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# Eco-friendly and facile synthesis of novel bayberry-like PtRu alloy as efficient catalysts for ethylene glycol electrooxidation

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## ABSTRACT

Direct fuel cells have attracted an increasing notice over last decade, while its large-scale commercial development is also seriously impeded by the lack of cost-efficient electrocatalysts. The shape-controlled syntheses of binary Pt-based nanocrystals bounded with abundant surface active areas and tunable atomic ratio have been of vital importance in the fabrication and modification of outstandingly excellent electrocatalysts. Therefore, embodying the morphology advantages and composition effects are significant for synthesizing the cost-efficient electrocatalysts. In view of this, we herein report our efforts for demonstrating an eco-friendly approach to successfully synthesize a novel type of bayberry-like PtRu nanocatalyst with different compositions. Different from some other reported PtRu binary nanostructures, such as-prepared bayberry-like PtRu nanocrystals with rough surface can meet the requirement of both high mass activity and long-term stability, which shed light for the commercial development of direct fuel cells.

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## Introduction

With the increasing depletion of transitional fossil fuels coupled with the serious environment crisis, direct fuel cells (DFCs) have attracted a growing attention for their enormous potential in converting the chemical energy of small organic molecule fuels directly into electricity [1,2]. Among multitudinous fuel cells, direct ethylene glycol fuel cells (DEGFCs) are nowadays considered as promising energy technology due to their promising features such as higher energy density, higher

boiling point, and less catalyst toxicity etc [3–6]. Regardless of these beneficial terms, the lack of cost-efficient anode electrocatalysts are also severely impeding the commercial development of DFCs [7–10]. As for anode catalyst, in virtue of its fascinating activity and durability, Pt has appeared to be the most promising and commonly used metal component. However, a great deal of obstructions along with the use of Pt [11], including its skyrocketing high cost but low natural abundance and susceptibly poisoning [12] by surface-adsorbed CO-like intermediates generated in the oxidation reaction still hinder the commercial application of DEGFCs [13–15].

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In this connection, developing effective strategies for engineering high performance electrocatalysts with less cost have been urgently sought. Up till now, many tactics have been put forward by pioneers, and one of the successful methods for addressing these challenges is to partially substitute Pt with a transition metal [16–18]. In this way, bimetallic nanostructures with a lower Pt content can not only cut the cost the catalysts but also lead to the superior performance as compared to monometallic Pt nanostructures. Accordingly, a wide range of transition metals such as Au [19], Ag [20], Cu [21], Bi [22] and Sn [15] have been applied to cooperate with Pt to form the stable alloy nanostructures with enhanced electrocatalytic performances for alcohol oxidation. Among these cooperated materials, PtRu was once thought to be the best CO-poisoning-tolerant catalyst, which could be accounted by the Watanabe–Motoo bifunctional mechanisms [23]: Ru atoms provide  $\text{OH}_{\text{ads}}$ -like adsorbed hydroxyl groups and serve as the oxidant to oxidize the  $\text{CO}_{\text{ads}}$  at a much lower potential, which are favorable for greatly reducing the CO-poisoning of PtRu electrocatalyst [24–27].

On the other hand, it has been well-known that the catalytic properties of nanocrystals (NCs) are strongly dependent on their morphologies, and many approaches till now have been proposed for manipulating the morphologies and structure of noble metal nanoparticles to maximize utilization efficiency and electrocatalytic performances [28,29]. Therefore, in this aspect, another promising procedure for addressing the highly expensive cost and insufficient activity issues of anode catalysts is to endow the catalysts with the desirable morphology and maximize the utilization efficiency of Pt [30,31]. Despite of the significant progresses have been made in the synthesis of PtRu NCs, those NCs with a smooth surface have either the limited catalytic activity or poor durability due to their restricted surface active areas. In this regard, if we can band the advantages of morphologies and compositions to engineer the ideal PtRu catalysts with porous active surface, it will be extremely favorable for providing abundant active sites and leading to a great enhancement of electrocatalytic performances [32,33].

Herein, we demonstrate an eco-friendly and facile strategy for synthesizing a novel class of bayberry-like PtRu alloy with brushy surface and abundant surface active sites as efficient catalysts for the electrooxidation of EG in the alkaline media. Apart from some previously reported PtRu catalyst, the strategy we developed in this work for the preparation of bayberry-like PtRu NCs is environmental benignity, which conducted in the ambient temperature with the assistant of PVP in the whole process. In addition, after a series of electrochemical measurements, the bayberry-like PtRu NCs exhibited the outstandingly high electrocatalytic activity and durability towards EG electrooxidation, demonstrating it as a promising alternative candidate for the commercial application of DEFCs.

## Experimental section

### Chemicals and materials

Ruthenium trichloride ( $\text{RuCl}_3$ ), chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ), ascorbic acid (AA), polyvinyl pyrrolidone (PVP), potassium

hydroxide (KOH), hydrochloric acid (HCl), ethanol (AR) and EG (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Commercial Pt/C catalyst (JM 20% Pt) was purchased from Shanghai Hesun Electric Co., Ltd. (China). Secondary distilled (DI) water was used throughout the whole experiments. All the chemicals were of analytical grade and used as received without any further purification.

### Preparations of electrocatalysts

For the typical preparation of PtRu NCs, 10 mg PVP (a colloidal stabilizer) were dissolved in 10 mL deionized water, followed by the addition of 0.8 mL aqueous solution of  $\text{RuCl}_3$  (19.3 mM), 1.0 mL  $\text{H}_2\text{PtCl}_6$  (7.7 mM). The mixture was stirred continuously for 10 min at room temperature. After that, 2 mL AA (20 mg) solution was added dropwise to the mixture and maintained at the ambient temperature with rapid stirring for 6 h. After the reaction, the product was collected by centrifugation and washed repeatedly with a sufficient amount of ethanol and acetone to remove excess residuum. The as-obtained product was then re-dispersed in 10 mL deionized water and denoted as  $\text{Pt}_1\text{Ru}_2$ , for a more detailed comparison,  $\text{Pt}_1\text{Ru}_1$  and  $\text{Pt}_1\text{Ru}_3$  were also prepared under the same conditions expect for the amount of the addition of  $\text{RuCl}_3$  (0.4 and 1.2 mL).

### Characterization

The morphology and microstructure of the as-prepared products were all firstly examined by a TECNAI-G20 electron microscope (TEM) conducted at an accelerating voltage of 200 kV. The microcrystal structure properties were also measured by X-ray diffraction (XRD) analysis, which operated on a PANalytical X'Pert Pro MPD system operating at 40 kV and the current at 30 mA with Cu  $K\alpha$  radiation source ( $\lambda = 1.54056 \text{ \AA}$ ) at a step scan of  $10^\circ \text{ min}^{-1}$  from  $5^\circ$  to  $90^\circ$ . Besides, for studying the element valences and compositions of different samples, the X-ray photoelectron spectroscopy (XPS) was performed on a VG Scientific ESCALab 220XL electron spectrometer using 300 W Al  $K\alpha$  radiation was also employed. Notably, some characterizations on commercial Pt/C have also operated for comparison.

### Electrochemical measurements

A standard three-electrode system with a CHI 760E electrochemical working station (CH Instrumental Co., Ltd, China) was employed to conduct a series of electrochemical measurements for all the samples. A platinum wire and a saturated calomel electrode (SCE) were applied as reference electrode and counter electrode, respectively. The glassy carbon electrode (GCE, diameter of 3.0 mm) in this work serves as working electrode, which need to be polished with alumina powders every time before examination. To fabricate the working electrode, 10  $\mu\text{L}$  of catalyst ink should be pipetted onto the surface of GCE. Additionally, we have also added 3  $\mu\text{L}$  of nafion (0.05%) to cover on the surface of catalysts power and dried in the oven at  $65^\circ\text{C}$  for further avoiding the dissolution of the catalysts ink. For activating the catalyst, the catalysts-coated GCEs were firstly tested in 1 M KOH solution by CVs from  $-0.8 \text{ V}$  to  $0.4 \text{ V}$  (vs. SCE) at a scan

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