

# Fabrication of platinum submonolayer electrodes and their high electrocatalytic activities for ammonia oxidation



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## ABSTRACT

Pt submonolayer with different coverage on the Au electrode for ammonia oxidation was prepared by Cu underpotential deposition (UPD) followed by redox replacement of UPD Cu by Pt. The effects of the Cu UPD potential and time on the deposited Cu and the redox replaced Pt layer on the electrode were investigated. The amount of the deposited Cu and Pt was determined by the anodic stripping method. The electrocatalytic activity of the Pt decorated electrodes for ammonia oxidation was characterized by cyclic voltammetry. The results showed that the Cu UPD potential has a significant influence on the formed Cu layer and the subsequent Pt submonolayer. The Cu deposition behaviour changes from UPD process to overpotential deposition (OPD) process with the decrease of deposition potential. Besides, the amount of the deposited Cu increases as the Cu deposition potential decreases. Consequently, Pt layer with different coverage on the electrode can be effectively controlled by adjusting the Cu UPD potential. The Pt submonolayer electrodes prepared by the redox replacement of Cu UPD layer have a high mass activity for ammonia oxidation, and their mass activities are more than two times higher than that of the Pt decorated electrodes obtained by redox replacement of Cu OPD layer. Besides, the Pt submonolayer electrodes also have a higher specific activity possibly due to the modification in structural and electronic properties of the Pt submonolayer induced by the Au substrate.

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## 1. Introduction

The electro-oxidation of ammonia has been attracted considerable and increasing attention from both the viewpoint of energy and environment. Ammonia is a carbon-free chemical energy carrier, and has high hydrogen storage capacity (17.7 wt.%) and energy density (3000 Wh kg<sup>-1</sup>) [1,2]. Ammonia is also easy to produce, store and transport. The development of direct ammonia fuel cell has been reported by using NH<sub>4</sub>OH in KOH as fuel [3,4]. On the other hand, ammonia is a common pollutant in wastewaters. Electro-oxidation of ammonia has been shown to be a promising technique for the removal of ammonia contamination [5–7]. Recently, a new technology has been developed for the production of high-purity hydrogen on demand by ammonia electrolysis, while simultaneously eliminating ammonia pollutants in wastewater [6–9]. It has been pointed out that ammonia

electro-oxidation consumes theoretically 95% less energy than water electrolysis for producing hydrogen [8]. Furthermore, decomposition of ammonia by electro-oxidation in alkaline solution at low overpotentials is free of NO<sub>x</sub> and CO<sub>x</sub> [10,11]. Therefore, electro-oxidation of ammonia also offers a significant advantage in clean energy supply.

Among various noble metals, platinum (Pt) has been so far acknowledged as the most effective electrocatalyst for the ammonia oxidation [12–15]. Since ammonia electro-oxidation is a sluggish reaction [15], high loading of Pt in the electrocatalysts is usually required to achieve acceptable reaction rates. However, the high cost and low abundance of Pt remain major obstacles for their widespread applications. Therefore, great efforts have been made over the years to develop electrocatalysts that can effectively improve their activity and simultaneously reduce the Pt loading. Several strategies, including decreasing particle size [16], alloying of Pt [17,18], dealloying of Pt-based alloys [19], engineering of core/shell structure [20] and development of Pt monolayer or submonolayer [21], have been tried theoretically to increase the Pt mass activity of the electrocatalysts. Of the various approaches, using Pt sub- or monolayer electrocatalysts has unique advantages

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such as ultralow Pt content, high utilization of Pt, and increased tunable activity and stability compared to the conventional Pt electrocatalysts [21–23]. An efficient technique for Pt monolayer deposition on various metal and alloy substrates, first demonstrated with Au(111) [24], involves the redox replacement of underpotentially deposited Cu adlayer by Pt. It has been found that the Pt mass activity of these Pt monolayer electrocatalysts for oxygen reduction reaction shows several times to more than an order of magnitude higher than that of the conventional all-Pt electrocatalysts [25–28]. However, to date, there has been no report of the application of Pt sub- or monolayer electrodes for electro-oxidation of ammonia. Furthermore, the parametric influence of the Cu underpotential deposition (UPD) process (e.g., deposition potential and time) on the formed Pt layer and the corresponding electrocatalytic activities has remained unclear.

In the present work, a Pt submonolayer was prepared on a Au electrode by Cu UPD combined with the redox replacement of UPD Cu by Pt. The effect of the Cu deposition potential and deposition time on the formed Pt layer was investigated by electrochemical methods. The amount of the UPD Cu was characterized by the anodic stripping method. The Pt submonolayer with different surface coverage on the Au electrode was effectively obtained by controlling the Cu UPD potential. Furthermore, the relationship between the electrodes decorated with different Pt coverage and their electrocatalytic activity for the ammonia oxidation were investigated by cyclic voltammetry.

## 2. Experimental

All the electrodeposition and electrochemical measurements were performed by using a PARSTAT 2273 electrochemical workstation (Princeton Applied Research) in a classical three electrode cell. A polycrystalline Au electrode was used as working electrode (WE), a saturated calomel electrode (SCE) as the reference electrode (RE) and a Pt plate as the counter electrode (CE).

Before use, the Au electrode was polished with 1, 0.3 and 0.05  $\mu\text{m}$  alumina paste sequentially and cleaned in ultrapure water by sonication. Experiments were carried out at  $25 \pm 1^\circ\text{C}$ . All the solutions were prepared with ultrapure water obtained from a water purification system (Millipore,  $18.2\text{ M}\Omega\text{ cm}$ ). Prior to and throughout the tests, the solution was deaerated by purging a high-purity  $\text{N}_2$  gas (99.999%).

Cu UPD was carried out in 0.05 M  $\text{CuSO}_4$  + 0.05 M  $\text{H}_2\text{SO}_4$  solution by a well-established method [29]. The Au working electrode was first held at 0.65 V(SCE) for 20 s to ensure the surface is free of Cu. The electrode potential was then scanned to the desired deposition potential at a scan rate of  $0.4\text{ V s}^{-1}$ , and held at the deposition potential for a certain time. After Cu deposition, the modified Au electrode was removed from the solution and rapidly transferred to 5 mM  $\text{K}_2\text{PtCl}_4$  + 0.05 M  $\text{H}_2\text{SO}_4$  solution. It was held in this solution for 10 min for the redox replacement of Cu layer by Pt. Afterward, the Pt decorated Au electrode was rinsed in ultrapure water and dried in air. For Cu anodic stripping tests, after holding at the Cu deposition potential for a certain time, the electrode potential was scanned back to 0.65 V(SCE) at sweep rate of  $0.4\text{ V s}^{-1}$ .

The electrochemically active surface area of the Pt decorated Au electrode was characterized by the steady-state cyclic voltammograms (CV) recorded at  $0.05\text{ V s}^{-1}$  in 0.5 M  $\text{H}_2\text{SO}_4$  solution. A three electrode cell was used, with the Pt decorated Au electrode as WE, a platinum plate as CE and a SCE as RE. The electrocatalytic activity of Pt decorated Au electrodes for ammonia oxidation was investigated by the CV measurements in 1 M  $\text{KOH}$  + 0.1 M  $\text{NH}_3$  solution at a scan rate of  $0.01\text{ V s}^{-1}$ . All the currents in the CV curves are normalized by the geometric surface area of the working electrode.

## 3. Results and discussion

### 3.1. Cu UPD and anodic stripping process

Fig. 1a shows the CV curve for Cu UPD on the Au electrode in 0.05 M  $\text{H}_2\text{SO}_4$  solution containing 0.05 M  $\text{CuSO}_4$ . A peak pair (A and A') is observed in the CV curve. When the potential is above 0.6 V (SCE), the current is very small, indicating that no UPD process occurs. A cathodic peak (A') at about 0.25 V(SCE) is observed during the negative-going scanning, which is related to the formation of UPD Cu on the Au electrode. When the negative-going potential decreases below 0.1 V(SCE), the current increases dramatically, showing the occurrence of the overpotential deposition (OPD). An anodic peak (A) at about 0.3 V(SCE) occurs on the positive-going scan, which corresponds to the dissolution process of the UPD Cu. Furthermore, the CV profile suggests that the Cu UPD process on the Au electrode occurs in a relatively wide potential region from about 0.1 to 0.3 V(SCE). Fig. 1b shows the CV curve of the bare Au electrode in 0.05 M  $\text{H}_2\text{SO}_4$  without Cu ions in the solution. No peak is observed in the potential region from 0 to 0.6 V(SCE), confirming the peak pair (A and A') is attributed to the Cu deposition and stripping in the solution containing  $\text{CuSO}_4$ . The reduction peak at around 0.91 V corresponds to the reduction of Au oxide.

Fig. 2 shows the anodic stripping curves after Cu UPD at 0.15 V (SCE) for 2, 10, 30 and 60 s, respectively. It is seen that there is a similar feature for all the curves and the current density of the stripping curves increases with the increase of the time of the Cu UPD process from 2 to 30 s. However, the stripping curve does not change obviously when the deposition time increases from 30 to 60 s, indicating that the Cu UPD process gets saturated after 60 s.

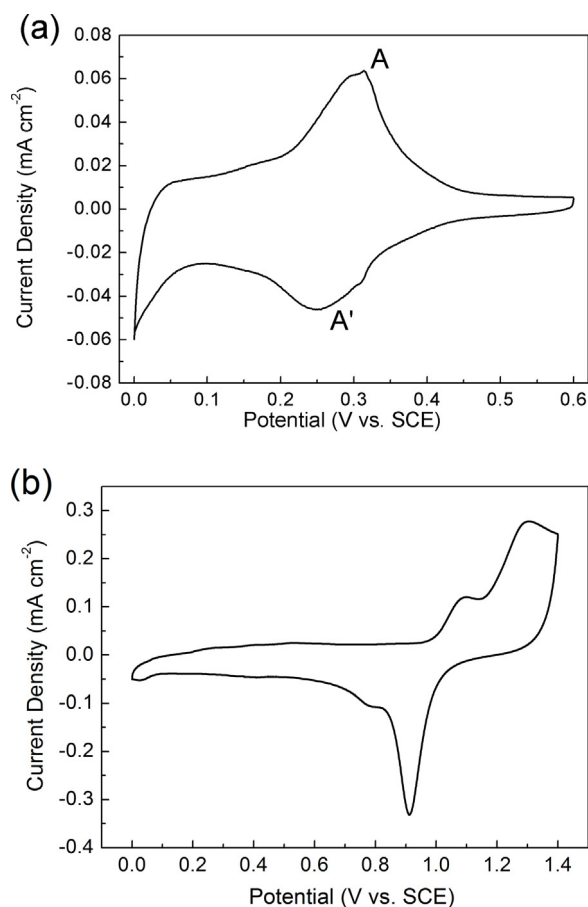
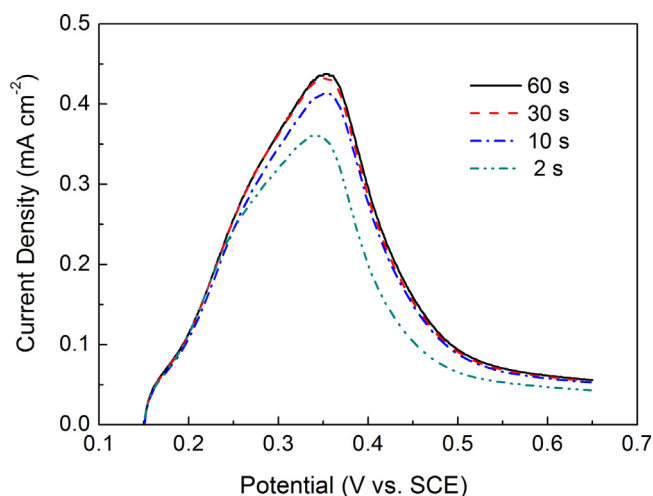
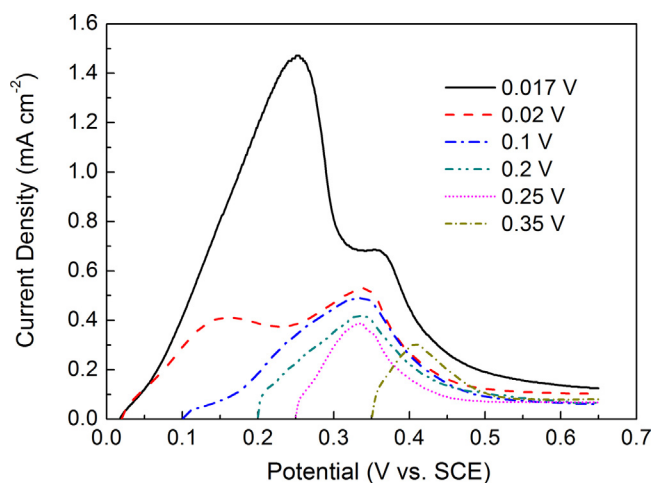


Fig. 1. CVs measured on the Au electrode in (a) 0.05 M  $\text{H}_2\text{SO}_4$  solution containing 0.05 M  $\text{CuSO}_4$  and (b) 0.05 M  $\text{H}_2\text{SO}_4$  without Cu ions in the solution at  $0.05\text{ V s}^{-1}$ .



**Fig. 2.** Anodic stripping curves after Cu UPD on the Au electrodes at 0.15 V(SCE) for 2, 10, 30 and 60 s respectively.



**Fig. 3.** Anodic stripping curves after Cu UPD on the Au electrodes at different deposition potentials for 60 s at  $0.4 \text{ V s}^{-1}$ .

Fig. 3 shows the anodic stripping curves of Cu after UPD for 60 s at various deposition potentials from 0.35 to 0.017 V(SCE). It is noticed that the Cu stripping behaviour depends on the Cu deposition potential. The stripping current density increases with the decrease of the Cu deposition potential from 0.35 to 0.1 V(SCE), and only one stripping peak could be observed. However, when the deposition potential drops to 0.02 V(SCE), the Cu stripping behaviour changes obviously and another shoulder peak is formed at about 0.15 V(SCE). When the deposition potential further decreases to 0.017 V(SCE), the current intensity of the shoulder peak increases obviously and surpasses the right UPD stripping peak. This suggests that the OPD process occurs and the shoulder peak overlaps with the stripping peak of OPD Cu.

### 3.2. Redox replacement of Cu by Pt

After Cu UPD process, the electrode was immersed into 5 mM  $\text{K}_2\text{PtCl}_4$  and 0.05 M  $\text{H}_2\text{SO}_4$  solution to achieve the Pt decoration through the reaction between Cu atoms and  $\text{PtCl}_4^{2-}$  ions. A series of the Pt decorated electrodes with different amount of Pt can be obtained by controlling the deposition potential of the Cu UPD process. In the present work, it is assumed that the efficiency of the redox replacement reaction between the UPD Cu and Pt ions is 100%. Correspondingly, the amount of the obtained Pt can be calculated from the stripping charge of the Cu adlayer. Table 1 shows the results of the oxidation charge of Cu deposited on the Au electrode at different potentials calculated from Fig. 3 and the calculated Pt amount is also given. The amount of the deposited Cu increases steadily with the decrease of the deposition potential from 0.35 to 0.1 V(SCE). It is worth noticing that when the deposition potential decreases from 0.02 to 0.017 V(SCE), the Cu stripping charge increases dramatically by more than two times, suggesting the occurrence of Cu OPD process.

### 3.3. Electrochemical measurements

The electrochemically active surface area (ECSA,  $\text{cm}^2 \text{ cm}^{-2}$ ) of the formed Pt layer is determined by the CV measurements in 0.5 M  $\text{H}_2\text{SO}_4$  solution at a scan rate of  $0.05 \text{ V s}^{-1}$ . Fig. 4 shows the CVs measured on the Pt decorated Au electrode prepared at different deposition potentials in 0.5 M  $\text{H}_2\text{SO}_4$  solution. All the CV curves show typical potential regions including the hydrogen adsorption/desorption region ( $-0.2$  to  $0.1 \text{ V(SCE)}$ ) and the formation/reduction of the surface Pt oxide,  $\text{Pt-OH}_{\text{ad}}$  ( $0.4$  to  $1.0 \text{ V(SCE)}$ ) [30]. The current density for the hydrogen desorption increases with the decreasing Cu deposition potential, indicating the increasing ECSA. ECSA is determined from the CVs according to the following equation [31]:

$$\text{ECSA} = Q_{\text{H}} / Q_{\text{H}}^0 \quad (1)$$

The mass specific, electrochemically active surface area (SSA,  $\text{cm}^2 \mu\text{g}^{-1}$ ) of Pt electrocatalysts is calculated by:

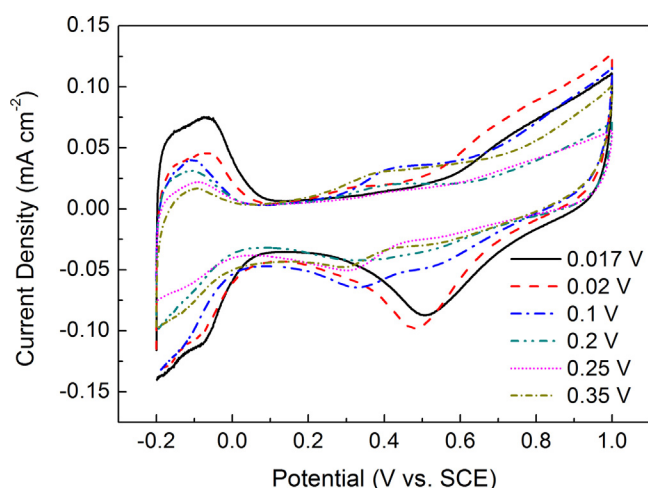
$$\text{SSA} = \text{ECSA} / L_{\text{Pt}} \quad (2)$$

where  $Q_{\text{H}}$  is the charge for the hydrogen desorption ( $\text{mC cm}^{-2}$ ),  $Q_{\text{H}}^0$  the specific charge for a monolayer of hydrogen on Pt ( $0.21 \text{ mC cm}^{-2}$ ) [32] and  $L_{\text{Pt}}$  is the amount of Pt ( $\mu\text{g cm}^{-2}$ ). The value of  $Q_{\text{H}}$  is calculated by integrating the area related to the hydrogen desorption after subtracting the contribution of the double-layer charge. Furthermore, the coverage of the Pt layer is obtained through dividing each ECSA by the geometrical surface area of the electrode. The calculated results are listed in Table 2. It is worth noticing that the calculated Pt coverage obtained at the Cu deposition potential of 0.017 V(SCE) is more than 100%, indicating that more than one monolayer is formed. In contrast, in the Cu UPD

**Table 1**

Calculated values of the Cu oxidation charge and the corresponding Pt amount under different Cu deposition potentials.

Deposition potential (V(SCE))	Cu oxidation charge ( $\text{mC cm}^{-2}$ )	Pt amount ( $\mu\text{g cm}^{-2}$ )
0.017	0.656	0.663
0.02	0.260	0.263
0.1	0.185	0.187
0.2	0.136	0.138
0.25	0.079	0.080
0.35	0.046	0.046

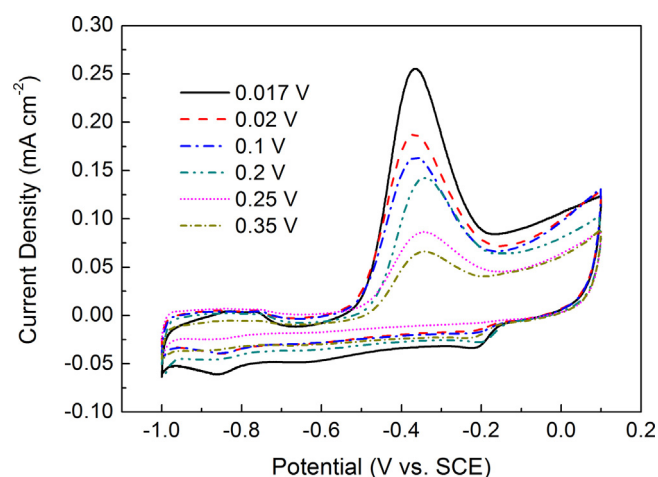


**Fig. 4.** CVs measured on the Pt decorated Au electrodes prepared at different Cu deposition potentials in 0.5 M  $\text{H}_2\text{SO}_4$  solution at  $0.05 \text{ V s}^{-1}$ .

region, the surface coverage of the Pt layer is below 100% and its value increases with the decrease of the Cu UPD potential. This demonstrates that the Cu UPD potential can be used to effectively control the surface coverage of the Pt submonolayer on the electrode. Besides, under the investigated conditions, the ECSA of the Pt on the electrode increases with the Pt amount.

The electrochemical activity of Pt decorated electrodes is determined in 0.1 M ammonia and 1 M KOH solution at a scan rate of  $10 \text{ mV s}^{-1}$ . Fig. 5 shows the CVs measured on the Pt decorated electrodes prepared at various Cu deposition potentials. There is a similar feature for all the CV curves, i.e., an anodic peak observed at about  $-0.37 \text{ V(SCE)}$ , which is attributed to the oxidation of ammonia [13,14]. There is no such characteristic current peak observed in the plot when CV is measured in the absence of ammonia in the solution, as reported in the previous work [33,34]. This confirms the electrocatalytic activity of the Pt decorated electrode for ammonia oxidation. Moreover, the peak current density increases with the decrease of the deposition potential. The amount and coverage of the Pt on the electrode increase with the decrease of the Cu deposition potential, contributing to the increased ECSA (Table 1) which provides more active sites for ammonia oxidation. This results in the enhancement of the overall electrocatalytic activity of the Pt decorated electrode. Similar results that the total electrocatalytic activity of the Pt catalysts increases with the Pt amount under certain condition have been reported in our previous studies [35,36].

The mass-specific activity (MA) of the prepared Pt decorated electrodes for ammonia oxidation is determined by  $Q_{\text{AOR}}/L_{\text{Pt}}$ , where  $Q_{\text{AOR}}$  is the charge required for the ammonia oxidation reaction ( $\text{mC cm}^{-2}$ ) and  $L_{\text{Pt}}$  is the amount of the decorated Pt on the electrode ( $\mu\text{g}$ ). The value of  $Q_{\text{AOR}}$  is determined from the area integrated under the anodic current peak in CV [35]. Fig. 6a shows the MA of the Pt decorated electrodes prepared at different Cu deposition potential. It is seen that the MA depends on the Cu deposition potential. The highest MA (about  $14 \text{ mC } \mu\text{g}^{-1}$ ) of the Pt



**Fig. 5.** CVs measured on the Pt decorated electrodes prepared at various Cu deposition potentials in 0.1 M ammonia and 1 M KOH solution at  $0.01 \text{ V s}^{-1}$ .

decorated electrode is achieved at the Cu UPD potential between 0.2 and 0.35 V(SCE). With the decrease of the Cu deposition potential from UPD region to the OPD region (i.e.,  $0.017 \text{ V(SCE)}$ ), the MA of the electrode decreases dramatically. Generally, for the Pt submonolayer electrodes obtained in the Cu UPD region, the MA values remain a stable high value irrespective of the Pt coverage. This suggests that the majority of the Pt atoms obtained by the redox replacement of UPD Cu are accessible for ammonia electro-oxidation. Beyond the UPD region, the increased Pt coverage lowers the MA, indicating the increased proportion of the unemployed Pt atoms. This is confirmed by Table 2, which shows that the SSA of the Pt submonolayer electrodes prepared in the Cu UPD region has a higher value than that of the Pt decorated electrodes obtained in the Cu OPD region. Noticeably, the Pt submonolayer electrodes prepared in the Cu UPD region exhibits more than one order of magnitude increase in the MA for ammonia oxidation compared with the Pt electrocatalysts reported in our previous studies [35,36]. A comparison between the SSA values shows that the greatly improved MA in the present work is mainly attributed to the extremely high surface area/volume ratio of the Pt electrocatalysts where nearly all the Pt atoms in the submonolayer are at the catalytic sites [37,38]. Besides, considering the MA of an electrocatalyst can also be simply expressed as [39]:

$$\text{MA} = \text{SSA} \times \text{SA} \quad (3)$$

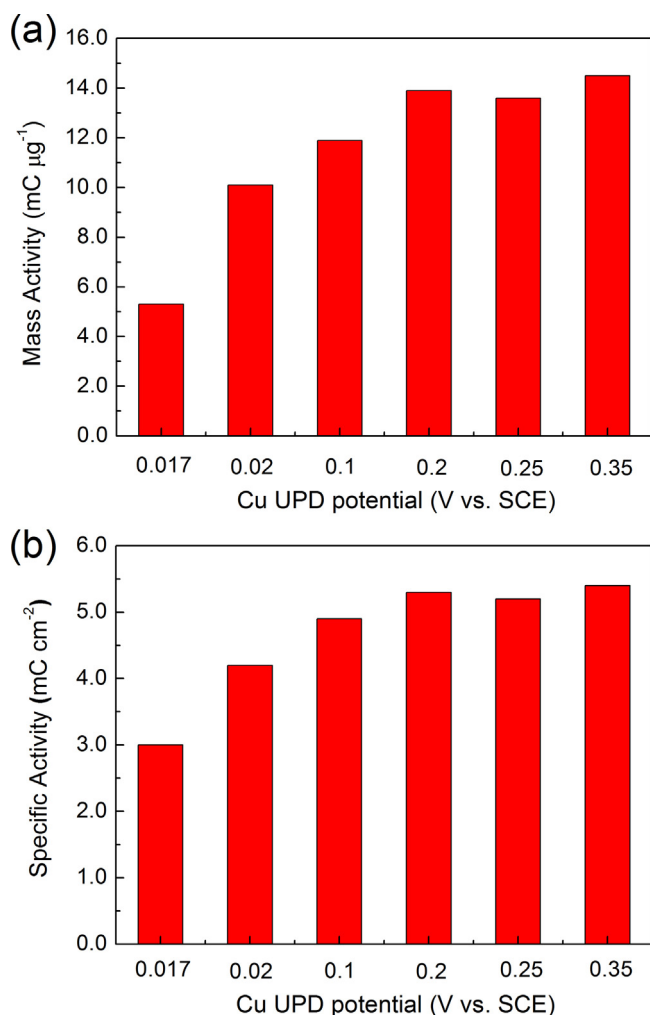
where SA is the specific activity and commonly depends on the intrinsic nature of the electrocatalyst, which is calculated as the  $Q_{\text{AOR}}$  normalized by the ECSA. Fig. 6b shows the calculated SA of the Pt decorated electrodes prepared at different Cu deposition potential. It is interesting to find that the Pt submonolayer electrodes also have a higher SA value than the decorated electrodes with Pt coverage above 100%. It has been widely reported that the electrocatalytic activity of Pt sub- or monolayer can be affected by the underlying substrate due to both geometric and ligand effects [26,40–42]. Nørskov et al. [43,44] reported that

**Table 2**

Calculated values of the ECSA, SSA and Pt coverage under different Cu deposition potentials.

Deposition potential (V(SCE))	ECSA ( $\text{cm}^2 \text{ cm}^{-2}$ )	SSA ( $\text{cm}^2 \mu\text{g}^{-1}$ )	Pt coverage (%)
0.017	1.17	1.76	117
0.02	0.62	2.37	62
0.1	0.46	2.44	46
0.2	0.36	2.62	36
0.25	0.21	2.61	21
0.35	0.12	2.65	12





**Fig. 6.** (a) MA (b) SA of the Pt decorated electrodes prepared at different Cu deposition potentials.

the characteristics of the surface metal  $d$ -band center ( $\varepsilon_d$ ), play an important role in determining surface reactivity. A more reactive surface is characterized by a higher-lying  $\varepsilon_d$ , which binds adsorbates more strongly and thus enhances the dissociation reaction kinetics producing these adsorbates [42–44]. Previous studies showed that the Au substrate exerts a tensile strain on the Pt monolayer due to the lattice mismatch between Au and Pt and upshifts the  $d$ -band centre. As a result, this increases the binding energy of the Pt monolayer for the adsorbates [42,43]. Besides, in situ infrared spectroscopy measurements [45] and density functional theory calculations [46] demonstrate that a Pt surface with higher binding energy of  $\text{NH}_2$  intermediate has a higher ammonia electro-oxidation activity since  $\text{NH}_2$  then serves as the key precursor for the formation of hydrazine ( $\text{N}_2\text{H}_4$ ) which is subsequently dehydrogenated quickly to  $\text{N}_2$  [47]. Therefore, the modification in geometric and electronic structure of surface Pt atoms by the Au substrate results in a Pt surface with increased binding energy for to adsorbates to activate ammonia oxidation and thus improves the SA. For practical electrocatalytic applications, it is suitable to support such Pt submonolayers on high surface area nanoparticles. However, this would introduce a wide range of parameters, such as the particle size, shape and composition of the electrocatalysts depending on the preparation method, which affect the ammonia oxidation activity. It would be thus difficult to illustrate the effects of the Cu UPD parameters on the formed Pt sub- or monolayers and the corresponding

electrocatalytic activity for ammonia oxidation. Therefore, a bare Au electrode has been used as the substrate in this study. Based on the results of the present work, preparation of Pt submonolayers on various metal core nanoparticles as practical electrocatalysts for ammonia oxidation is currently underway in our group.

#### 4. Conclusion

Pt submonolayer on the Au electrode was prepared by redox replacement of UPD Cu by Pt. The surface coverage and the electrocatalytic activity of the formed Pt layer depend on the Cu UPD potential. With the decrease of Cu UPD deposition potential from 0.35 to 0.02 V(SCE), the Pt coverage increases from 12 to 62%. As the Cu deposition potential further decreases to 0.017 V(SCE), Cu OPD process occurs and the obtained Pt becomes more than one monolayer. The ECSA of the Pt layer increases with the increase of the Pt amount and coverage on the electrode as the Cu deposition potential decreases, contributing to the increase of the total electrocatalytic activity. However, the MA of the Pt submonolayer electrodes prepared in the Cu UPD region for ammonia oxidation has a higher value, which exhibits more than 100% increase compared to the Pt overlayer electrodes obtained in the Cu OPD region. Furthermore, Pt submonolayer electrodes also have a higher SA than the electrodes decorated with non-monolayer Pt possibly due to the modification in structural and electronic properties of Pt submonolayer induced by the Au substrate.

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