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Full Length Article

Concave Pd–Ru nanocubes bounded with high active area for boosting ethylene glycol electrooxidation

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ABSTRACT

This paper reported our extensive efforts in the design of concave PdRu nanocubes via a facile wet-chemical strategy. Different from the previously reported PdRu nanostructures, the as-prepared concave PdRu nanocubes combined the advantages of fascinating nanocube structure, synergistic and electronic effect as well as high surface area. All of these beneficial terms endow them to exhibit superior electrocatalytic activity and long-term stability towards ethylene glycol oxidation as compared with commercial Pd/C. Our work highlights the significance of shape-controlled of PdRu nanostructures over the electrocatalytic performances towards the electrooxidation of ethylene glycol (EG), which will pave up a new strategy for boosting the development of renewable and clean energy technology.

1. Introduction

The increasing consumption of traditional fossil fuels coupled with the serious environment crisis have stimulated the rapid development of renewable and clean energy technology [1,2]. Direct fuel cells (DFCs), with the features of easily-available, high-energy and non-toxic, have attracted an increasing notice for serving as promising energy conversion and storage devices [3,4]. Among multitudinous fuel cells, direct ethylene glycol fuel cells (DEGFCs) are nowadays considered as advanced energy technologies due to their remarkable features such as higher boiling point (198 °C), higher energy density and less catalyst toxicity etc. [5,6]. In addition, some previously published researches have demonstrated that the EG can primarily be produced from the cellulose with high yield, all of which make them as safe and attractive energy carrier in the field of DEGFCs [7,8]. Regardless of these beneficial properties, the lack of cost-efficient catalysts for the electrooxidation of EG still seriously hinder its practical application [9].

Noble metal nanomaterials represent a novel class of catalysts for the electrooxidation reaction in DFCs, but its large-scale commercial application is also impeded by their limited electrocatalytic activity and stability [10]. Update, Pt-based nanomaterials, one of the most effective electrocatalysts used in DFCs, have also met the challenges of scared natural abundance and unsatisfied activity [11,12]. In order to get over these difficulties, extensive efforts have been paid to engineer the hopefully alternative electrocatalysts with both enhanced activity and durability but less cost. In this regard, many less expensive and more plentiful non-platinum electrocatalysts with satisfactory performances have been widely applied [13,14]. Especially for Pd and Pd-based materials, which can be widely applied as lead electrocatalysts towards liquid fuel oxidation with comparable or even superior performances to Pt [15–17]. As for Pd, it has been proved that the catalytic properties of Pd-based electrocatalysts are strongly dependent on their morphologies and compositions [18–21]. With respect to this, alloying Pd with a secondary metal may be one of efficient strategies to boost the commercial development of DFCs, for which can reduce the usage of noble Pd metal while simultaneously improving performance as compared with that of pure Pd on mass activity [22–25]. Among a wide range of transition metals, Ru has been undoubtly considered as excellent ligand to form the stable PdRu alloy with greatly enhanced catalytic activity for liquid fuel oxidation reactions due to the Watanabe–Motoo bifunctional mechanisms: Ru atoms provide OH_{ads}-like adsorbed hydroxyl groups and serve as the oxidant to oxidize the CO_{ads} at a much lower potential [26,27], which are favorable for greatly reducing the CO-poisoning of PdRu electrocatalyst [7,28].

In addition, tuning and optimizing the exposed surface active area through engineering the morphology and structure is also believed to be a fruitful approach to enhance the electrocatalytic performances [29]. Up till now, many typical nanostructures have been developed to greatly enhance the electrocatalytic perfor-

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mances such as nanowire [30], dendrites [31], nanosphere [32], core–shell [33] and so on. Among these special nanostructures, concave nanocubes have been highly expected to exhibit outstandingly excellent electrocatalytic performances for DEGFCs due to their fascinating properties of high surface area, self-supporting capacity, as well as high surface permeability [34–36].

Based upon these analyses, we herein designed a novel class of binary PdRu concave nanocubes with abundant exposed surface area and tunable compositions via a facile wet-chemical strategy. Owing to the fascinating concave nanocube structure, synergistic and electronic effects between Pd and Ru, the as-prepared PdRu concave nanocubes exhibited considerable high electrocatalytic activity with the mass activity of 3345 mA mg_{Pd}^{-1}, 3.86-fold enhancements than that of commercial Pd/C (866 mA mg_{Pd}^{-1}). We confirmedly trust that this proposed plot is important for the fabrication and modification for future metallic catalysts and the as-prepared PdRu concave nanocubes (PdRu CNCs) with outstandingly excellent electrocatalytic performances can be well applied for boosting the development of DEGFCs.

2. Experimental section

2.1. Preparations of electrocatalysts

In the standard synthesis of PdRu CNCs, 40 mg cetyltrimethylammonium bromide (CTAB) was firstly dissolved in 8 mL H_2O in a flask. Subsequently, 2.2 mL $RuCl_3$ (19.3 mM) and 2 mL L-ascorbic acid ($C_6H_8O_6$, 60 mg, 99%) were added dropwise to above mixture under vigorous stirring. The reaction flask was then transferred to an oil bath and heated from room temperature to 85 °C. 1 mL H_2PdCl_4 (22.6 mM) was also added dropwise to above solution as soon as the temperature raised to 85 °C and kept reacting for 4 h at this temperature. The as-obtained PdRu CNCs denoted as Pd_1Ru_2 were collected via centrifuging and washing with ethanol and double-distilled water for several times. For comparison, the other two types of PdRu CNCs were also prepared just by changing the amount of $RuCl_3$.

2.2. Physicochemical characterization

For characterizing the physicochemical properties of the as-obtained products, a series of analyses have been employed. The morphologies and microstructures of the as-prepared products were all firstly investigated by a HITACHI HT7700 transmission electron microscope operating at an acceleration voltage of 120 kV. After an initial assessment, then the scanning transmission electron microscopy (STEM) and high-magnification transmission electron microscopy (TEM) operated on an FEI Tecnai F20 transmission electron microscope at an accelerating voltage of 200 kV were also employed to further characterize their morphological features. X-ray diffraction (XRD) analysis operated on a PANalytical X'Pert Pro MPD system at 40 kV and the current at 30 mA with Cu Kα radiation source (λ = 1.54056 Å) at a step scan of 20° min^{-1} from 5° to 90° was also measured to investigate microcrystal structure properties. Besides, the X-ray photoelectron spectroscopy (XPS) performed on a VG Scientific ESCALab 220XL electron spectrometer using 300 W Al Kα radiation was also employed to study the element valences and compositions of different samples.

2.3. Electrochemical measurements

A series of electrochemical measurements of all the as-prepared samples were conducted in a typical three-electrode system with a CHI 760E electrochemical working station (CH Instrumental Co., Ltd., China). A platinum wire and a saturated calomel electrode (SCE) were applied to serve as reference electrode and counter electrode, respectively. In this work, we used the glassy carbon electrode (GCE, diameter of 3.0 mm) as working electrode, which needs to be polished with alumina powders every time before examination. For modifying the working electrode, 10 μL of catalyst ink and 3 μL of nafion (0.05%) were added to the surface of GCE and dried ambient temperature. The cycle voltammetries (CVs) of all the catalysts were performed in a solution contained 1 M KOH and 1 M EG. Successive CVs of 1000 cycles have also been operated to investigate the long-term stability of the as-prepared catalysts. On purpose of comparison, commercial Pd/C was also used as contrastive catalyst, and the uniform processes as mentioned above were applied to perform the electrochemical measurements.

3. Results and discussion

3.1. Physicochemical characterization

The concave PdRu nanocubes have been synthesized via a facile wet-chemical with the assistance of CTAB. The morphological features of the as-obtained PdRu CNCs were firstly analyzed through TEM. Fig. 1(a)–(c) shows the typical TEM images of Pd_1Ru_2 CNCs with different magnifications and their size distributions. The results reveal that the as-obtained PdRu nanocrystals with a high yield approaching 100% exhibit a distinct cubic shape with concave structures, indicating that it can be produced at a large scale. The diameter distribution of this unique PdRu CNCs in Fig. 1(c) displays the narrow average diameter of approximately 28.7 ± 2.3 nm, which may help the fascinating PdRu CNCs with enormous improvement of electrocatalytic performances.

Moreover, for making a detailed analyses of the role of composition played in affecting the morphology of catalysts, the other two types of PdRu CNCs have also prepared by regulating the amount of $RuCl_3$ while kept the other conditions unchanged. More interestingly, the TEM images in Fig. 2 display almost the same

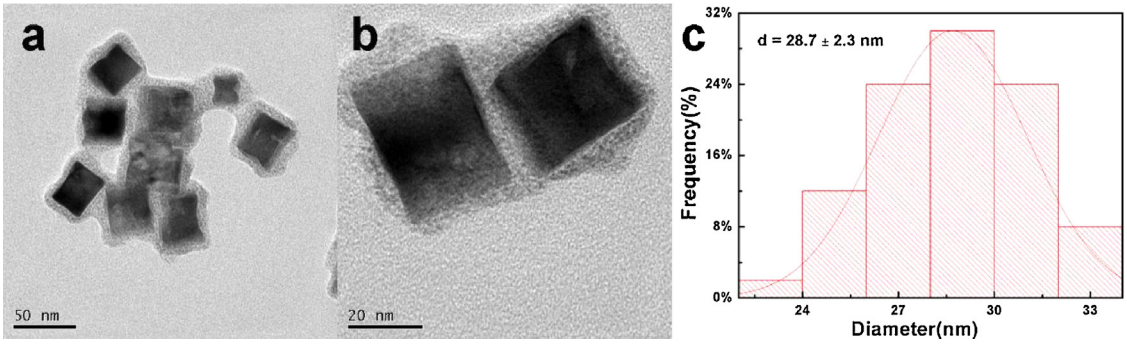

Fig. 1. TEM images of the Pd_1Ru_2 nanocubes (a and b) and diameter size distribution of Pd_1Ru_2 nanocubes (c) from Fig. 1 (a).