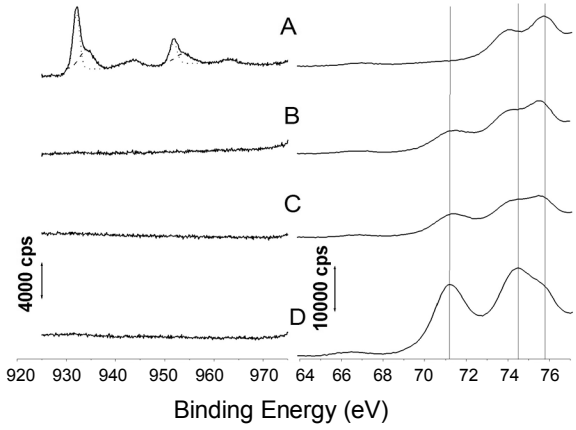


Figure 1. XP Cu 2p and Pt 4f spectra of the UPD Cu/Au(111) electrodes immersed in $PtCl_4^{2-}$ solution at different replacing time; (A) 0 minute (before the replacement), (B) 10 minutes, (C) 20 minutes, and (D) 240 minutes.

Fig. 1 shows the XP spectra of Cu and Pt regions as a function of time. The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks range 932 to 934 eV and 951 to 954 eV, respectively, and each of them can be best fitted with two peaks. Each of these two peaks corresponds to metallic Cu (dotted line) and copper oxide (dashed line). The Cu $2p_{3/2}$ (932.2 eV) and Cu $2p_{1/2}$ (952.0 eV) peaks in Fig 1A totally disappeared after 10 minutes incubation (Fig. 1B). Simultaneously Pt $4f_{7/2}$ (71.2 eV) and Pt $4f_{5/2}$ (74.5 eV) peaks[12] appeared, reflecting that the Pt/Cu SLR^3 rapidly occurred. The four other peaks in XP spectra of Cu 2p (Fig. 1A) with the binding energies of 933.4, 941, 953.2 and 962 eV are identical to those in the XP spectra region of Cu oxides and similar to the XP spectra of UPD Cu on Au reported previously.[13,14] The appearance of CuO is due to exposure of the sample electrode to the ambient environment before the XPS measurements. It was reported that only a moderate amount of copper oxide was formed on UPD Cu/Au surface even when the UPD Cu surface was deliberately oxidized by oxygen plasma.[13,14] A Au $5p_{1/2}$ peak (75.8 eV) was found in the similar intensities through Fig. 1A to 1D. Another peak (66.5 eV) was also found with the same behavior as Au $5p_{1/2}$ peak in Fig 1. This peak temporarily assigned to the unidentified species existed in the chamber of XPS. One should note that the Pt 4f signal does not remain the same after replacement, Pt $4f_{7/2}$ peak intensity was found to be 5011, 5000 and 15660 cps for the replacement time of 10, 20 and 240 min, respectively. The relative amount of UPD Cu and formed Pt at different replacement time on the Au surface was determined by Cu_{UPD} : $Pt_{10\,min}$: $Pt_{20\,min}$: $Pt_{240\,min}$ = (A_{Cu}/R_{Cu}) : $(A_{Pt,10\,min}/R_{Pt})$: $(A_{Pt,20\,min}/R_{Pt})$: $(A_{Pt,240\,min}/R_{Pt})$, where A is the peak area and R is the atomic sensitivity factor.[12,15,16] Using R_{Cu} and R_{Pt} of 4.4 and 6.3, respectively,[16] the ratio was found to be 1 : 0.17 : 0.23 : 0.93.

The Pt/Au electrodes with different incubation time were also tested by CV measurements in 0.05 M H_2SO_4 solution (Figure 2a). The potential was initially scanned from 0.1 V to negative direction. The platinum oxide reduction peak around 0.4 V as well as a well-shaped hydrogen adsorption/desorption feature in the potential region of +0.1 V to −0.20 V were observed, similar to that of a polycrystalline Pt reported previously.[17] The voltammogram is different from that of Pt film formed *via* replacement of UPD Cu from $PtCl_6^{2-}$ solution but similar to the one through $PtCl_4^{2-}$.[8] The charges associated with the desorption of hydrogen on the platinum were found to be 62, 107, 103

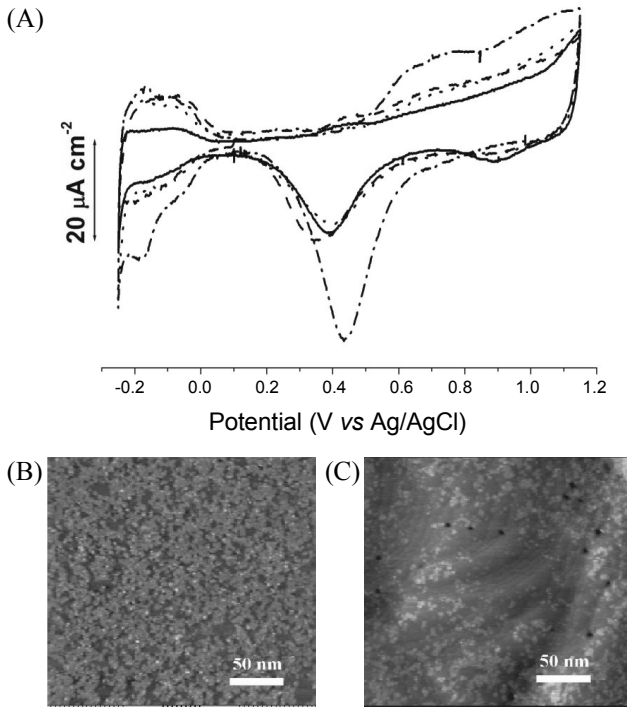


Figure 2. (A) Cyclic voltammogram of Pt/Au electrode in 0.05 M H_2SO_4 solution with potential scan rate of 20 mV s^{-1}. Incubation time in 0.5 mM $PtCl_4^{2-}$ solution; (solide) 5 minutes, (dash) 10 minutes, (dot) 20 minutes, and (dash dot) 4 hours. (B) & (C) STM images (U_t = 100 mV, I_t = 100 pA) of Pt film on Au(111) electrode obtained after 240 (B) and 10 (C) minutes replacement of Cu adlayer in 0.5 mM K_2PtCl_4 solution. The electrodes were rinsed by Pt ions free sulfuric acid solution before CV and STM measurements.

and 155 μC cm^{-2} at the incubation time of 5, 10, 20 and 240 min, respectively. These values are equal to about 30%, 51%, 49% and 74% of the charge associated with the adsorption/desorption of one hydrogen full monolayer on a Pt(111) surface (210 μC cm^{-2}),[18] suggesting that even after 4 hours immersion, a full monolayer of Pt was not formed and bare Au surface still existed as was found in XPS experiments. The voltammogram little changed with further incubation time.

The STM images of the electrodes taken after 240 and 10 minutes incubation are shown in Figure 2B and C, respectively. Pt nano-clusters and bare Au(111) surface are seen in both cases. The data show that larger and more uncovered Au(111) surface was found with the smaller incubation time. The STM images are different from the one in the previous report,[7] where apparently the entire Au(111) surface was covered by a uniform Pt film and no large gold surface was observed. However, Pt clusters with 0.3 to 0.5 nm high were found in the close up STM image. In addition, ultrafine and narrow regions of bare gold surface were seen between the Pt nano-clusters in the STM image of the original work. The difference between this study and the previous work may come from the use of different platinum ions. In the present case $PtCl_4^{2-}$ ions were hired, one Pt atom replaced one Cu atom on the Au surface and the significant congregation of deposited Pt atoms could occur at first and then the atomic rearrangements proceed as time passed out.

When the sizes of the atomic nuclei (Cu: 0.256 nm, Pt: 0.278 nm, Au: 0.288 nm) are considered, the commensurate Pt(111) surface may be expected if all the Cu atoms were replaced by Pt atoms at the same location. The above results of XPS, CV, and STM demonstrate that the UPD copper was completely removed upon electron transfer, that the adsorption of Pt atoms was less than 100% with aggregation in some preferred locations so that significant portion of Au substrate was unoccupied, and that the deposited platinum atoms were mobile for hours after replacing copper atoms. SLR^3 is composed of charge transfer, adsorption of the reduced particles, and the rearrangement of the adsorbed atoms. Except the electron transfer, the other processes are slow and the details of SLR^3 remain to be explored. This is the first example to show the long-term atomic rearrangement or relaxation in SLR^3.

In summary, kinetic aspects of Pt monolayer formation by a spontaneous redox replacement of UPD Cu adlayer on Au(111) surface were studied. UPD Cu adlayer was totally removed immediately after it was exposed to the solution containing $PtCl_4^{2-}$ ions. The deposited platinum atoms were mobile for hours that atomic rearrangements took place. Pt clusters and uncovered Au surface were detected.

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