

## Electrooxidation of Formic Acid at Platinum–Gold Nanoparticle-modified Electrodes

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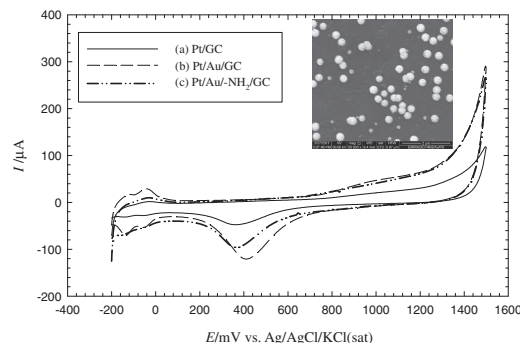
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The electrocatalytic oxidation of formic acid (FA) at Pt–Au nanoparticle (NP)-modified glassy carbon (GC) electrode has been investigated. The catalytic activity toward the electrooxidation of FA was greatly influenced by the method of the electrode preparation. The highest catalytic activity was obtained on Pt/Au/–NH<sub>2</sub>/GC electrode in which the GC electrode was chemically modified with gold nanoparticles (AuNPs) and Pt nanoparticles (PtNPs) were next electrochemically deposited on top of AuNPs.

Direct FA fuel cells (DFAFCs) have attracted continuously growing attention because of their advantages over the traditional hydrogen and direct methanol fuel cells (DMFCs).<sup>1</sup> So far, platinum is among the best electrocatalysts for DFAFCs. The electrooxidation of FA on Pt catalysts adopts a dual path mechanism, that is, a dehydrogenation path and a dehydration path. However, the surface poisoning resulting from the adsorption of the intermediate CO from the dehydration path hinders significantly the catalytic activity.<sup>2</sup> In practical applications, the modification of the Pt surface by some foreign atoms may overcome the CO poisoning. This surface modification could result in improving the catalytic activity of the electrode, as has been observed on Pt–Ru, Pt–Bi, and Pt–Au surfaces on the basis of the bifunctional mechanism, the electronic effect, or the ensemble effect.<sup>3–5</sup>

Au-modified Pt electrodes have strongly been recommended for FA electrooxidation because of their high stability and electrocatalytic activity.<sup>6</sup> Herein, we report on the superior electrocatalytic activity of a nanoparticle-based Pt/Au/–NH<sub>2</sub>/GC electrode toward the electrooxidation of FA.

Freshly prepared glassy carbon electrode (GC, *d* = 3.0 mm) was used as a working electrode in this investigation. A Ag/AgCl/KCl(sat) and a spiral Pt wire were used as the reference and counter electrodes, respectively. Several modifications for the GC electrode were employed for the sake of comparison. Two different methods (electrochemical and chemical) were employed to assemble AuNPs onto the GC electrode. In the electrochemical method, the deposition took place in 0.1 M H<sub>2</sub>SO<sub>4</sub> containing 1.0 mM Na[AuCl<sub>4</sub>] solution, and the potential was cycled from 0 to 1.1 V vs. Ag/AgCl/KCl(sat) at 100 mV s<sup>–1</sup> for 10 times (with a loading of 0.43 μg cm<sup>–2</sup>). However, in the chemical assembling procedure, carbamate was used as a linker, and AuNPs were grafted on the surface of the GC electrode (with a loading of 0.82 μg cm<sup>–2</sup>).<sup>7</sup> The electrodeposition of PtNPs on GC and Au/GC electrodes was done in 0.2 M H<sub>2</sub>SO<sub>4</sub> containing 1.0 mM H<sub>2</sub>[PtCl<sub>6</sub>] solution at a constant potential of 1 V for 300 s (with a loading of 23.8 μg cm<sup>–2</sup>). For the Pt/Au/



**Figure 1.** CVs obtained at (a) Pt/GC-, (b) Pt/Au/GC-, and (c) Pt/Au/–NH<sub>2</sub>/GC-modified electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Potential scan rate: 100 mV s<sup>–1</sup>. Inset: SEM image of Pt/Au/–NH<sub>2</sub>/GC electrode (magnification: 50000×).

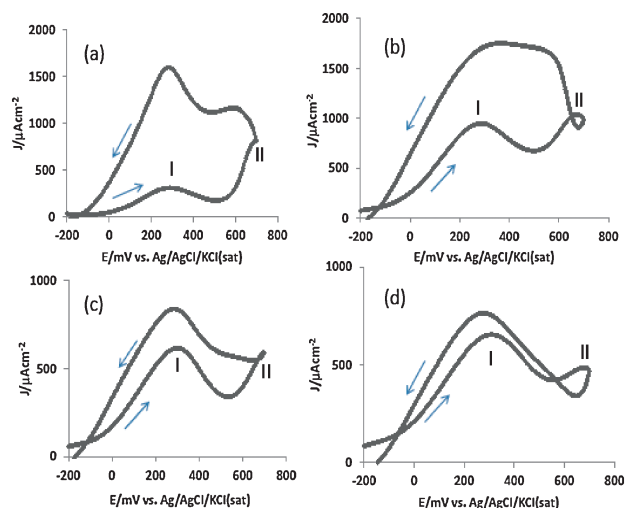
GC electrode, AuNPs were directly electrodeposited on the GC; however, for the Pt/Au/–NH<sub>2</sub>/GC electrode, AuNPs were chemically assembled onto the amino-group-grafted GC (–NH<sub>2</sub>/GC) electrodes. For both electrodes, round PtNPs (particle size of ca. 80 nm, see for example inset of Figure 1) were electro-deposited on the AuNP-modified GC electrodes.

The electrochemical measurements were performed at room temperature (25 ± 1 °C) in a two-compartment three-electrode cell. The measurements were performed using an EG&G potentiostat (model 273A).

Fortunately, in our case of Au and Pt surfaces, the methods of electrochemical characterization are powerful and sensitive to very low amounts of both species and can, moreover, distinguish firmly between the different types of surface atoms.

Figure 1 shows the cyclic voltammograms (CVs) in 0.5 M H<sub>2</sub>SO<sub>4</sub> for the Pt/GC-, Pt/Au/GC-, and Pt/Au/–NH<sub>2</sub>/GC-modified electrodes. Interestingly, for the three electrodes, the typical response characterizing a clean poly-Pt surface appeared; the Pt oxidation, extending over a wide range of potential, is coupled with the reduction peak at ca. 0.3–0.4 V. In addition, the hydrogen adsorption–desorption peaks are shown in the potential range from 0.0 to –0.2 V.

With a careful inspection of Figure 1 and alternatively by calculating the charge consumed with the reduction of PtO, one can be convinced that the real surface area of Pt in the Pt/Au/GC electrode is the highest, and that of the Pt/GC electrode is the lowest among the three electrodes. Needless to say, the increase in the Pt surface area in the Pt/Au/GC- and Pt/Au/–NH<sub>2</sub>/GC- modified electrodes results from the increase in the surface area of the underlying AuNPs. However, when AuNPs were chemically assembled on the –NH<sub>2</sub>-grafted GC substrate,



**Figure 2.** The CVs obtained at (a) bare Pt, (b) Pt/GC, (c) Pt/Au/GC, and (d) Pt/Au/ $-\text{NH}_2$ /GC electrodes in 0.3 M HCOOH (pH 3.5). Potential scan rate:  $200 \text{ mV s}^{-1}$ .

the steric hindrance of the amino group forced a certain separation between AuNPs which ultimately lowered the amount and the surface area of AuNPs and PtNPs. One more interesting observation from Figure 1 is the absence of the characteristic peaks for Au surface for the Pt/Au/GC- and Pt/Au/ $-\text{NH}_2$ /GC-modified electrodes. This means that PtNPs could preferentially cover the entire surface of AuNPs.

Figure 2 shows the CVs of the formic acid oxidation at the bare Pt, Pt/GC, Pt/Au/GC, and Pt/Au/ $-\text{NH}_2$ /GC electrodes in a 0.3 M aqueous solution of formic acid (pH 3.5). The pH was adjusted by adding a proper amount of NaOH (usually equivalent to 0.1 M). For the bare Pt (Figure 2a) and Pt/GC (Figure 2b) electrodes, two peaks were observed in the forward scan, at ca. 0.3 (peak I) and 0.65 V (peak II). The first peak at 0.3 V (peak I) was assigned to the direct oxidation of HCOOH to  $\text{CO}_2$ , while the second peak at 0.65 V (peak II) was assigned to the oxidation of the poisonous  $\text{CO}_{\text{ads}}$  species to  $\text{CO}_2$ . At low potential range, the Pt sites are partially poisoned by  $\text{CO}_{\text{ads}}$  from the dissociative adsorption step. The measured current then mainly comes from the FA oxidation on the unoccupied Pt sites through the dehydrogenation pathway. The peak current indicates the level of Pt surface poisoning by  $\text{CO}_{\text{ads}}$ . At high potential, the  $\text{CO}_{\text{ads}}$  is oxidized by Pt–OH species that starts to be formed at around 0.5 V during the forward scan, which releases most Pt sites for FA oxidation. In the backward scan (cathodic scan), while most of the poisonous intermediates have been oxidized at high potential, some of the poisonous intermediates still existed, so the indirect peak was still observed at the high potential region.<sup>8</sup> After the complete oxidation of the poisonous intermediates, the FA oxidation then can proceed on the clean Pt surface through the dehydrogenation pathway. Therefore, the current intensity which is proportional to the surface area, which initially was poisoned with CO, is expected to be high as depicted in Figures 2a and 2b.

We wish here to emphasize that the adsorption of CO on Pt surface requires the existence of three adjacent Pt sites (with a definite atomic spacing), and any interruption in this continuity may impede or prevent its adsorption.<sup>9</sup> In this regard, the modification of GC substrate with AuNPs before the deposition of PtNPs in the Pt/Au/GC- and Pt/Au/ $-\text{NH}_2$ /GC-modified electrodes is intended to interrupt the Pt atom contiguity required for CO adsorption. It worth mentioning that Au itself is a poor catalyst for the electrooxidation of FA, where it can easily adsorb neither the reactant nor the intermediates.<sup>10</sup> The AuNPs-modified GC (Au/GC) electrode was as well catalytically inactive toward the FA oxidation under the experimental conditions studied here (the results are not shown).

Two functions will next be employed to account for the degree of catalytic enhancement toward FA oxidation; one is the ratio of the current intensities of the direct peak (peak I) to the indirect peak (peak II) ( $I_p^{\text{d}}/I_p^{\text{ind}}$ ), and the second is ratio of the current intensities of the forward direct peak and the backward direct peak ( $I_p^{\text{d}}/I_p^{\text{b}}$ ).

At the Pt/Au/GC electrode, the ratio ( $I_p^{\text{d}}/I_p^{\text{ind}}$ ) was comparable to that obtained at the Pt/GC electrode (ca. 2.3); however, the ratio ( $I_p^{\text{d}}/I_p^{\text{b}}$ ) was largely increased. This increase in ( $I_p^{\text{d}}/I_p^{\text{b}}$ ) indicates improvement in catalytic activity of the Pt/Au/GC electrode toward FA oxidation, presumably, via lowering the CO adsorption and favoring the direct oxidation path. Interestingly, at the Pt/Au/ $-\text{NH}_2$ /GC electrode, a better enhancement toward the electrooxidation of FA could be observed, where a significant increase in the  $I_p^{\text{d}}/I_p^{\text{ind}}$  (ca. 9) and  $I_p^{\text{d}}/I_p^{\text{b}}$  (ca. 0.8) were obtained. The reason behind the difference in the catalytic enhancement observed at the Pt/Au/GC- and Pt/Au/ $-\text{NH}_2$ /GC-modified electrodes might relate to the degree of interrupting the contiguity of Pt sites necessary for CO adsorption.<sup>1</sup> The different crystallographic orientation of AuNPs might also have a role in the obtained behavior.<sup>7</sup>

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