Highly active Pd and Pd–Au nanoparticles supported on functionalized graphene nanoplatelets for enhanced formic acid oxidation

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Pd and Pd–Au nanoparticles supported on poly(diallyldimethylammonium chloride) (PDDA) functionalized graphene nanoplatelets (GNP) have been synthesized by the ethylene glycol reduction method and characterized by transmission electron microscopy (TEM) and electrochemical measurements for formic acid oxidation. TEM analysis shows that the Pd–Au nanoparticles are uniformly distributed on the surface of graphene nanoplatelets with an average particle size of 6.8 nm. The Pd–Au nanoparticles supported on PDDA–xGNP show higher activity for formic acid electro-oxidation than Pd nanoparticles supported on PDDA–xGNP and Pd or Pd–Au supported on traditional Vulcan XC-72 carbon. The higher catalytic activity of Pd–Au/PDDA–xGNP is mainly due to the alloying of Pd with Au. The promotional effect of Au and the absence of continuous Pd sites significantly suppress the poisoning effects of CO, enhancing the catalytic activity for formic acid oxidation and making them promising for direct formic acid fuel cells (DFAFC).

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1. Introduction

Direct formic acid fuel cells (DFAFCs) are attractive as a power source for portable devices due to their advantages, such as higher theoretical open-circuit potential, lower crossover of the formic acid fuel through the polymer membrane, nonflammability of formic acid, and safe storage and transportation, compared to direct methanol fuel cells (DMFC).^{1–3} Although formic acid (2086 W h l^{−1}) has a lower energy density than methanol (4690 W h l^{−1}), it can be offset by employing a higher concentration of formic acid due to the lower fuel crossover.^{4,5} However, there are two key issues blocking the commercialization of DFAFC: (i) low efficiency and (ii) poor stability of the catalysts. Although enormous attention has been focused on Pt as the major electrocatalyst, Pt is easily poisoned, resulting in a loss of its catalytic activity during long-term operation. In addition, the high cost and low abundance of Pt limits its application as an electrocatalyst.

Considerable efforts and progress have been made in understanding the mechanisms of formic acid electro-oxidation and maximizing the performance of DFAFCs. Pd is less expensive than Pt (the current price is only 40% that of Pt) and shows higher catalytic activity than Pt for formic acid oxidation due to the different mechanisms of formic acid electro-oxidation on Pd

compared to that on Pt.⁴ Formic acid electro-oxidation on a Pd catalyst mainly proceeds in a facile dehydrogenation pathway.

However, CO is generated during formic acid oxidation and poisons the Pd active sites, leading to rapid decay in catalytic activity.^{5,6} The introduction of a second metal into the Pd lattice could increase the adsorbing ability for active oxygen and thereby help prevent the formation of strongly adsorbed CO on Pd surface. It is well-known that Au is an active catalyst for CO electro-oxidation in aqueous acidic medium.^{7–10} The hydroxyl groups adsorbed on Au surface can promote oxidation of CO and enhance the catalytic activity.^{11–13}

Pd–Au black alloys and Pd–Au nanoparticles supported on carbon have shown higher CO tolerance than Pt and Pt–Ru catalysts.⁶ Incorporation of Au improves the stability of Pd catalysts and helps in preventing the electro-catalyst degradation to a certain extent and suppresses the dissolution of Pd under highly oxidizing conditions.¹⁴ Thus, Pd–Au bimetallic catalysts show electro-catalytic activity for formic acid oxidation superior to that of monometallic Pd catalysts. Pd–Au/C catalyst with core-shell structure show higher electro-catalytic performance for formic acid oxidation by weakening the Pd–CO bond.¹⁵ Also, Pd–Au supported on multiwalled carbon nanotubes have shown remarkable activity for formic acid electro-oxidation than carbon supported Pd catalyst.¹⁶

It has been shown that the electro-catalytic activity not only depends on size, morphology, and distribution of Pd nanoparticles, but also on the nature of the support.^{17,18} A support

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with the ability to control, stabilize, and disperse the metal nanoparticles can greatly enhance the performance. In particular, there has been increased interest in graphene nanoplatelets (GNPs). They have been explored as durable catalyst supports for fuel cells due to the following distinct characteristics: (1) superior conductivity and (2) strong corrosion resistance.^{19–22} We demonstrate here, for the first time, that Pd–Au nanoparticles supported on graphene exhibit enhanced electrocatalytic activity and stability for formic acid oxidation compared to Pd supported on carbon (Pd/C).

2. Experimental

2.1. Functionalization of graphene nanoplatelets by PDDA (PDDA–xGNP)

All the chemicals are of analytical grade and were used as received. The graphene nanoplatelets (xGNP) (purity $\geq 99.5\%$) were obtained commercially from XG Sciences (USA).^{23,24} These nanoplatelets were small stacks of graphene sheets, about 5–10 nm in thickness with a specific surface area of $112 \text{ m}^2 \text{ g}^{-1}$.²⁵ xGNP was functionalized with a long-chain positively charged polyelectrolyte, poly (diallyldimethylammonium chloride) (PDDA) (MW = 200k to 350k, Sigma-Aldrich). PDDA can be easily adsorbed onto the hydrophobic surface of xGNP *via* the π – π interaction between the unsaturated C=C contaminant in the PDDA chains^{22,25} and graphene planes of xGNP. Typically, 300 mg of xGNPs was dispersed in 500 mL of 0.5 wt% PDDA aqueous solution and ultrasonicated for 3 h, which yielded a stable dispersion of xGNP. Then, the dispersed solution of xGNP was stirred for 24 h. After that, 2.5 g of KNO_3 was added to increase the binding between PDDA and xGNP surface, resulting in a highly functionalized xGNP with PDDA.²¹ The solution was stirred for another 24 h, filtered, and washed with ultrapure deionized water (18.2 M Ω cm, Mill-Q Corp.) to remove the free polyelectrolyte and then dried for 3 h at 90 °C in vacuum, which is hereafter denoted as PDDA–xGNP.

2.2. Synthesis of Pd–Au/PDDA–xGNP catalysts

First, 0.9433 g of sodium citrate was dissolved in 165 mL of water–ethylene glycol mixture solution (volume/volume = 1 : 1), and then 160 mg of functionalized PDDA–xGNP was transferred into the above solution to obtain the sodium citrate suspension, which was stirred and ultrasonically mixed for 2 h. 44.5 mg of K_2PdCl_4 and 44.5 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (aqueous solution containing 1 g per 100 mL) were dissolved in another 40 mL of water–ethylene glycol solution. The sodium citrate suspension was refluxed at 170 °C in argon atmosphere for 5 min. The catalyst precursor solution was then added drop-wise into the heated sodium citrate suspension and the solution was diluted by adding 40 mL of water–ethylene glycol solution (volume/volume = 1 : 1) and continued to be heated for another 2 h. The catalyst thus obtained with 20 wt% metal loading was then filtered, washed with water and ethanol, dried at 60 °C for 12 h, and then reduced in hydrogen at 150 °C for 2 h. The as synthesized catalyst is hereafter denoted as Pd–Au/PDDA–xGNP. The Pd supported on PDDA–xGNP sample with 20 wt%

Pd was prepared by the same process, but without including the Au precursor in the synthesis, and this sample is hereafter denoted as Pd/PDDA–xGNP. Commercial Pd/C catalyst was obtained from Johnson Matthey.

2.3. Preparation of working electrode

The Glassy Carbon (GC) electrode was polished before each experiment to a mirror finish with 0.05 μm alumina suspensions and rinsed thoroughly with double distilled water. The electrode was dried in a high purity nitrogen stream. The catalyst ink suspensions were prepared by mixing the required amount of catalyst in 0.5% Nafion solution. The mixture was sonicated for 30 min in an ultrasonication bath and 7 μL of the resulting catalyst ink was cast onto the surface of the GC electrode (5 mm diameter, 0.196 cm^2). The modified electrode was allowed to dry at 80 °C for 5 min to obtain a uniform catalyst film. All electrochemical experiments were carried out at room temperature and ambient pressure, employing 0.5 M sulphuric acid as the electrolyte solution.

2.4. Characterization methods

X-ray diffraction (XRD) patterns were recorded with a Philips Xpert X-ray diffractometer using $\text{Cu K}\alpha$ radiation. For transmission electron microscopy (TEM) studies, the catalysts dispersed in ethanol were placed on a copper grid and the TEM images were collected with a JEOL 2010 TEM equipped with an Oxford ISIS system. The operating voltage on the microscope was 200 keV. All images were digitally recorded with a slow-scan charge-coupled device (CCD) camera.

2.5. Electrochemical measurements

All electrochemical studies were carried out with an Autolab PGSTAT 30 (Eco Chemie) potentiostat/galvanostat. A classical three-electrode cell consisting of Ag/AgCl (3 M KCl) reference electrode, a platinum plate (5 cm^2) counter electrode, and a glassy carbon working electrode (the diameter of working electrode is 5 mm, 0.196 cm^2) was used for the cyclic voltammetry (CV) studies. The CV experiments were performed with 0.5 M H_2SO_4 solution in the absence and presence of 0.5 M HCOOH at a scan rate of 50 mV s^{-1} . All the solutions were prepared with ultra-pure water (Millipore, 18 M Ω). The electrolytes were degassed with nitrogen gas before the electrochemical measurements. All the electrochemical data were collected at room temperature.

3. Results and discussion

3.1. Physiochemical characterization of the catalysts

The XRD patterns of the Pd/C, Pd/PDDA–xGNP, and Pd–Au/PDDA–xGNP samples are shown in Fig. 1. All the three samples show reflections characteristic of a face-centered cubic (fcc) lattice, corresponding to the structures of Pd or Pd–Au.^{26,27} The reflections of Pd–Au (3 : 1 atomic ratio) are shifted to lower angles compared to those of Pd due to the larger size of Au, confirming the alloying of Au with Pd. The

Fig. 1 X-ray diffraction patterns of (a) Pd/C and (b) Pd/PDDA-xGNP, and (c) Pd-Au/PDDA-xGNP catalysts.

crystallite size of the Pd-Au nanoparticles obtained by using the Scherrer equation is 5.9 nm.

Fig. 2 shows the TEM images of the Pd/C, Pd/PDDA-xGNP, and Pd-Au/PDDA-xGNP electrocatalysts. It can be observed from Fig. 2(a) and (e) that the particles in Pd-Au/PDDA-xGNP are dispersed more uniformly compared to that in Pd/PDDA-xGNP. The particle size distribution obtained from the TEM images are shown in Fig. 2(b), (d), and (f). The Pd-Au/PDDA-xGNP sample exhibits larger particle size than Pd/PDDA-xGNP, but exhibits higher catalytic activity (see later). The HRTEM image of the Pd-Au/PDDA-xGNP catalyst (Fig. 2(g)) with a Pd : Au ratio of 3 : 1 shows that the interplanar spacing (2.285 Å) of the (111) planes matches closely that of the Pd_{0.5}Au_{0.5} alloy (2.299 Å) with a Pd : Au ratio of 1 : 1,^{28,29} confirming the formation of Au-Pd alloy.

3.2. Electrochemical characterization of the catalysts

Fig. 3 displays the CVs of the Pd/C, Pd/PDDA-xGNP, and Pd-Au/PDDA-xGNP electrodes in 0.5 M H₂SO₄ solution at a sweep rate of 50 mV s⁻¹. Two pairs of hydrogen adsorption peaks are observed for the Pd/C and Pd/PDDA-xGNP samples, while the intensity of the second peak is much diminished in the case of Pd-Au/PDDA-xGNP. However, the hydrogen adsorption peak current is higher for Pd-Au/PDDA-xGNP compared to those for Pd/PDDA-xGNP and Pd/C, suggesting a larger electrochemically active surface area (EASA) for Pd-Au/PDDA-xGNP. Also, the surface oxide formation on Pd-Au/PDDA-xGNP occurs at a higher potential than that on Pd/PDDA-xGNP. In contrast to Pt, the main problem with Pd alloys is the difficulty to distinguish adsorbed hydrogen on the Pd surface from absorbed hydrogen in the bulk due to Pd dissolution.^{30,31} The EASA values for the catalysts were calculated by the coulombic charge associated with palladium oxide reduction using a conversion value of 0.424 mC cm⁻²,^{32,33} and the values are given in Table 1. The higher EASA of Pd-Au/PDDA-xGNP indicates that Au incorporation increases particle dispersion.

Fig. 2 TEM images of (a) Pd/C, (c) Pd/PDDA-xGNP, and (e) Pd-Au/PDDA-xGNP electrocatalysts. Histograms of (b) Pd/C, (d) Pd/PDDA-xGNP, and (f) Pd-Au/PDDA-xGNP electrocatalysts. (g) HRTEM of Pd-Au/PDDA-xGNP electrocatalyst.

3.3. Electrochemical oxidation of formic acid

Fig. 4 presents the CVs of the Pd-Au/PDDA-xGNP catalyst with various Pd : Au ratios for formic acid oxidation in 0.5 M H₂SO₄ + 0.5 M HCOOH solution in comparison to those of Pd/C, Pd/PDDA-xGNP, and Pd-Au(3 : 1)/C. The catalytic currents are normalized to the mass of Pd and the values are given per mg of Pd in Table 1. The peak current density of Pd/PDDA-xGNP is 274 mA mg⁻¹ compared to 194 mA mg⁻¹ for Pd/C. Pd/graphene catalysts have been reported to show higher electrocatalytic activity due to the unique interaction between Pd and the graphene support.³⁴ In addition, the PDDA in our study can assist

Fig. 3 Cyclic voltammograms of (a) Pd/C, (b) Pd/PDDA-xGNP, and (c) Pd-Au/PDDA-xGNP catalysts in 0.5 M H₂SO₄ recorded at 50 mV s⁻¹.

Table 1 Comparison of the catalytic activities for formic acid oxidation

Electrocatalyst	Particle size (nm)		EASA (m ² g ⁻¹)	Mass specific activity (mA mg _{Pd} ⁻¹)
	XRD	TEM		
Pd/Vulcan XC-72 ³⁴	—	—	—	193
Pd/graphene ³⁴	—	10	—	210
Pd/CNT ³⁵	—	—	—	200
Nanoporous palladium ³⁶	—	3–6	23	262
Pd/Vulcan XC-72	4.2	4.4	36.4	196
Pd/PDDA-xGNP	5.7	5.1	42	274
Pd-Au (3 : 1)/PDDA-xGNP	5.9	6.8	58	580

in stabilizing the catalyst particles effectively, and the larger EASA can offer more active sites for chemisorption of formic acid. Interestingly, Pd-Au/PDDA-xGNP with a Pd : Au ratio of 3 : 1 exhibits the highest peak current density of 580 mA mg⁻¹ for formic acid oxidation, which is higher than those for Pd/C, Pd/PDDA-xGNP, and Pd-Au(3 : 1)/C (Fig. 4 and Table 1) despite the larger particle size of Pd-Au/PDDA-xGNP (Fig. 2) and those reported before in the literature.^{34,35} Also, among the various Pd-Au/PDDA-xGNP catalysts investigated, the sample with a Pd : Au ratio of 3 : 1 shows the highest activity for formic acid oxidation (Fig. 4).

The catalytic activity increases with Au content, but not linearly (Fig. 4), Pd₃Au showing the highest activity. This indicates that the atomic ratio and arrangement of Au and Pd sites is critical for enhancing the catalytic activity. It is known in the literature that pure Au has negligible catalytic activity for formic acid oxidation.^{15,37–39} Of note is the improved catalytic activity of Pd-Au catalysts toward formic acid oxidation through the pure “ensemble effects”⁴⁰ and the particle interfaces in the graphene support. Au content >50% results in a drop in catalytic activity due to the formation of isolated Pd sites. The higher catalytic

Fig. 4 Cyclic voltammograms of formic acid electro-oxidation on (a) Pd/C, (b) Pd/PDDA-xGNP, (c) Pd-Au (3 : 1)/C, (d) Pd-Au (3 : 1)/PDDA-xGNP, (e) Pd-Au (1 : 1)/PDDA-xGNP, (f) Pd-Au (2 : 1)/PDDA-xGNP, and (g) Pd-Au (4 : 1)/PDDA-xGNP in 0.5 M H₂SO₄-0.5 M HCOOH solution at a scan rate of 50 mV s⁻¹ (recorded after 20 scans) at 25 °C. The ratios refer to atomic ratios.

activity of Pd-Au/PDDA-xGNP could be due to the better particle dispersion, shifts in the d-band center of Pd, and the donation of electron density from Au to Pd, which can weaken the adsorptive strengths of the reaction intermediates during formic acid oxidation.^{41,42} This is consistent with the DFT calculations, showing that the addition of Au significantly improves the activity of a Pd-Au catalyst and the Au-induced ligand effect on both O and CO chemisorptions.⁴³ Also, the mechanism involving formic acid adsorption on Pd surface and hydroxyl species formation on Au surface could promote the bifunctional effect and thereby enhance the catalytic activity.

3.4. Stability of the electrocatalysts

The stability of catalysts is critical for application in fuel cells. Fig. 5 shows the chronoamperometry (CA) curves recorded at 0.3 V for 1 h in 0.5 M HCOOH-0.5 M H₂SO₄. The CA curves obtained with Pd/C and Pd/PDDA-xGNP show a significant decay in the current initially, reaching a steady state after 700 s. In contrast, Pd-Au/PDDA-xGNP exhibits higher current and superior stability over the entire length of time (1 h) in Fig. 5. The enhanced stability of Pd-Au/PDDA-xGNP is due to the promotional effect of Au on the catalytic activity of Pd.^{44,45} Au plays a major role in enhancing the stability and on the CO tolerance of the catalyst. The recurrent spike in the CA curve for Pd-Au/PDDA-xGNP in Fig. 5 is due to the removal of CO₂ bubbles produced during the oxidation process of formic acid. Overall, the higher activity and better stability of Pd-Au/PDDA-xGNP is due to the better dispersion and the enhanced interaction between catalyst nanoparticles and the graphene nanoplatelets support. The results demonstrate the potential of xGNP as a durable electrocatalyst support to replace carbon black in formic acid fuel cells.

Fig. 5 Current density versus time curves of (a) Pd–Au/PDDA–xGNP, (b) Pd–Au/C, (c) Pd/PDDA–xGNP, and (d) Pd/C catalysts measured in 0.5 M H₂SO₄ + 0.5 M HCOOH at 0.3 V vs. Ag/AgCl.

4. Conclusions

Pd and Pd–Au supported on polyelectrolyte-functionalized graphene nanoplatelets have been synthesized and their catalytic activities for formic acid oxidation have been compared with that of Pd supported on traditional Vulcan XC-72 carbon. Both the Pd/PDDA–xGNP and Pd–Au/PDDA–xGNP catalysts show higher activity for formic acid than the traditional Pd/C catalyst. More importantly, the Pd–Au/PDDA–xGNP catalyst with a Pd : Au atomic ratio of 3 : 1 exhibit nearly three times higher activity for formic acid oxidation and better stability than Pd/C, despite a larger particle size. The better performance of the Pd–Au/PDDA–xGNP catalyst is due to the better dispersion of the Pd–Au particles on the PDDA functionalized graphene nanoplatelets and the bifunctional promotional effect of Au through the hydroxyl groups adsorbed on the Au surface. In addition, the functionalized graphene nanoplatelets facilitate good contact between the reactant and the catalyst particles through improved metal–support interaction. The study demonstrates that optimized catalyst compositions and catalyst–support interactions could enhance the commercialization feasibilities of formic acid fuel cells.

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