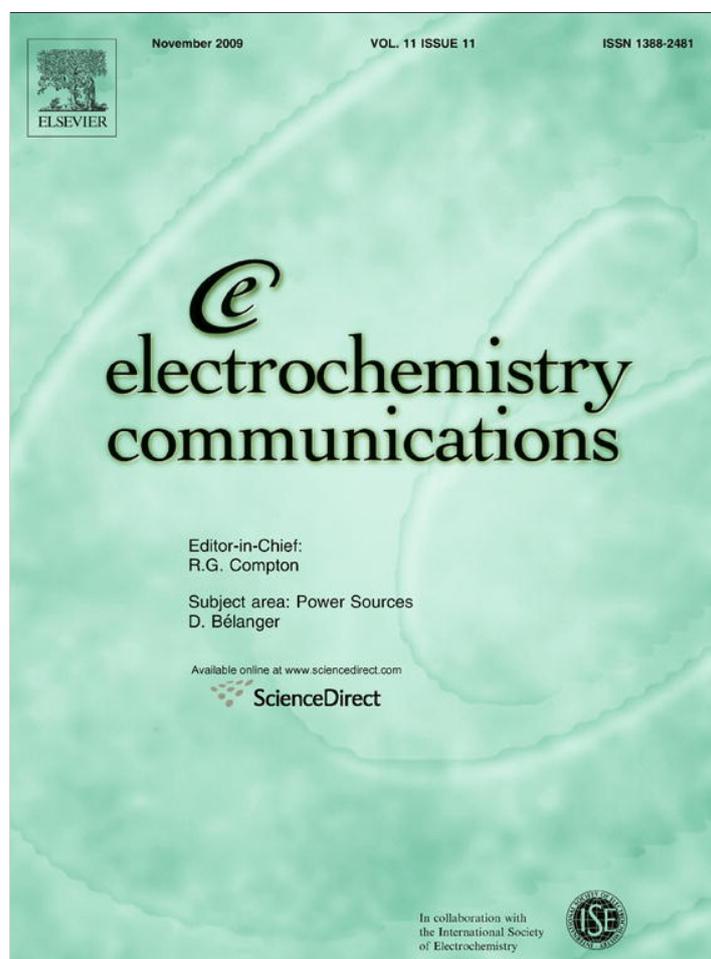


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Electrocatalytic oxidation of formic acid on functional MWCNTs supported nanostructured Pd–Au catalyst

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ABSTRACT

In this work, PdAu nanocatalysts with different weight ratio of Pd and Au supported on functional multi-walled carbon nanotubes (f-MWCNTs) were prepared, and their electrocatalytic activity for the oxidation of formic acid was also studied. The electrocatalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electrochemical results showed that the 4Pd1Au/f-MWCNTs (by weight) catalyst, exhibited distinctly higher activity and better stability in formic acid electrooxidation than the Pd/f-MWCNTs catalyst. The Nano-Au improves potentially the performance of Pd-based electrocatalysts for the direct formic acid fuel cells (DFAFCs).

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1. Introduction

As an attractive candidate to replace methanol and hydrogen, formic acid (FA) has considerable advantages in polymer electrolyte membrane (PEM) fuel cells for powering portable devices [1,2]. FA is nontoxic, nonflammable and has lower penetration efficiency through the Nafion membrane to methanol due to the repulsion between HCOO^- and SO_3^- ions. These extraordinary properties of FA make it possible to use highly concentrated fuel solutions in DFAFCs [3], which compensates the low volumetric energy density of FA and improves the overall cell efficiency. In addition, FA has a higher electronic motive force (EMF, 1.45 V) than either hydrogen or methanol [1,3].

Recent studies showed that the electrocatalytic activity of Pd for FA oxidation is higher than that of Pt [4,5], because Pd catalysts can overcome the CO poisoning effect mainly through the direct pathway. In many studies, considerable effort has been made to develop the Pd and Pd-based binary metallic catalyst [6–14]. For example, Ha et al. [10] first reported the use of pure Pd as the anode catalyst in DFAFCs, and they [11] also studied the addition of other metals to Pd/C, such as gold, which show beneficial effect for the oxidation of FA. Zhou et al. [13] prepared carbon supported Au–Pd catalysts with the core–shell structure, which improve the catalytic activity and stability of Pd for the electrooxidation of FA. Little research has been conducted in applying Pd–Au catalysts

with different weight ratio of Pd/Au to electrocatalyze FA oxidation reaction in these studies.

It has been proved that the catalytic activity of Pd appears to be associated with the size, morphology and distribution of nanocatalysts but also with the nature of the support [1]. Carbon nanotubes (CNTs), as a new branch of carbon materials, have been found numerous applications in catalytic field. In recent years, increasing attention has been paid to its serving as the support for the development of fuel cells due to its high surface area, excellent electronic properties, special chemical stability, and hollow geometry [15,16]. Furthermore, the surface modification of CNTs is necessary to create more surface binding sites and anchoring groups for precursor metal ions or metal nanoparticles [17]. Thus the f-MWCNTs supported Pd–Au catalysts could catalyze the oxidation reaction of FA more effectively. However, related studies are scarce so far.

In present work, Pd/f-MWCNTs and a series of bimetallic PdAu/f-MWCNTs catalysts were synthesized by a mild impregnation reduction method. FA oxidation reaction of the catalysts were investigated, and compared with that of Pd catalyst.

2. Experimental

2.1. Reagents

Chloroauric acid tetrahydrate ($\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$) and Nafion (5%) solution were obtained from Aldrich. Palladium chloride (PdCl_2)

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was purchased from Shanghai Chemical Company. All other chemicals in this study are of analytical grade.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) was carried out on the H-600–2 microscope. X-ray diffraction (XRD) was recorded on Bruker D8 Advance X-ray diffractometer with Cu K α radiation of wavelength $\lambda = 0.15406$ nm.

All electrochemical measurements were carried out with a CHI 660B electrochemistry workstation at 30 °C. The Pd or PdAu/f-MWCNTs pyrolytic graphite (PG) electrode was used as the working electrode (geometric surface area, 0.06 cm²). A Pt wire and saturated calomel electrode (SCE) were used as counter and reference electrode respectively. The electrolyte used was 0.5 M H₂SO₄ + 0.5 M HCOOH.

2.3. Catalyst preparation

f-MWCNTs supported Pd nanoparticles catalysts were prepared as follows: firstly, an ordered 4-aminobenzenesulfonic monolayer was grafted onto MWCNTs surface according to literature [8]. Then, 60 mg f-MWCNTs were ultrasonically suspended in a mixed solution of 16 ml water and 4 ml ethanol for 1 h. The resulted ink was mixed with 2.8 mL 0.05 M PdCl₂ solution and then stirred for 2 h before the superfluous tri-sodium citrate and sodium borohydride were slowly dropped in. After that, the above mixed suspension was stirred for another 8 h to complete the reaction under the protection of high purity nitrogen. At last, the suspen-

sion was filtered, washed with the doubly distilled water until no Cl⁻ was detected and then dried in vacuum at 50 °C overnight. In the case of PdAu/f-MWCNTs electrocatalysts with various Pd/Au weigh ratios, an aqueous solution of HAuCl₄ (0.05 M) was added to the above system and the weight ratio of Pd to Au was kept constant at 5:1, 4:1, 3:1, 1:1, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of Pd/f-MWCNTs and 4Pd1Au/f-MWCNTs catalysts. It is shown in Fig. 1.(curve a) that the peak located at a 2θ value of about 26° is attributed to the graphite (0 0 2) plane of the MWCNTs and other four peaks at 40.1°, 46.7°, 68.1° and 82.1° corresponds to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) facets of palladium crystal. In the XRD pattern of the 4Pd1Au/f-MWCNTs catalyst (Fig. 1. curve b), the peaks at 40.0°, 46.5°, 68.0° and 82.0°, corresponding to Pd, slightly smaller than that of the Pd/f-MWCNTs catalyst. Furthermore, the strong diffraction peaks with the 2θ values of 38.2°, 44.5°, 64.5° and 78.2°, corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) facets of gold crystal, indicates the coexistence of Pd and Au in the catalyst. In addition, the average size of metal particles on 4Pd1Au/f-MWCNTs and Pd/f-MWCNTs is 4.0 and 4.3 nm respectively, calculated from (1 1 1) peak by the Scherrer formula [18], which suggests that the nanoparticles size on the various catalysts is similar.

Fig. 2 shows the TEM images of Pd/f-MWCNTs and 4Pd1Au/f-MWCNTs catalysts. It can be seen from Fig. 2B that many fine Pd and Au particles with well uniformed dispersion formed on the outer walls of the CNTs, which is slightly better dispersion than the Pd particles on Pd/f-MWCNTs (Fig. 2 image A). This illustrates that Au can prevent the aggregation of Pd nanoparticles. The mean particle size of the well dispersed nano-PdAu from counting 150 particles was about 3.9 nm, which is in good agreement with the value calculated from the XRD results.

Fig. 3 shows the cyclic voltammograms in 0.5 M H₂SO₄ solution on the two different electrodes. It is found that the hydrogen adsorption and desorption peaks on the 4Pd1Au/f-MWCNTs/PG (Pd loading = 0.4 mg cm⁻²) electrode are larger than that on Pd/f-MWCNTs/PG (Pd loading = 0.5 mg cm⁻²) electrode. The coulombic charges of the hydrogen desorption peaks for the 4Pd1Au/f-MWCNTs and Pd/f-MWCNTs catalysts are 21.2 × 10⁻³ and 13.0 × 10⁻³ C cm⁻² respectively. And it is observed from Fig. 3 that 4Pd1Au/f-MWCNTs/PG and Pd/f-MWCNTs/PG electrodes deliver reduction peaks at ca. 0.503 V and 0.509 V, respectively, attributing to the reduction of the oxide formed on the Pd and nanoPd/Au during the forward scan. According to the integrated intensity of these peaks, the real surface area of the PdAu is approximately 1.5 × larger than that of the Pd electrode. The results further reveal that the adsorption/desorption of hydrogen is more active on 4Pd1Au/f-MWCNTs/PG than that on Pd/f-MWCNTs/PG.

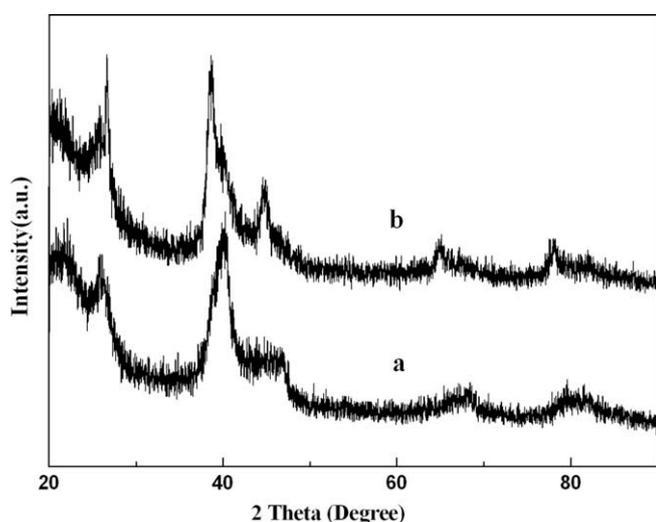


Fig. 1. XRD patterns of: (a) Pd/f-MWCNTs and (b) 4Pd1Au/f-MWCNTs.

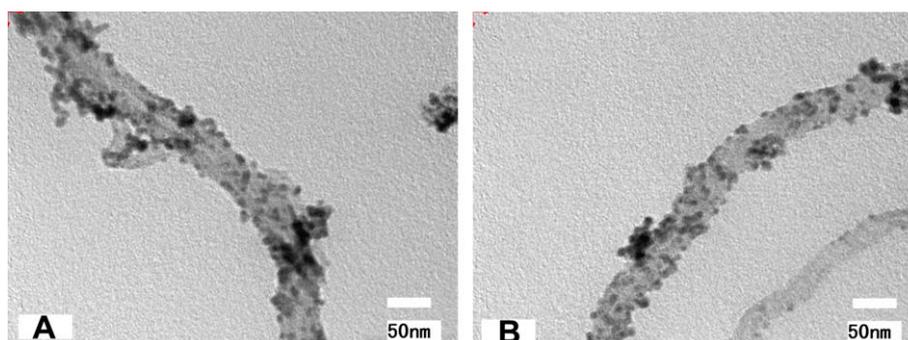


Fig. 2. TEM images of: (A) Pd/f-MWCNTs and (B) 4Pd1Au/f-MWCNTs.

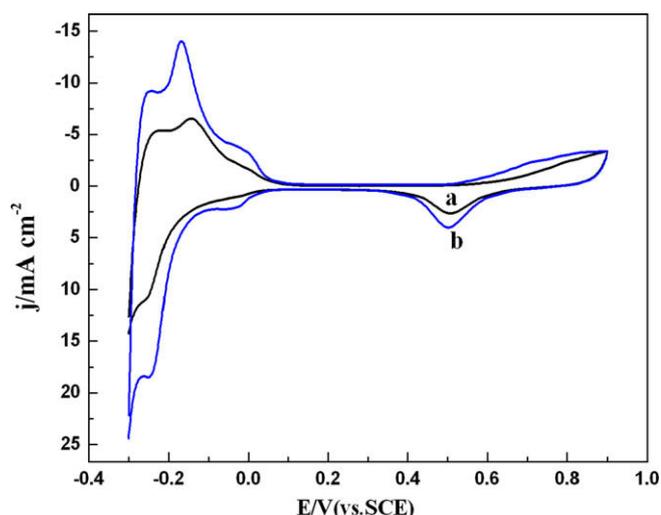


Fig. 3. Cyclic voltammograms of 0.5 M H_2SO_4 on (a) Pd/f-MWCNTs and (b) 4Pd1Au/f-MWCNTs electrodes.

Fig. 4 is a comparison of FA oxidation on the catalysts with different ratio of Pd/Au. The strong oxidation peaks belong to the oxidation of FA and the corresponding intermediates. From the curve (e), the main oxidation peak potential in the positive-scan direction for the 4Pd1Au/f-MWCNTs catalyst is located at ca. 0.211 V, and the corresponding peak current density is ca. 59.3 mA cm^{-2} , displaying the highest catalytic activity for FA. FA oxidation current density is shown to change in the order: 4Pd1Au/f-MWCNTs > 3Pd1Au/f-MWCNTs > 5Pd1Au/f-MWCNTs > Pd/f-MWCNTs > 1Pd1Au/f-MWCNTs. The corresponding oxidation peak current densities on these catalysts are 59.3, 35.6, 29.8, 25 and 18.8 mA cm^{-2} , respectively.

The stability of FA oxidation on Pd/f-MWCNTs and 4Pd1Au/f-MWCNTs electrodes were investigated in 0.5 M H_2SO_4 containing 0.5 M HCOOH at a constant potential of 0.1 V. The rapid current decrease shows the poisoning of the electrocatalysts. Fig. 5 shows that, the current density of the 4Pd1Au/f-MWCNTs after 6000 s is higher than that of Pd/f-MWCNTs at the corresponding time. Nevertheless, at the same time, the oxidation current is larger on 4Pd1Au/f-MWCNTs than that on Pd/f-MWCNTs. This indicates that

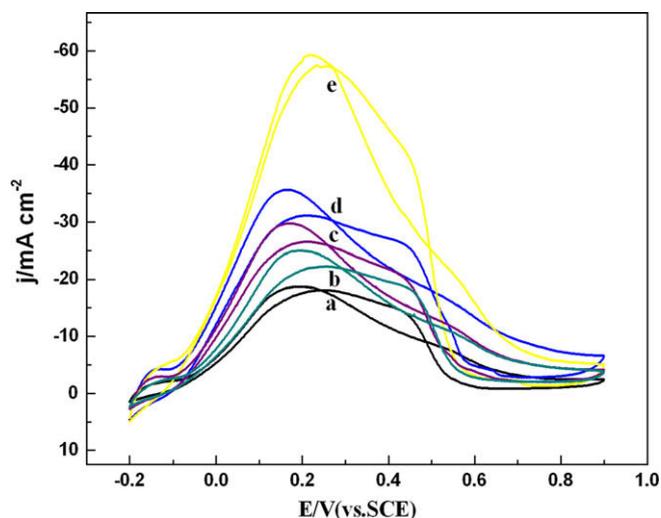


Fig. 4. Cyclic voltammograms of 0.5 M HCOOH in 0.5 M H_2SO_4 solution on (a) 1Pd1Au/f-MWCNTs, (b) Pd/f-MWCNTs, (c) 5Pd1Au/f-MWCNTs, (d) 3Pd1Au/f-MWCNTs and (e) 4Pd1Au/f-MWCNTs catalyst electrodes.

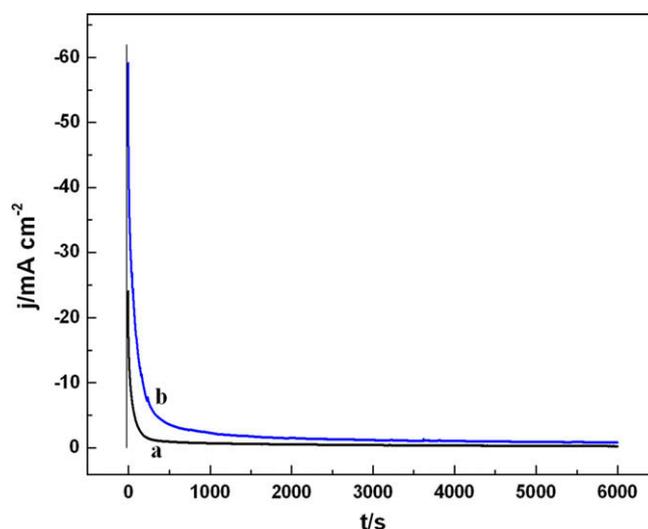


Fig. 5. Chronoamperometric curves of (a) Pd/f-MWCNTs and (b) 4Pd1Au/f-MWCNTs electrodes in 0.5 M H_2SO_4 containing 0.5 M HCOOH at 0.1 V.

certain content of Au enhances the stability and poisoning tolerance of Pd.

The above results illustrate that Au can promote the oxidation of FA in PdAu/f-MWCNTs electrocatalysts, possibly due to the weakening of the adsorptive strengths of the CO-like intermediates. Au has negligible electrocatalytic activity for the oxidation of FA, but exhibits good activity for CO oxidation [19]. CO-like intermediate species on the gold surface can be oxidized to produce CO_2 or other products. The synergistic effects between Pd and Au may prevent the accumulation of CO-like intermediates and consequently more Pd active sites are available for further electrochemical reaction through the direct pathway.

4. Conclusions

With suitable weight ratio of Pd and Au, PdAu/f-MWCNTs catalysts could provide higher electrochemical surface area, catalytic performance and better stability for FA oxidation than the Pd/f-MWCNTs catalyst. The Au nanoparticles show potential in further improving the performance of Pd-based electrocatalysts for the DFAFCs.

Acknowledgements

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