



# One-pot synthesis of Pd@PtNi core-shell nanoflowers supported on the multi-walled carbon nanotubes with boosting activity toward oxygen reduction in alkaline electrolyte



Sa Liu<sup>a,\*</sup>, Yan Wang<sup>a</sup>, Liwen Liu<sup>a</sup>, Mengli Li<sup>a</sup>, Wenjie Lv<sup>a</sup>, Xinsheng Zhao<sup>b</sup>, Zhenglong Qin<sup>a</sup>, Ping Zhu<sup>a</sup>, Guoxiang Wang<sup>c</sup>, Zhouyang Long<sup>a</sup>, Fangmin Huang<sup>a</sup>

<sup>a</sup> School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, PR China

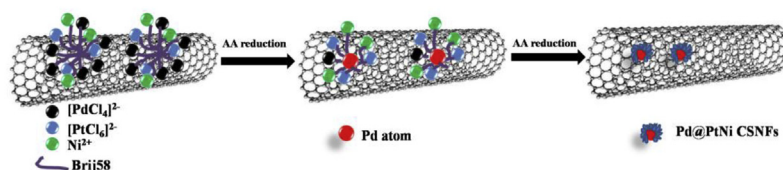
<sup>b</sup> School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, PR China

<sup>c</sup> School of Light Industry & Chemical Engineering, Dalian Polytechnic University, Dalian 116034, PR China

## HIGHLIGHTS

- The Pd@PtNi/MWCNTs core-shell nanoflowers are synthesized by one-pot method.
- The core-shell and porous flower-like structure boost the ORR activity.
- An excellent catalytic activity can be obtained by tuning the ratio of Pd and Pt.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 19 April 2017

Received in revised form

25 July 2017

Accepted 18 August 2017

### Keywords:

Core-shell

Nanoflower

Electrocatalyst

Oxygen reduction

## ABSTRACT

Pt-based nanocrystals with controlled morphologies and structures are one of most promising electrocatalysts for oxygen reduction reaction (ORR). Herein, a facile one-pot wet-chemical method is developed to synthesize Pd@PtNi core-shell nanoflowers (CSNFs) supported on the multi-walled carbon nanotubes (MWCNTs). Brij 58 is demonstrated as a structure-directing agent to generate the nanoflower and ascorbic acid acts as a reductant to form a core-shell structure. By tuning the molar ratio of Pd and Pt, Pd@PtNi/MWCNTs CSNFs show obviously improved ORR activity and durability in alkaline electrolyte compared with PtNi/MWCNTs nanoflowers and commercial Pt/C. The results illustrate that the core-shell structure and porous feature of nanoflower are both beneficial to the enhancement of the catalytic properties.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered as a promising candidate for the power of automobiles and electronic devices due to its high power density, high efficiency and low emission [1,2]. However, the widespread application of PEMFCs is limited by the high cost, low performance and poor durability of

the cathode catalysts, because of the expensive platinum (Pt) and the sluggish oxygen reduction reaction (ORR) kinetics [3]. To solve these problems, many efforts have been made to develop relatively inexpensive cathode catalysts with sufficient catalytic activity and high durability [1–6]. One of the most effective strategies is to form PtM (3 d transition metals, Ni, Co, Cu, Fe, etc.) alloys, which can significantly reduce Pt loading and improve the ORR activity, owing to the electronic effect and synergetic effect [7–10]. Among the PtM alloys, PtNi alloy catalysts have been most fascinated in recent years for their efficiently improved catalytic performance towards ORR [11–13]. Stamenkovic et al. reported that the (111) surface of Pt<sub>3</sub>Ni

\* Corresponding author.

E-mail address: [liusa@jsnu.edu.cn](mailto:liusa@jsnu.edu.cn) (S. Liu).

showed 10-fold and 90-fold higher ORR activity than Pt (111) and commercial Pt/C, respectively [12]. Xia and co-authors synthesized uniform 9 nm Pt-Ni octahedra with a record high ORR activity of 3.3 A mg<sub>Pt</sub><sup>-1</sup> by using oleyamine and oleic acid as surfactants and W(CO)<sub>6</sub> as a structure-directing agent [14].

Recently, ternary PtNi-based nanocrystals (NCs) catalyst was also prepared to further boost the catalytic activity and stability [15–19], which is mostly attributed to more variables to be available for tuning [20]. Among numerous alternative metals, palladium (Pd) has similar properties with Pt while the less expensive than Pt, and it exhibits high electrochemical activity and CO-tolerance towards alcohol oxidation, especially in alkaline media [21–23]. Furthermore, Pd@Pt core-shell structure has attracted much interest for high Pt utilization and excellent activity [4,24–27], because the core-shell nanostructure could provide three major effects in deciding the electrocatalytic activity: ligand effects, ensemble effects, and geometric effects [28]. Shao and Xia et al. synthesized Pd@Pt–Ni core-shell octahedral catalyst with high activity and exceptional durability under ORR conditions, and its mass activity was enhanced by 12.5-times compared with that of commercial Pt/C [27]. Feng et al. synthesized core-shell PdPt@Pt/reduced graphene oxide NCs by one-pot wet-chemical method, which displayed improved electrochemical activity toward ethylene glycol oxidation reaction [25].

On the other hand, many studies have illuminated that not only the compositions of alloy catalysts, but also the shapes and nanostructures are necessary to their activity [16,21,29,30]. More recently, the Pt-based nanoflowers, nanodendrites and nanoclusters with three-dimensionally (3D) interconnected porous structure have attracted extensive attentions [16,21,29–38] for their enlarged surface area to volume ratios, low density and open structures to be favorable for O<sub>2</sub> mass transport and interaction with catalyst.

By above knowable, the core-shell and porous structure (e.g. nanoflower) can both improve the electrocatalytic activity. Inspired by this, a one-step synthesis of Pd@PtNi core-shell nanoflowers (CSNFs) well-dispersed on the multi-walled carbon nanotubes (MWCNTs; denoted as Pd@PtNi/MWCNTs) was reported by the reduction of Pt, Ni and Pd precursor with ascorbic acid (AA) in the presence of Brij 58 as soft template. The core-shell nanostructure was formed through the different reduction rate of PdCl<sub>4</sub><sup>2-</sup>/Pd, PtCl<sub>6</sub><sup>2-</sup>/Pt and Ni<sup>2+</sup>/Ni precursors by AA, and the flower-like structure was decided by the assembly of Brij 58 micelles with metal ions in aqueous solution. Moreover, the ORR performance of the CSNFs in alkaline electrolyte was investigated in details.

## 2. Experimental section

### 2.1. Chemicals and materials

MWCNTs (30–50 nm in diameter and 10–20 μm in length) were purchased from Beijing Boyu Gaoke Co., Ltd., Beijing, China, and further purified prior to use by stirring in the mixture of concentrated nitric acid and sulfuric acid (3:1 v/v) at 80 °C for 10 h. H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and PdCl<sub>2</sub> were purchased from Shenyang Nonferrous Metal Research Institute, Shenyang, China. Brij 58, AA, NiCl<sub>2</sub>·6H<sub>2</sub>O and commercial Pt/C (20 wt% Pt) were purchased from Alfa Aesar Company. For preparation of stock H<sub>2</sub>PdCl<sub>4</sub> solution (20 mM) [24], 0.177 g PdCl<sub>2</sub> was dissolved with 40 μL HCl (37%), and then diluted to 50 mL with deionized water (18.2 MΩ).

### 2.2. Synthesis of Pd@PtNi/MWCNTs CSNFs

In a typical synthesis of Pd<sub>2</sub>@PtNi/MWCNTs CSNFs, 100 mg of Brij 58 was dissolved into 5 mL of H<sub>2</sub>O, followed by adding 24.08 mg

of MWCNTs under constant sonication for 1 h. Then, 1 mL of 20 mM H<sub>2</sub>PtCl<sub>6</sub> aqueous solution, 2 mL of 20 mM H<sub>2</sub>PdCl<sub>4</sub> aqueous solution, and 1 mL of 20 mM NiCl<sub>2</sub> aqueous solution were added, respectively. After they were mixed thoroughly, 1 mL of 0.25 M AA aqueous solution was added slowly to the mixed solution at 60 °C, which kept stirring for 1 h. Finally, the black precipitates were collected, cleaned, and dried for further characterization. PtNi/MWCNTs, Pd<sub>1</sub>@PtNi/MWCNTs and Pd<sub>3</sub>@PtNi/MWCNTs were synthesized by the same procedure except for 0, 1 and 3 mL of H<sub>2</sub>PdCl<sub>4</sub> aqueous solution (20 mM) was added, respectively. In addition, Pd/MWCNTs was also synthesized. The theoretical loading of platinum group metal (PGM, Pt and Pd) was 20 wt %.

### 2.3. Characterization of catalysts

The size and morphology of the catalysts were characterized by JEOL JEM-2000EX transmission electron microscope (TEM) and JEOL JEM-2000F high resolution TEM (HRTEM) with energy dispersed X-ray spectroscopy (EDS). The elemental mapping and line profiles were recorded on the high-angle annular dark-field scanning TEM (HAADF-STEM). The composition of the catalysts was also determined by inductively coupled plasma-atomic mass spectrometer (ICP-MS, Thermo ICAP-QC). Power X-ray diffraction (XRD) measurements were conducted using a Bruker AXS D8 ADVANCE power X-ray diffractometer with a Cu Kα (λ = 1.5418 Å) radiation source.

### 2.4. Electrochemical measurements

5 mg Pd@PtNi/MWCNTs CSNFs were ultrasonically dispersed in a mixed solution of isopropyl alcohol (1.2 mL) and Nafion (50 μL, 5 wt %, DuPont) to obtain a well-dispersed suspension. Afterwards, 5 μL of the suspension was dropped onto a glassy carbon rotating disk electrode (RDE, 0.1256 cm<sup>2</sup>) to form the working electrode. Similarly, working electrodes with PtNi/MWCNTs and commercial Pt/C (20%) were prepared following the same process as Pd@PtNi/MWCNTs. The total loadings of PGM were 4 μg or 31.85 μg cm<sup>-2</sup> for the Pd@PtNi/MWCNTs (both Pt and Pd), PtNi/MWCNTs and Pt/C catalysts (only Pt), respectively. Before all electrochemical measurements, the RDE was mechanically polished with 0.3 and 0.05 μm alumina powder successively until a mirror finish surface was obtained. The polished electrode was rinsed with ultrapure water and then sonicated in ethanol and water, respectively. A Pt plate and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All the potentials in this paper were reported with respect to the reversible hydrogen electrode (RHE).

The electrochemical measurements were carried out on a CHI660E electrochemical workstation (CHI Instruments, Shanghai Chenhua Co., China). Cycle voltammetry (CV) experiments were conducted in a N<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> electrolyte at a scan rate of 50 mV s<sup>-1</sup> to evaluate the electrochemical active surface area (ECSA) using Equation (1) from the hydrogen desorption charge (Q<sub>H-desorption</sub>) in the positive-going potential scan (0.05–0.4 V) after correction for double-layer charging (by subtracting the current at 0.4 V from the total current) [39].

- Q<sub>H</sub> = 210 μC cm<sup>-2</sup> is associated to the adsorption/desorption of one hydrogen monolayer on 1 cm<sup>2</sup> of polycrystalline Pt and/or Pd;
- L<sub>PGM</sub> is the PGM loading on GDE (0.03185 mg<sub>PGM</sub> cm<sup>-2</sup>);
- A<sub>geo</sub> (cm<sup>2</sup>) is the geometric surface area of the GDE (0.1256 cm<sup>2</sup>).

Download English Version:

<https://daneshyari.com/en/article/5148782>

Download Persian Version:

<https://daneshyari.com/article/5148782>

[Daneshyari.com](https://daneshyari.com)