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Atomic Scale Deposition of Pt around Au Nanoparticles to Achieve Much Enhanced Electrocatalysis of Pt

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We report an electrochemical method to deposit atomic scale Pt on 5 nm Au nanoparticle (NP) surface in N₂-saturated 0.5 M H₂SO₄. Pt is provided by the Pt wire counter electrode via one-step Pt wire oxidation, dissolution, and deposition realized by controlled electrochemical scanning. Scanning from 0.6-1.0 V (vs. RHE) for 10000 cycles gives Au_{98.2}Pt_{1.8}, which serves as an excellent catalyst for the formic acid oxidation reaction, showing 41 times higher specific activity (20.19 mA/cm²) and 25 times higher mass activity (10.80 A/mg_{Pt}) with much better CO-tolerance and stability than the commercial Pt. Our work demonstrates a unique strategy to minimize the use of Pt as a catalyst for electrochemical reactions.

Minimizing the use of Pt as a catalyst component without compromising Pt catalysis is one of the focal studies in current catalysis field, especially in the area of using Pt for energy conversion reactions.¹⁻⁷ An obvious approach to this goal is to reduce the sizes of the catalysts based on Pt nanoparticles (NPs) to the cluster or even atomic scale.⁸⁻¹⁵ Recent studies have shown that at the cluster or atomic scale, low-coordinated atoms tend to function as active sites.^{10,16} Experimentally, it has become essential to prepare such catalysts and to test their catalysis for chemical reactions. This preparation can be realized by atomic layer deposition (ALD) that requires physical evaporation of atoms in a high vacuum condition.^{8,17} To make the deposition process more easily accessible, solution phase deposition induced by chemical reduction of metal salts or organometallic complexes is also explored.¹⁷ In this approach, an oxide support is often used to anchor/stabilize the clusters or atoms generated from the solution phase reaction, as demonstrated in the syntheses of atomic scale catalysts of Pt-FeO_x¹⁰, Pd-Al₂O₃¹¹, Pt-CeO₂^{12,13}, Ir-FeO_x¹⁴ and Pd-TiO₂¹⁵. Despite the promising catalysis demonstrated, these composite systems are often applied to thermal catalysis, not for electrocatalysis related to energy conversions in acidic environment.

Here we report a convenient, one-step electrochemical method to deposit atomic scale Pt on 5 nm Au NPs through Pt wire oxidation, dissolution and selective deposition to achieve much enhanced electrocatalysis of Pt in acid. It is known that in an acid electrolyte at a positive potential, Pt wire can be slowly oxidized and dissolved in the acid as Pt²⁺.¹⁸ When the Au NPs deposited on an amorphous carbon support are coupled as a working electrode (WE) to the Pt wire counter electrode (CE), the oxidation of the Pt wire and dissolution of Pt²⁺ should allow Pt²⁺ to be attracted to the surface of Au NPs that protrude as an antenna on the carbon support, concentrating more negative charge on the electrode surface

and facilitating the selective reduction of Pt²⁺ to Pt on each Au NP, as illustrated in **Fig. 1A**. By controlling electrochemical cycling potentials in N₂-saturated 0.5 M H₂SO₄, we could deposit atomic scale Pt selectively on Au NPs, which can be characterized by high-resolution electron microscopy analysis, electrochemistry and electrocatalysis. The C-Au_{98.2}Pt_{1.8} catalyst with only 0.9 wt% Pt loading showed much enhanced catalysis for the formic acid oxidation reaction (FAOR) without obvious CO poisoning issue, achieving 10.80 A/mg_{Pt} mass activity (MA) and 20.19 mA/cm² specific activity (SA), which is 25 times (in MA) and 41 times (in SA) higher than the commercial Pt (20 wt%). Our study provides a simple approach to atomic scale modification of metal NPs with catalytically active component for catalytic applications.

The key to the successful synthesis is to deposit Pt selectively on Au NPs. Here we chose Au NPs as a sub-support for Pt because Au NPs are much more stable and conductive in an acidic solution than other metal NPs.¹⁹ The presence of Au NPs should also help to concentrate the charge when the Au NP electrode is applied a negative potential, and to adsorb Pt²⁺ present in the acid solution for selective Pt deposition. In performing the controlled electrochemical deposition, we first prepared monodisperse 5 nm Au NPs according to the previously reported method²⁰ (**Fig. S1**). We then loaded these NPs onto KetjenBlack EC-300-J carbon at a mass loading of 1:1, denoted as C-Au NPs, and further onto the WE at the loading mass of 0.1 mg_{Au}/cm². This WE was then coupled with Ag/AgCl (4 M KCl) as the reference electrode (RE) and Pt wire (exposed surface area 15.57 mm²) as the CE in 50 mL N₂-saturated 0.5 M H₂SO₄ solution (Setup details in supporting information). We applied the cycling potentials from -0.1 - 0.2 V, 0.2 - 0.6 V, 0.6 - 1.0 V, 0.8 V - 1.2 V or 1.0 - 1.4 V (vs. RHE) and the cycling scan rate for deposition was kept same at 100 mV/s.

Figure 1. (A) Schematic illustration of the atomic scale Pt deposition on Au NPs surface, (B) TEM image of the Au NPs loaded onto carbon before CV cycles, (C) Pt composition change with different numbers of CV cycling from 0.6 V to 1.0 V, (D) TEM image of the Au NPs loaded onto carbon after 10000 CV cycling from 0.6 V to 1.0 V, (E) HER polarization curves of the Au NPs after different CV cycles from 0.6 V to 1.0 V without iR correction (Au: before cycles; Au_{98.9}Pt_{0.2}: 4000 cycles; Au_{99.0}Pt_{0.7}: 7000 cycles; Au_{98.2}Pt_{1.8}: 10000 cycles). The scan rate: 100 mV/s for atomic Pt deposition and 2 mV/s for HER LSV curve.

Scanning between 0.6 - 1.0 V, which is the common potential range used for the accelerated Pt durability tests in studying Pt electrocatalysis in an acid solution,^{4,6,21} we first tested the effect of number of cycling on the Pt deposition. The results are summarized in **Fig. 1B-D** and **Fig. S2**. Before the cycling, Au NPs are dispersed well on the carbon support as shown from the transmission electron microscope (TEM) image (**Fig. 1B**). In the first 3000 cycles, we observed no change in NP sizes and morphology and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses of the samples showed no detectable amount of Pt (**Fig. 1C**). After 4000 potentials cycles, the Au NPs were "contaminated" by 0.2 at% Pt. From 4000 to 10000 cycles, the Pt compositions increase linearly with the number of potential cycles (**Fig. 1C**), indicating that the deposition of Pt on Au is limited by Pt-oxidation, dissolution and diffusion to the surface of Au NPs. The NP size and morphology is well maintained without obvious Au NP sintering or aggregation (**Fig. S2A-I** and **Fig. 1D**). However, after 11000 cycles, the NPs are prone to aggregate into larger NPs (**Fig. S3**), similar to what was observed in the CV cycling effect on Pt NPs.²² The successful deposition of Pt was further

verified with the dramatic activity increase of the NPs in their catalyzing the hydrogen evolution reaction (HER) in 0.5 M H₂SO₄ (**Fig. 1E**). The HER overpotential (at 10 mA/cm²) is reduced to 22 mV for the C-Au_{98.2}Pt_{1.8} NPs obtained after the 10000 potential cycles. As a comparison, the commercial C-Pt has an overpotential of 26 mV (**Fig. S4**).

Figure 2. (A) HAADF-STEM image of a single Au_{98.2}Pt_{1.8} NP. (B) High resolution image from the selected area in (A) showing the atoms arrangements. (C) CVs for C-Au_{98.2}Pt_{1.8}, C-Au and commercial C-Pt, obtained in N₂-saturated 0.5 M H₂SO₄ with a scan rate of 50 mV/s. (D) CO stripping for C-Au_{98.2}Pt_{1.8}, commercial C-Pt and C-Au, obtained in 0.1 M HClO₄ with a scan rate of 20 mV/s. Solid line is first scan cycle, dashed line is second scan cycle.

Potential cycling range has drastic effects on the Pt deposition over the Au NPs. While keeping the cycling number consistent (10000 cycles) and scanning from negative to positive potential ranges, Pt contents on the Au NPs show an exponential decay from 11.2 to 0.2 at% (**Fig. S5**). NP sizes and morphology could not be readily preserved under most of these different potential ranges (**Fig. S6**). When the Au NPs are exposed to a negative potential scan from -0.1-0.2 V, the Pt wire is under more oxidative environment and is prone to Pt oxidation and dissolution, leading to an uncontrolled Pt deposition on Au NPs (**Fig. S6A**). In contrast, cycling in 1.0-1.4 V, the Au NPs are put under more oxidative environment, which makes Au NPs less attractive to Pt²⁺ and prone to self-aggregation (**Fig. S6D**). The deposition was further confirmed by HER catalysis of the modified Au NPs (**Fig. S7**), as the Au NPs prepared from 1.0-1.4 V deposition show very poor HER activity in 0.5 M H₂SO₄. Considering all the tested electrochemical conditions, 10000 CV cycles from 0.6 V to 1.0 V gave us the best catalyst in C-Au_{98.2}Pt_{1.8}.

We characterized the Pt distribution around each Au NP in the C-Au_{98.2}Pt_{1.8} structure. The electron energy loss spectroscopy (EELS) line-scan across one single Pt-deposited Au NP could only give the Au signal, not Pt signal (**Fig. S8**). X-ray diffraction (XRD) patterns for the NPs before and after Pt

deposition are nearly identical (**Fig. S9**). However, if we focus on one Pt-deposited Au NP carefully, as demonstrated in **Fig. 2A**, we can see Au lattice fringes at a spacing of 0.24 nm that is close to *fcc*-Au (111) (0.236 nm). Focusing on the selected square area in **Fig. 2A**, we obtained **Fig. 2B**, from which we can see a set of lattice fringes (yellow dots) with their spacing measured to be 0.25 nm, which is different from what is measured from the Au. This new set of atoms must be atomic scale Pt, but with a shorter Pt-Pt distance compared to the bulk Pt at 0.28 nm. The shortened Pt-Pt distance is a good indication of the formation of atomic scale Pt clusters, as predicted previously.^{10,23} To further confirm the atomic scale deposition of Pt around each Au NP, we measured cyclic voltammetry and CO stripping properties of the C-Au_{98.2}Pt_{1.8}. **Fig. 2C** demonstrates the cyclic voltammogram (CV) of the C-Au, C-Au_{98.2}Pt_{1.8} and commercial C-Pt NPs. The two peaks from 0 to 0.29 V in the anodic scan of the commercial Pt are related to the hydrogen underpotential desorption (H_{UPD}). ~0.9 V is the Pt oxidation and 0.63 V is the corresponding Pt reduction peak.²⁴ For the Au NPs, there is no H_{UPD} peak, the peak at 1.4 V is due to the Au oxidation, and the one at 1.15 V is the corresponding Au-reduction peak.²⁴ The C-Au_{98.2}Pt_{1.8} shows a feature of Au and Pt, indicating that 1) Pt is successfully deposited onto the Au surface; and 2) Pt and Au form separate phases without noticeable alloy formation. We also studied CO stripping properties of the NPs and measured their electrochemical surface area (ECSA) of Pt. **Fig. 2D** shows the CO stripping curves for the C-Au_{98.2}Pt_{1.8}, C-Au and commercial C-Pt. The theoretical maximum ECSA of Pt is 237 m²/g_{Pt} when every single Pt atom gets exposed.^{25,26} In our CO stripping test, the ECSA of the commercial Pt is 64 m²/g_{Pt}, which is similar to the reported.^{7,25} However, for the C-Au_{98.2}Pt_{1.8}, the ECSA is measured to be 228 m²/g_{Pt}. This gives a strong evidence that single Pt atoms are deposited on the Au surface. Another noticeable feature is that the tiny CO oxidation peak of the C-Au_{98.2}Pt_{1.8} is negatively shifted compared with that of the commercial C-Pt. Considering that there is no CO adsorption on the pure Au surface, this further confirms the improved CO tolerance of Pt when it attaches to Au. In comparison, CO stripping for the C-Au_{88.8}Pt_{11.2} (10000 cycles, -0.1 V to 0.2 V) was also obtained (**Fig. S10**), the ECSA was decreased to 76 m²/g_{Pt}, which is also consistent with the TEM analysis on the sample showing Pt aggregation around Au NPs.

To further prove that the presence of Au NPs does help Pt deposition at the cycling potentials, we performed two control experiments. In one experiment, we replaced the Pt wire with a graphite rod as the CE. After 10000 cycling from 0.6 V to 1.0 V, we obtained no evidence of Pt deposition and the NPs show no change in HER (**Fig. S11**). In another experiment, Pt wire was used as the CE but the WE was modified only with the carbon support without the presence of Au NPs. Using TEM, we could not detect the presence of any form of Pt. The corresponding HER activity is too low (even worse than the C-Au NP sample) to confirm the presence of metallic Pt on the carbon support (**Fig. S12**). These two control experiments indicate that without the both presence of Au NPs and Pt CE,

the same potential cycling condition could not lead to the deposition of metallic Pt.

Figure 3. (A) FAOR CVs of the NPs obtained from different cycles of Pt depositions on Au NPs from 0.6 - 1.0 V (Au: before cycles; Au_{98.2}Pt_{0.2}: 4000 cycles; Au_{98.2}Pt_{1.0}: 7000 cycles; Au_{98.2}Pt_{1.8}: 10000 cycles) (B) FAOR CVs of the NPs obtained from 10000 cycles of Pt depositions on Au NPs from different potential cycling, (Au_{98.2}Pt_{0.2}: 1.0 - 1.4 V; Au_{88.8}Pt_{11.2}: 0.1 - 0.2 V; Au_{98.2}Pt_{1.8}: 0.6 - 1.0 V) (C) FAOR CVs of the NP catalysts obtained before and after 10 h chronoamperometry i-t test at 0.4 V, (D) FAOR CVs plotting mass activity vs. the oxidation potentials. Inset: the zoom-in CV from the C-Pt. FAOR CVs were obtained in N₂-saturated 0.1 M HClO₄ + 0.1 M HCOOH with a scan rate of 50 mV/s.

The atomic scale modification of Au NPs with Pt should provide an ideal catalyst system for studying electrochemical reactions. Such Pt-stained Au NPs can be an excellent catalyst for HER, as described above, but not so for electrochemical reduction of oxygen due to the negative electronic effect of Au over Pt.^{27,28} Previous studies have suggested that the formic acid dehydrogenation to CO₂ can better proceed on single Pt atoms^{29,30} than on larger Pt surface.^{29,31} This infers that our Pt-stained Au NPs may serve as an excellent catalyst for formic acid oxidation reaction (FAOR).²⁴ We tested the FAOR in 0.1 M HClO₄ + 0.1 M HCOOH with Au NPs decorated with different degree of Pt. **Fig. 3A&B** summarize the FAOR CVs (normalized to ECSA from CO stripping) of the Pt-deposited Au NPs obtained by different cycling numbers from 0.6-1.0 V (A) or after 10000 cycles at different potential ranges (B). Increasing Pt content from 0 to 1.8 at% leads to a significant increase in activity with the onset HCOOH oxidation potential negatively shifting to below 0.2 V and with the maximum catalytic activity reaching 20.19 mA/cm² at around 0.6 V. It is also interesting to see that for the NPs with Pt content at 0.5 - 1.8 at%, the CO-poisoning peak that is often associated with Pt catalyst at around 0.9 V is absent and the FAOR anodic scan peak and cathodic scan peak positions start to overlap. This indicates that atomic scale deposition of Pt over Au NPs promotes the formic acid dehydrogenation, facilitating the FAOR.^{24,32,33} However, the NPs with Pt content at 0.2 at% (deposited from 1.0 -1.4 V scanning range) have no FAOR activity and those

with Pt at 11.2 at% (deposited from -0.1 – 0.2 V) show the obvious CO poisoning peak (Fig. 3B).

The optimal C-Au_{98.2}Pt_{1.8} catalyst was compared much favorably with the commercial Pt one for the FAOR, as shown in Fig. 3C. The SA (by normalizing the FAOR peak current to the ECSA from CO stripping) of C-Au_{98.2}Pt_{1.8} is 41 times higher than the value of the commercial Pt. After 10 h chronoamperometry i-t test at 0.4 V, the SA of the commercial Pt drops 63% (from 0.49 mA/cm² to 0.18 mA/cm²) with the CO-poison peak dominates the oxidation feature at 0.88 V. For the C-Au_{98.2}Pt_{1.8}, however, the SA only decreases 8% (from 20.19 mA/cm² to 18.65 mA/cm²). We also obtained their MA (Fig. 3D) by normalizing the FAOR peak current to the Pt mass (from ICP-AES measurements). The C-Au_{98.2}Pt_{1.8} NPs have the MA of 10.80 A/mg_{Pt}, which is 25 times higher than the value of the commercial Pt (0.44 A/mg_{Pt}). Our studies are consistent with what have been predicted that the single Pt atoms are active for formic acid dehydrogenation,^{29,30,34} and further prove that Pt deposited on the Au NPs is in atomic scale and Au helps to stabilize the atomic scale Pt in the FAOR condition.

In summary, we have reported a simple electrochemical method of depositing atomic scale Pt on 5 nm Au NPs in N₂-saturated 0.5 M H₂SO₄. In this controlled deposition approach, the Pt wire acts as one electrode to provide Pt²⁺ via the wire surface Pt oxidation and dissolution and Au NPs on another electrode serve as stable antenna to enrich negative charge for selective Pt²⁺ attraction and reduction. The Pt²⁺ deposition and reduction process is controlled by electrochemical potentials. Cycling in a positive potential range (1.0 -1.4 V) causes Au NPs to aggregation, while cycling in a negative potential range (-0.1 - 0.2 V) leads to an uncontrolled Pt deposition on Au NPs. The optimized deposition condition is found to be cycling 10000 times between 0.6 - 1.0 V, giving Au_{98.2}Pt_{1.8}. The Au NPs modified with atomic scale Pt demonstrate the excellent catalytic performance for the FAOR, showing 41 times higher SA and 25 times higher MA with much better CO-tolerance and stability than the commercial Pt. The reported method is not limited to deposition of Pt over Au NPs, but can be generalized to modify other metal NPs with atomic scale Pt or other catalytic component with much enhanced catalysis for electrochemical and chemical reactions.

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