



Research paper

Hollowed structured PtNi bifunctional electrocatalyst with record low total overpotential for oxygen reduction and oxygen evolution reactions



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ABSTRACT

Oxygen electrocatalysis plays a critical role in numerous energy storage/conversion devices, but the sluggish kinetics of both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) has greatly restricted the broad-based applications of such devices, especially for those requiring bifunctional electrocatalysts towards both reactions (e.g., regenerative fuel cells, metal-air batteries). Herein, we demonstrate that hollow structured bimetallic PtNi/C synthesized through a facile solution-based approach can be employed as a highly active bifunctional electrocatalyst for both ORR and OER, showing a combined ORR and OER overpotential of 0.69 V, which represents a record low value for a bifunctional electrocatalyst. Rotating ring disk electrode (RRDE) technique discloses that ORR was proceeding predominantly through the desired 4-electron pathway on the PtNi/C catalyst. Moreover, the PtNi/C is also found rather stable for both ORR and OER, with small activity lost after the accelerated durability test. These data echo the importance of innovative bi-/multi-metallic nanostructures for highly efficient catalysts that depend critically on using precious metals, for application in energy storage/conversion technologies.

1. Introduction

Electrochemical devices as unitized regenerative fuel cells (URFCs), and rechargeable metal-air batteries, which enable the facile interconversion between chemical and electrical energy, are considered as ideal solutions for the renewable energy storage/conversion [1–4]. One of the key challenges in commercialization of such devices is to search for highly efficient bifunctional electrocatalysts with low overpotential for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), because of their slow reaction kinetics while different requirements on the nature of active sites for these two reactions [5–10]. Pt-based electrocatalysts are well known for their excellent activity for ORR but exhibit rather poor performance for OER, while in contrast, IrO₂ and RuO₂ are active catalysts for OER but barely active for ORR [11]. The state-of-the-art approach to a bifunctional electrocatalyst is to use Pt and IrO₂/RuO₂ in physical mixture or double-layer form, while the electrocatalytic performance of the mixed catalysts is usually compromised in presence of the second component [12–14]. Composite electrocatalysts prepared by alloying Pt with Ir or Ru have also been investigated as the bifunctional catalysts, but only moderate ORR and OER activities can be achieved [15–17]. High loadings of the noble metal electrocatalyst are thus needed to compensate the activity loss by using these mixed/composite electrocatalysts and also to overcome the

sluggish reaction kinetics of both ORR and OER [12,18], while the resulting high cost have greatly hindered the broad based application of the URFC and rechargeable metal-air batteries technology. Efforts were also made to develop non-precious-metal catalysts (NPMCs, e.g., metal oxides, perovskites oxides, carbon-based materials) as a bifunctional electrocatalyst [2,11,19], however, the synthesis of NPMCs usually involves tedious procedures and/or high temperature treatment, while satisfactory activity/stability can still be hardly achieved. Therefore, it remains a challenge to integrate efficient ORR and OER bifunctionality into one single catalyst.

PtNi nanoparticles represent one of the most active electrocatalysts for ORR [20,21], while it is also well documented that Ni-containing materials (e.g., oxides, (oxy)hydroxide) can exhibit excellent performance for OER [22–24]. Therefore, it can be expected that a proper combination of Pt with Ni could have great potential to give birth to efficient bifunctional electrocatalysts for both ORR and OER. Herein, as a proof-of-concept, we investigated carbon supported PtNi hollow nanoparticles with opened porous structure (PtNi/C) as a bifunctional electrocatalyst for ORR and OER in alkaline electrolyte. It turns out that the PtNi/C exhibits 3 times higher specific activity for ORR relative to the reference Pt/C. Moreover, PtNi/C is also found to be highly active and stable for OER, achieving a current density of 10 mA cm⁻² at an overpotential of 350 mV, which even outperforms the benchmark IrO₂/

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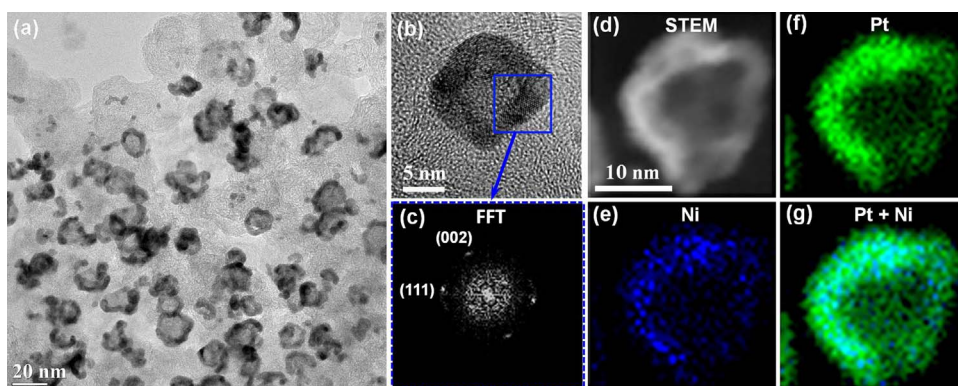


Fig. 1. Representative TEM (a), HRTEM/FFT (b, c), STEM (d) and EDS elemental mapping images (f–g) of PtNi/C sample.

C catalysts. The total overpotential, which is defined as the gap between the ORR half wave potential and OER overpotential at 10 mA cm^{-2} [5,6], is around 0.69 V on the PtNi/C, which represents the record low value to date for a bifunctional electrocatalyst. These data demonstrate the great promises of the PtNi/C as a new benchmark bifunctional electrocatalyst to be used in practical applications of URFC and/or rechargeable metal-air battery technologies.

2. Experimental

2.1. Synthesis of PtNi/C catalysts

The carbon supported PtNi hollow structured nanoparticles was synthesized by modifying a literature protocol [21]. Briefly, 137 mg of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 176 mg of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ and 300 mg of carbon support (Ketjenblack EC300J, AkzoNobel) was firstly dispersed in 150 mL of deionized water-ethanol mixed solution (14:1, v/v) under vigorous stirring. After 30 min ultrasonic treatment of this mixture, a freshly prepared 1 mL of NaBH_4 (0.22 M) solution was added at a rate of 5 mL/min by using a syringe pump. After stirring the mixture for 1 h at room temperature, the solid sample was collected by filtration, intensively washed with deionized water and vacuum-dried at 80°C overnight. The reference Pt/C and Ni/C catalysts were prepared by using the same procedure but without adding Ni or Pt precursor. The PtNi/C sample was further subject to acid treatment in 1 M H_2SO_4 for 22 h (R.T.) before electrochemical measurements.

2.2. Structural analysis

(Scanning) Transmission electron microscopy (STEM) analysis was performed on JEM-2100F (JEOL) operating at 200 kV. Energy dispersive spectroscopic (EDS) elemental mapping measurements were carried out in STEM mode with an X-ray detector (X-max80, Oxford Instruments). X-ray diffraction (XRD) was conducted in transmission geometry on an X-ray powder diffractometer (StadiP, Stoe & Cie GmbH) using $\text{Cu K}\alpha 1$ radiation ($\lambda = 1.540598 \text{ \AA}$) and Ge[111] monochromator. The porous property analysis was performed on a Quantachrome NOVA gas sorption analyzer using N_2 -sorption. The surface area was calculated by using the Brunauer-Emmett-Teller (BET) equation. ICP analyses were carried out at the Institute of Inorganic Chemistry and Analytical Chemistry (Johannes Gutenberg-University, Mainz, Germany). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a SSX 100 ESCA Spectrometer using monochromatic Al $\text{K}\alpha$ radiation, and the binding energies were calibrated using the adventitious C 1s line at 284.8 eV. Spectra were evaluated using CasaXPS software with the Shirley type background.

2.3. Electrochemical measurements

Electrochemical measurements were conducted on a PARSTAT 4000

Potentiostat/Galvanostat controlled by a Versastudio software (AMETEK). A Hg/HgO electrode and Pt wire were used as reference and counter electrodes respectively. All potentials reported here in this work were calibrated against the reversible hydrogen electrode (RHE). A glassy carbon rotating disk electrode (RDE, $d = 5 \text{ mm}$, PINE) was used as the working electrode. Prior to use, the RDE was polished to a mirror finish using $0.05 \mu\text{m}$ γ -alumina suspension (Buehler), followed by ultrasonic cleaning with ethanol, acetone and deionized water to remove any contaminants. To prepare the working electrode, a catalyst suspension was firstly prepared by dispersing the catalyst powder in a mixed solvent of deionized water, isopropanol, and Nafion solution with the volume ratio of 4:1:0.025. Then $10 \mu\text{L}$ of the catalyst suspension ($2 \mu\text{g}/\mu\text{L}$) was deposited onto RDE. The electrochemistry measurements were carried out at room temperature in N_2 or O_2 saturated 0.1 M KOH electrolyte. Prior to the ORR and OER measurements, the electrolyte was purged with high purity O_2 for at least 30 min, followed by repeated cyclic voltammetry pretreatment (100 mV/s) of the electrocatalyst for up to 20 cycles until a stable voltammetry curve can be obtained. The ORR and OER performance was then evaluated by recording the ORR and OER linear scan voltammetry (LSV) curve at a scan rate of 10 mV/s and RDE rotation rate of 1600 rpm for each sample. Before determining the electrochemically active surface area (ECSA), the electrolyte was saturated with high purity N_2 for 30 min. The ECSA value of Pt was evaluated by measuring the charges associated with the reductive adsorption of protons on Pt surfaces, as detailed in the Supporting Information. The iR-drop effect was compensated for all the measurements, and the solution resistance was determined by conducting AC impedance analysis (10 kHz , 5 mV).

3. Results and discussion

3.1. Structural and morphological characterization

To probe the morphology and structure of the as-synthesized PtNi/C sample, TEM and EDS elemental mapping analyses were carried out. As shown in Fig. 1, the majority of the particles featured an irregular shape with an average diameter of 15.0 nm. The brighter contrast in the center evidenced the formation of the hollow structure of these PtNi nanoparticles. The HRTEM in combination with fast Fourier-transform (FFT) analyses revealed that the shell is comprised of crystalline structures with lattice spacings of 0.221 and 0.231 nm which are in agreement with (002) and (111) planes in a fcc PtNi phase, respectively. Fig. 1d–e display the STEM-EDS elemental mapping for a typical PtNi hollow nanoparticle, showing that Pt and Ni are homogeneously distributed within the shell while the outermost surface is enriched in Pt as a result of the acid leaching treatment. Moreover, the EDS elemental analysis indicates that the atomic Pt:Ni:C ratio is around 4.38:0.44:100, as shown in Fig. S1 of the Supporting Information. Although this value deviates from the ICP analysis result which gives an atomic Pt:Ni:C ratio of 1.86:0.45:100.00 (Table S1) probably due to the semi-

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