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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 in a layer by layer growth mode to form a multilayer of Pt,3 with a layer by layer growth mode to form a multilayer of Pt,3 Au(111) surface from platinum complex solutions.3,4 Recently a new method, which is now recognized as surface limited redox replacement reaction (SLR3),5 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 PtCl6 -2 versus PtCl4 2- and a single UPD Cu replacement with Pt(II) ions can yield a full monolayer but the previous elaboration was limited to PtCl6 -2 case only,7 we investigated the redox replacement of UPD Cu adlayer on Au(111) in PtCl4 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

Fig. 1 shows the XP spectra of Cu and Pt regions as a function of time. The Cu 2P3/2 and Cu 2P1/2 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 2P3/2 (932.2 eV) and Cu 2P1/2 (950.2 eV) peaks in Fig 1A totally disappeared after 10 minutes incubation (Fig. 1B). Simultaneously Pt 4f7/2 (71.2 eV) and Pt 4f5/2 (74.5 eV) peaks12 appeared, reflecting that the Pt/Cu SLR3 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 5p1/2 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 5p1/2 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 4f7/2 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 CuUPD : Pt10 min : Pt20 min : Pt240 min = (ACu/RCu) : (APt,10 min/RPt) : (APt,20 min/RPt) : (APt,240 min/RPt), where A is the peak area and R is the atomic sensitivity factor.12,15,16 Using RCu and RPt of 4.4 and 6.3, respectively, 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 H2SO4 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 PtCl6 2- solution but similar to the one through PtCl4 2- .8 The charges associated with the desorption of hydrogen on the platinum were found to be 62, 107, 103...
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 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 remain to be explored. This is the first example to show the long-term atomic rearrangement or relaxation in SLR.

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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References