



## Short communication

## Copper@palladium–copper core–shell nanospheres as a highly effective electrocatalyst for ethanol electro-oxidation in alkaline media



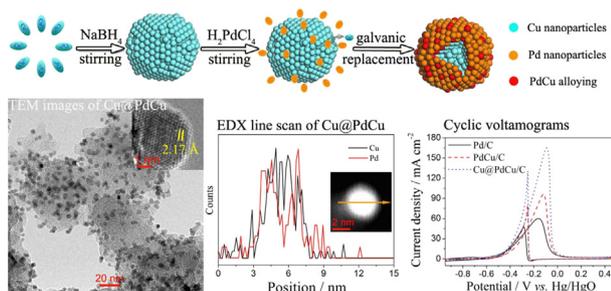
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## HIGHLIGHTS

- The Cu@PdCu/C catalyst is synthesized via the galvanic replacement method.
- The nanoparticles present core–shell structure with the shell thickness of about 0.5 nm.
- Ethanol oxidation peak current on Cu@PdCu/C is 2.78 times higher than that on Pd/C.
- Durability and anti-poisoning ability of Cu@PdCu/C toward ethanol oxidation are greatly promoted.
- The promoted effect is due to the synergistic effect between Pd and Cu.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel Cu@PdCu/C catalyst with the core–shell structure is prepared by the galvanic replacement between Pd<sup>2+</sup> ions and Cu particles. It is characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy-dispersive X-ray spectra (EDX) and electrochemical measurements. The Cu@PdCu nanoparticles are composed of the Cu core and PdCu alloying shell with a thickness of ca. 0.5 nm. The peak current density of ethanol oxidation on Cu@PdCu/C is 166.0 mA cm<sup>-2</sup>, which is 2.78 times higher than that on Pd/C catalyst (59.8 mA cm<sup>-2</sup>). Durability and poisoning tolerance of this catalyst are also greatly improved.

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## 1. Introduction

Recently, direct ethanol fuel cell (DEFC) has received a great number of attentions. This is because ethanol has non-toxicity, low permeability and high theoretical mass energy density

(8.01 kWh kg<sup>-1</sup>) as compared with methanol. And ethanol can be easily produced in great quantities from the fermentation of biomass [1–3]. A lot of researches showed that the electro-oxidation reaction of ethanol presented high activity in alkaline medium [4,5]. Pd is considered to be a promising alternative to Pt on alcohol electro-oxidation in alkaline medium [6]. It is well known that the alloying of Pd with other metals or its combination with metal oxides can remarkably enhance both their catalytic activity and stability for alcohol oxidation in alkaline solution [6,7].

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Apart from the effects by elements, the sizes and morphologies of electrocatalysts also have a crucial influence on the catalytic activity [8,9].

The tailored design and synthesis of core–shell nanoparticle catalyst is an effective method to enhance the catalytic activity [10–14]. The design with noble metal as thin shell on proper non-noble metal core not only reduces the usage of noble metal, but also significantly enhances the catalytic performance due to the so-called strain and ligand effect between the core substrate and the noble metal shell [15–17]. The polyvinylpyrrolidone (PVP) is used to synthesize core–shell catalysts in numerous researches. However, the capping agents are difficult to be removed completely and prone to block the catalytic active sites and enlarge the nanoparticle size [18]. A galvanic displacement method is developed to prepare core–shell catalysts without the use of capping agents. The catalysts with ultralow noble metal loadings can be easily synthesized by this method.

The cheap cupreous material is a promising assistant for Pt-based catalysts, but only a handful of studies focus on alcohol oxidation using Pd–Cu catalysts with well-defined morphologies in alkaline media [19–21]. In this study, the Cu@PdCu core–shell nanoparticles were prepared by the galvanic replacement between Pd<sup>2+</sup> ions and Cu particles. The Cu@PdCu/C catalyst has much higher catalytic activity and stability toward ethanol oxidation as compared with state-of-the-art Pd/C and PdCu/C catalysts.

## 2. Experimental

### 2.1. Synthesis of Cu@PdCu/C catalyst

The active carbon black (Vulcan XC-72R) used in this work was purchased from Cabot Corp. (USA). The processes of purification and acid-functionalization are described in detail elsewhere [22]. Prior to the synthesis, all solvents used were de-aerated with N<sub>2</sub> for 30 min. 17.8 mg of Vulcan XC-72R carbon and 0.3 g sodium citrate were dissolved in 50 ml of ethylene glycol (EG) under ultrasonic stirring. 4 ml of CuSO<sub>4</sub> (18.9 mM) solution was added into the suspension with constant stirring for 30 min. Then 25 ml of freshly prepared NaBH<sub>4</sub> (20 mM) solution was added dropwise under vigorous stirring at room temperature. The mixture was stirred for one night to decompose any remaining NaBH<sub>4</sub>. After that, 1 ml of H<sub>2</sub>PdCl<sub>4</sub> (37.8 mM) solution was added into the mixture. The Cu@PdCu/C catalyst was synthesized by the galvanic displacement reaction of PdCl<sub>4</sub><sup>2-</sup> to Pd via oxidizing Cu. The reaction in the mixture was conducted for one day under stirring. The entire reaction process was performed under N<sub>2</sub> atmosphere to prevent oxidation of Cu nanoparticles. Finally, the black product was filtered, washed and dried in a vacuum oven at 80 °C for 8 h. For comparison, PdCu/C and Pd/C were synthesized directly by co-reduction of the metal precursor using the dropwise addition of NaBH<sub>4</sub> under nitrogen atmosphere at room temperature.

### 2.2. Physical and electrochemical characterization

Characterization of as-prepared catalysts was tested under similar conditions as reported in Ref. [22]. Atomic adsorption spectroscopy (AAS, TAS-686G) was used to analyze the compositions of as-prepared catalysts. The XRD patterns were obtained from an X-ray powder diffractometer (Philip X' Pert Pro MPP) using a CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at the scan rate of 2° min<sup>-1</sup> with a step of 0.02°. The chemical valence states of the catalysts were analyzed by the X-ray photoelectron spectroscopy (XPS, VG ESCA-LAB 250) using an Al K $\alpha$  X-ray source of 1486.6 eV. The morphology and size distribution of the catalysts were examined using a transmission electron microscope (TEM, JEOL JEM-2010). Energy-

dispersive X-ray (EDX) analysis was carried out by a microanalyser. And an FEI Tecnai G2 F20 S-Twin TEM equipped with an EDX detector was employed for the high-angle annular dark-field scanning TEM (HAADF-STEM) images and EDX line analysis.

Electrochemical measurements were carried out by a CHI 660C electrochemical working station (CH Instrument Inc.) in a typical three-electrode electrolytic cell. Glassy carbon electrode (GCE, 0.1256 cm<sup>2</sup>) was used as the working electrode to support the catalysts. A piece of Pt foil and the mercuric oxide electrode (Hg/HgO/1 M KOH, 0.098 V vs. SHE) were used as the counter and reference electrodes, respectively. For the working electrode preparation, 5.0 mg as-prepared catalyst was dispersed in 1 ml solution of 985  $\mu$ l isopropyl alcohol and 15  $\mu$ l Nafion solution (15 wt %, DuPont) under ultrasonic stirring for 30 min. A 4  $\mu$ l aliquot of the slurry was transferred onto the pre-polished GCE by using a micropipette and dried under an infrared lamp. Before measurements, the electrolyte was first de-aerated with high purity N<sub>2</sub>. All electrochemical measurements were performed at 30  $\pm$  1 °C, as reported in Ref. [22].

## 3. Results and discussion

The Pd loadings and chemical compositions of the as-prepared Pd/C, PdCu/C and Cu@PdCu/C catalysts were determined using AAS analysis, respectively, as shown in Table 1. It is found that the galvanic replacement of Cu nanoparticle core with Pd<sup>2+</sup> was not completed for the Cu@PdCu/C catalyst because its theoretical content of Pd is 20 wt% and atomic ratio of Pd:Cu is 1:1. The XRD patterns of Pd/C, PdCu/C and Cu@PdCu/C catalysts are shown in Fig. 1A. At about 25°, all diffractograms show a broad peak which refers to graphite (002) facet of carbon black. In the XRD pattern of Pd/C, the four main diffraction peaks located at about 39.8°, 46.3°, 67.6° and 81.2° are ascribed to the (111), (200), (220) and (311) reflections of face centered cubic (*fcc*) Pd crystal (JCPDS Card No. 05-0681), respectively. For PdCu/C and Cu@PdCu/C catalysts, these four main diffraction peaks shift in positive position, which suggests the alloying between Pd and Cu. Fig. 1B shows the survey XPS spectra of these three catalysts. All catalysts have Pd 3d spectra, as shown in Fig. 1C. The binding energy of Pd signals have shifted negatively on PdCu/C and Cu@PdCu/C catalysts as compared with that on Pd/C catalyst, indicating the electronic interaction between Pd and Cu atoms. Pd 3d spectra can be deconvoluted into two pairs of peaks, which are ascribed to metallic Pd(0) and Pd(II) species. Moreover, the Cu 2p spectra can be found in the XPS spectra of PdCu/C and Cu@PdCu/C catalysts (shown in Fig. 1D). In the Cu 2p region, the deconvoluted peaks are assigned to metallic Cu(0) and Cu(II) species as well as the satellite peak of CuO (at  $\sim$ 943.0 eV) [20]. The Cu 2p signal of Cu@PdCu/C is intense, which suggests that part of Cu exists on the catalyst surface [23]. In addition, the compositions of these three catalysts analyzed by XPS are also shown in Table 1. It is found that the content of Cu in Cu@PdCu/C obtained from XPS is obviously lower than that in the nomenclature of Cu@PdCu/C analyzed by AAS, demonstrating that part of Cu atoms at the surface of the Cu core is displaced by Pd<sup>2+</sup> to form the

**Table 1**

The compositions obtained from AAS and XPS as well as particle sizes from TEM images for as-prepared catalysts.

Samples	Contents of Pd (wt%)	Atomic ratios from AAS (Pd:Cu)	Atomic ratios from XPS (Pd:Cu)	Particle sizes (nm)
Pd/C	19.68	/	/	3.0
PdCu/C	20.16	1:0.84	1:0.78	2.7
Cu@PdCu/C	16.92	1:1.46	1:0.46	3.9

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