

The Improvement of Pd Nanoclusters Electro-catalytic Properties for FAO by the Addition of Co Element

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Keywords: Pd-based nanoclusters catalysis, Physical vapor deposition, Formic acid oxidation

Abstract. Near-monodisperse Pd and PdCo nanoclusters were synthesized by physical vapor deposition using a plasma-gas-condensation cluster deposition system and tested for catalyzing formic acid oxidation. Under the condition of high vacuum and inert gas, NCs with clean surface and uniform size were obtained. The cyclic voltammetry tests revealed that the electrochemical surface area was increased from 49.7 m² g⁻¹ to 51.7 m² g⁻¹ and the peak current density of catalyzing FAO was raised from 0.115 mA cm⁻² to 0.125 mA cm⁻² when about 12wt. % Co element was added. Additionally, the tolerance to CO poisoning of Pd could also be improved by the addition of Co. The result indicated that this method offered a chemical-free way to prepare clean and efficient Pd-based nanoscale catalytics and encouraged deeper exploration for electrochemical catalytic reactions.

Introduction

Nowadays, the interests in the energy-converting and energy-saving technology of direct formic acid fuel cell (DFAFC) are raised significantly, due to its higher theoretical electromotive potential and less fuel crossover comparing with those of direct methanol fuel cell (DMFC) [1]. Pt as its general catalyst was challenged on account of large cost, slow reaction kinetics and the intermediate CO poisoning [2]. So one of the key issues in practical applications was to explore less or non-platinum catalytics which also could catalyze more efficiently and tolerate CO poisoning better. Recent researches showed that Pd-based catalyst could be an effective alternative to Pt in this field, due to their lower cost and higher active surface area, besides, it almost could avoid CO poisoning more effectually by the direct 2-electron catalytic process which was different from the process with the nocuous oxidation product CO of Pt-catalysts [3]. Moreover, some authors have supported that PdCo bimetallic nanoparticles (NCs) could improve the Pd electrocatalytic activity and stability for formic acid oxidation (FAO), which could be attributed to the synergistic effects within the two parts [4-6]. At present, the most commonly method to prepare bimetallic NCs was liquid-phase synthesis [7-9], however, there were several limitations, such as bad size distribution, poor surface cleanness and weak attachment. Different from the traditional liquid-phase route, the physical vapor-phase deposition method (PVD) was carried out at a high vacuum and inert gas conditions which were allowed to avoid the surface pollution and oxidation efficiently.

In this paper, the plasma-gas-condensation cluster deposition (PGCCD, see Fig. 1) system developed according to PVD technique was used to prepare Pd and PdCo bimetallic NCs. The catalytic activity and utilization efficiency of Pd could be approved by the addition of Co element. The NCs assembled films prepared by PGCCD whose packing density (P) was only about 30 % of

the bulk one^[10] had a narrow size distribution and good morphology consistency. In this device, the NCs were deposited onto the glassy carbon plate (GCP) directly, therefore, the preferable contact area and adhesive strength could be maintained even without any additives. Even more important, the catalytic performance of Pd NCs for FAO and the influences of Co on the structure, morphology and electrocatalytic properties of Pd NCs were also investigated systematically in this work.

Experimental

A PGCCD system (Fig. 1) was used to synthesize Pd and PdCo NCs, and the experiment principle has been described in detail in our earlier work^[11]. High-purity Pd and Co (99.99%) metal targets were installed as 100 mm apart distance, and an Ar flow rate of 350 sccm adjusted by a fine mass flow controller was injected steadily into the Sputtering chamber. In the experiment process, the pressure of the Sputtering chamber and Assembling chamber was maintained at about 100 Pa and 5×10^{-3} Pa, respectively. The high concentration Pd or Pd/Co mixed atomic vapor was generated by dc sputtering with a power of 400 W. Vapor atoms lost their kinetic energy rapidly and nucleated by collision with insert gas molecules. Then the nucleated NCs were extracted into the Assembling chamber through the nozzle located in Filter region accompanied by the Ar gas flow under the pressure differential produced by the pumping system. The NCs obtained a drift rate for the isentropic and adiabatic expansion process and softly landing and assembling onto the GCP ($S = 1 \text{ cm}^2$).

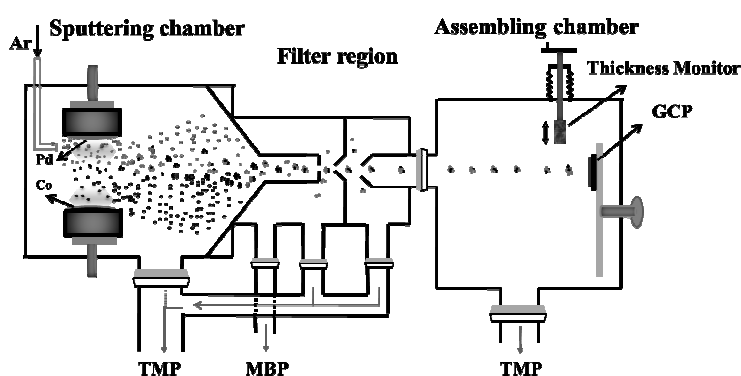


Fig. 1. Schematic Diagram of the Plasma-gas-condensation Clusters Deposition System (PGCCD)

The deposition rate of NCs was measured by a quartz oscillator-type thickness monitor located on the top of the Assembling chamber. The mass fraction of Co was measured by wavelength dispersive spectrometer (WDS, EPMA JEOL8100). The morphology and size distribution of NCs (with effect thickness of about 2.0 nm) loaded on the Cu micro grids were characterized by a transmission electron microscope (TEM, JEM2100HC). The surface morphology of the NCs assembled films (~100 nm) deposited on silicon wafers was observed through a scanning electron microscope (SEM, LEO-1530FE). Moreover, the crystalline structure of the as-prepared samples was analyzed by X-ray diffraction (XRD, Panalytical X'pert-PRO).

Electrochemical measurements were performed on an electrochemical workstation (Autolab PGSTAT302N). A standard three-electrode cell was used, which consisted of a Pt net counter electrode, an Ag/AgCl (in saturated KCl) reference electrode and a GCP covered with 100 nm Pd or PdCo bimetallic NCs working electrode. Before deposition, the GCPs were polished with 0.3 μm alumina powder and then washed twice for 10 min each by ultrasonic in alcohol. The cyclic voltammograms (CVs) were measured in the electrolytes of 0.5 M H_2SO_4 and 0.5 M $\text{H}_2\text{SO}_4 + 0.5$ M HCOOH at $-0.21 \sim +1.0$ V with a scan rate of 50 mV s^{-1} . The potentials in electrochemical curves were reported with respect to Ag/AgCl (0.210 V vs. SHE).

Results and Discussion

The XRD patterns of the Pd and PdCo NCs assembled films were shown in Fig. 2. The main diffraction peaks located at 40.473° and 47.046° can be assigned to (111) and (200) planes of Pd_{fcc}, respectively. Besides, the additions of Co (the mass fraction was measured by WDS as 12%) didn't change the phase structure of Pd but made its crystallinity better. Fig. 3 shows the TEM and SEM images of Pd and PdCo bimetallic NCs. It can be seen from the TEM images that the Pd and PdCo NCs were spherical with small size and narrow size distribution. The particle size of PdCo NCs (6.44 nm) was larger than Pd NCs (5.15 nm), which was in accordance with the result of XRD. The SEM images show that the NCs were loosely packed on the surface of silicon wafers and formed porous films, which will be conducive to obtain large specific surface area.

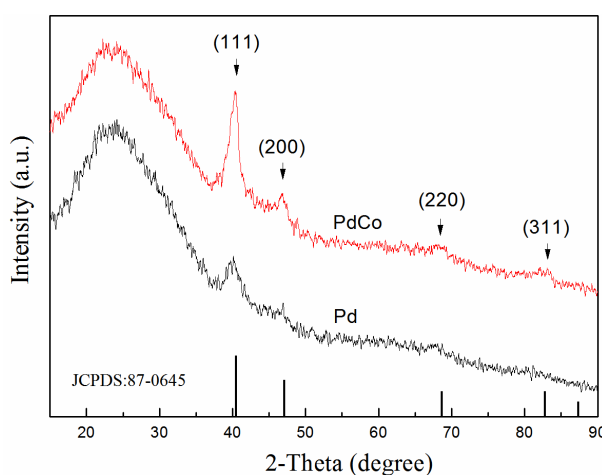


Fig. 2. XRD Patterns of Pd and PdCo NCs Synthesized by PGCCD

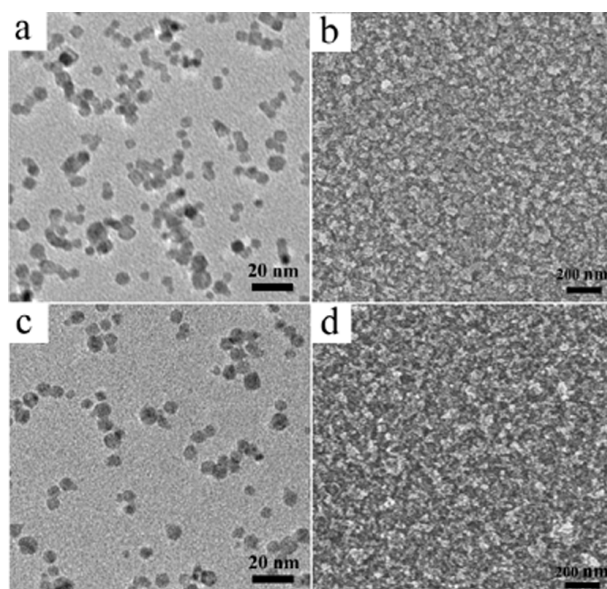


Fig. 3. TEM and SEM Images of Pd (a, b) and PdCo (c, d) NCs

Fig. 4a shows the stable CVs of Pd and PdCo NCs prepared by PGCCD and their current densities were normalized by the geometric area of catalysts. It could be found that two peaks current density (I_p) of hydrogen adsorption/desorption in the lower-potential region (-0.21 V \sim 0.1 V). The electrochemical active area (ECSA) calculated from the integration value of the charge involved in hydrogen desorption area to reflect the real surface area of electrodes were 49.7 and 51.7 $\text{m}^2 \text{g}^{-1}_{\text{Pd}}$ for Pd and PdCo, respectively^[12]. Here, the catalysts assembled by NCs with big specific surface area and their unique spongy-network nature could enlarge the effective contact

area (ECA) and provide more active sites. On the other hand, in the anodic scan of the higher-potential region, the Pd surface oxidation could be seen at +0.55 V in forward scan and the reduction of Pd oxides (PdO) appeared at about +0.5 V in the reverse scan. It was noticed that PdCo NCs reduction peak potentials was shifted more positively than the Pd NCs, which indicated that the oxidized PdCo NCs was reduced more effortlessly. So the CVs results suggested that PdCo NCs showed a more “noble” metal character than Pd NCs.

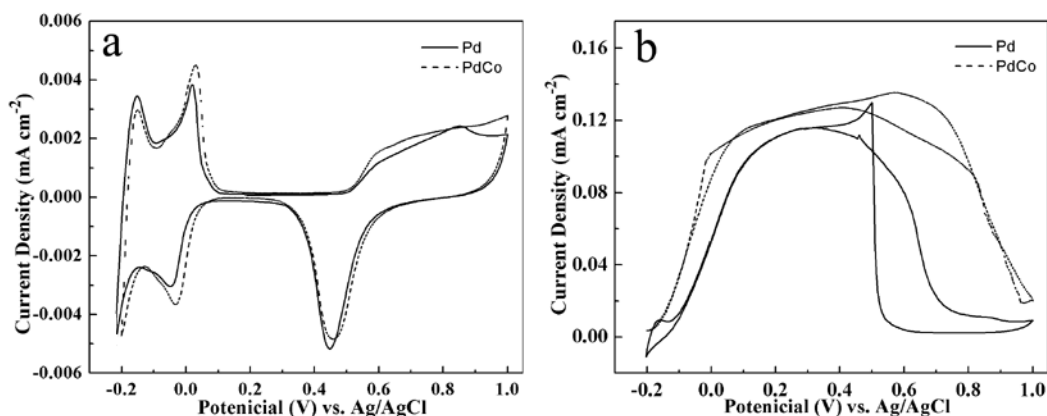


Fig. 4. CVs in N_2 Saturated 0.5 M H_2SO_4 (a) and Specific Activities (b) in 0.5 M H_2SO_4 + 0.5 M $HCOOH$ of the As-prepared Pd and PdCo NCs

Fig. 4b reveals the responses of above-mentioned NCs catalyzing FAO and the current densities were obtained by normalizing the currents to the ECSAs (specific activities). It was observed that in the forward scan, there was a high I_p appeared near 0.3 V (the direct oxidation of formic acid to form CO_2) and a shoulder I_p near 0.6 V (the formation of intermediate CO generated from the dissociative adsorption step)^[13]. The I_p of PdCo was 0.125 mA cm^{-2} which was higher than Pd (0.115 mA cm^{-2}), and its peak potential related appeared at -0.2V which was lower than Pd (-0.1V). The meaningful higher I_p of the first peak and much broader contour indicated the preferable catalytic activity to FAO and significant tolerance to CO poisoning^[14]. So the PdCo NCs was capable of more rapid $HCOOH$ absorption and activation which led to a kinetically faster catalytic reaction. The CVs in FAO indicated that Co doped into Pd could improve the electro-catalytic activities of Pd catalyst.

Conclusions

In this paper, a new physical vapor method to prepare Pd-based NCs catalysts was developed. By the addition of Co, the cost of Pd catalysts was reduced, and the electro-catalytic activities of Pd were improved. The ECSA was increased from $49.7 \text{ m}^2 \text{ g}^{-1}$ to $51.7 \text{ m}^2 \text{ g}^{-1}$ and the I_p of catalyzing FAO was raised from 0.115 mA cm^{-2} to 0.125 mA cm^{-2} when about 12wt. % Co element was added. Therefore, the PVD exhibits a broad application prospect in synthesizing metal NCs for applications of electrochemical catalysis.

Acknowledgements

The authors gratefully acknowledge financial support from the National Basic Research Program of China (grant no. 2012CB933103), National Outstanding Youth Science Foundation of China (grant no. 50825101), and the National Natural Science Foundation of China (grant nos. 51171158, 51371154 and 51301145).

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