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Short communication

Palladium–iridium nanowires for enhancement of electro-catalytic activity towards oxygen reduction reaction

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ABSTRACT

In this work, palladium–iridium nanowires with a Pd/Ir atomic ratio of 2/1 are synthesized through a facile hydrothermal method. Transmission electron microscopy images show that the palladium–iridium nanowires have a uniform diameter below 2 nm and a rough surface with many atomic steps. The electro-catalytic performance of the carbon supported palladium–iridium catalyst towards oxygen reduction reaction has been examined in 0.1 M $HClO_4$ solution. The carbon supported palladium–iridium catalyst displays comparable catalytic activity but much higher durability in comparison with those of the commercial carbon supported platinum catalyst. The excellent electro-catalysis might be attributed to the high accessible area, rough surface and iridium introduction. The work demonstrates that palladium–iridium nanocrystals are promising electro-catalysts for oxygen reduction electro-catalysis in acid media.

1. Introduction

Palladium nanoparticles have attracted great interest as alternatives to platinum-based catalysts for oxygen reduction reaction (ORR) owing to their relatively low cost and improvable catalytic activity [1–6]. Alloying with transition metals is an effective way that can not only improve the inherit catalysis but also enhance the utility of palladium constituent. Recently, significant progress has been made in the bimetallic palladium-based nanocrystals, such as PdFe, PdCo and PdCu [7–14]. However, the durability of palladium-based catalysts in acid solution remains still a critical challenge, because that the redox-potentials of palladium and other alloying metallic elements are lower than that of Pt (Pt^{2+}/Pt 1.19 V, Pd^{2+}/Pd 0.915 V). In contrast to Fe, Co and Cu, iridium is electrochemically stable in acid media (Ir^{3+}/Ir 1.16 V). Consequently, iridium has been successfully used to improve the durability of Pd–Co, Pd–Cu and Pd–Ce catalysts [15–17]. Though palladium–iridium bimetallic nanocrystals have been used as electro-catalysts for formic acid/borohydride/CO oxidation, little work has been focused on their electro-catalytic activities towards ORR [18–20]. In addition, previously reported Pd–Ir bimetallic nanoparticles were universally spherical in shape with very small size. Different from the other morphologies, nanowires are more promising in catalysis field owing to their relatively large accessible area and low aggregation [21–25]. Therefore, the synthesis of palladium–iridium nanowires is still costly and far from trivial.

In this report, palladium–iridium nanowires were synthesized through a facile one-pot process. The obtained bimetallic nanowires possessed markedly enhanced electro-catalytic activity towards ORR and high durability in acid media.

2. Experimental

2.1. Synthesis

Palladium (II) chloride ($PdCl_2$), ammonium hexachloroiridate (IV) ($(NH_4)_2IrCl_6$), polyvinylpyrrolidone (PVP, Mw = 40,000) and sodium iodide (NaI) were purchased from Sinopharm Chemical Reagent Co. Ltd. 2,7-dihydroxynaphthalene (2,7-DHN) was purchased from Aladdin Industrial Corporation. All the reagents were used as received without further treatment.

Pd–Ir nanowires were synthesized by using a hydrothermal method. $PdCl_2$ (10.6 mg, 0.06 mmol), $(NH_4)_2IrCl_6$ (13.3 mg, 0.03 mmol), NaI (300.0 mg) and PVP (800.0 mg) were dispersed into 12.0 mL of deionized water by stirring at 50 °C for 3 h. 9 mg of 2,7-DHN was dissolved into 3.0 mL of deionized water and quickly added into the above dark red solution. The mixed solution was transferred into a 25 mL Teflon-lined stainless-steel autoclave which was heated at 210 °C for 2 h. The products were precipitated by isopropanol, washed with ethanol and centrifuged for at least five times. For comparison, palladium nanowires were obtained through the same synthesis strategy by using only $PdCl_2$ as the precursor.

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2.2. Characterization

Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and energy dispersive X-ray spectroscopy (EDS) were performed on a JEM-2100 TEM equipped with EDXA. The metal compositions were determined by a Brucker ICP-MS (M90) system. The catalysts loading amount on carbon black were measured by thermo-gravimetric analysis (TGA) on a STA449F3 (METZSCH).

2.3. Electrochemical measurements

A mixed solution of 5 mL of ethanol and 5 mL of methanol consisting of 2 mg of palladium–iridium or palladium catalyst and 8 mg of carbon black (Cabot, Vulcan XC-72) were ultrasonically dispersed for 60 min and magnetically stirred for 3 h. The carbon supported catalysts were collected by centrifuge and dried for use. Nafion solution was prepared by mixing 4 mL of deionized water, 1 mL of isopropanol and 25 μL of Nafion (Sigma-Aldrich, 5 wt.%) together and stirred to be a homogeneous solution. 5 mg of Pd–Ir/C, Pd/C or commercial Pt/C (Johnson Matthey, 20 wt.%) were dispersed into 5 mL of Nafion solution, respectively. The working electrode was a glassy-carbon rotating disk electrode (RDE, Pine Instruments, 0.196 cm^2). 20 μL of catalyst ink was dropped onto the working electrode and dried naturally, the catalyst loading was 0.02 mg cm^{-2}.

All the electrochemical measurements were carried out on an Autolab potentiostat/galvanostat (PGSTAT-302N) workstation in a three electrodes cell at room temperature. A pure platinum foil with an area of 1.0 cm^2 and a saturated calomel electrode (SCE) in a separate compartment were used as the counter and reference electrodes, respectively. All the potentials in this paper are given with respect to the reversible hydrogen electrode (RHE). The electrolyte for cyclic voltammetry (CV), oxygen reduction reaction (ORR) and accelerated durability test (ADT) was 0.1 M perchloric acid ($HClO_4$, Sinopharm Chemical Reagent Co. Ltd.). Cyclic voltammetry (CV) curves were recorded in Ar-purged 0.1 M $HClO_4$ in the potential range of 0.05–1.0 V with a sweep rate of 50 mV s^{-1}. Before each test, the electrode was pretreated by carrying CV until a stable voltammogram was obtained. ORR polarization curves were recorded in oxygen-saturated 0.1 M $HClO_4$ solution from 0 to 1.1 V with a sweep rate of 10 mV s^{-1} and a rotation rate of 1600 rpm. Polarization curves at rotation rates ranging from 400 to 2400 rpm were recorded to examine the electrons transfer number for oxygen reduction. Stability of the carbon supported catalysts were examined by ADT, which was performed by repetitive potential cycling between 0.6 and 1.0 V for 10,000 cycles with a sweep rate of 50 mV s^{-1} in oxygen-saturated 0.1 M $HClO_4$ solution. CV and ORR polarization curves were recorded after 10,000 ADT cycles to detect the change.

The electrochemical active surface area (EASA) was evaluated by integrating the charge associated with the H_{upd} adsorption–desorption in the CV curves. 210 μC cm^{-2} (q_H) was assumed to be the charge associated with the monolayer of hydrogen adsorption on the nanoparticle surface [26,27]. EASA was calculated by the below equation:

$$EASA = S_H / (q_H \times v \times m) \quad (1)$$

where, S_H is the integral of H_{upd} adsorption in CV curves, m is the metal catalyst loading amount on the working electrode, v is the sweep rate of scanning.

3. Results and discussion

3.1. Characterization of palladium–iridium bimetal catalyst

Fig. 1 presents the results of the structural and compositional measurements of the as-made product. Almost all the produced nanoparticles are in nanowire shape (Fig. 1A). The nanowires show high uniformity in diameter averaged at 1.5–2.0 nm and are connected with each other

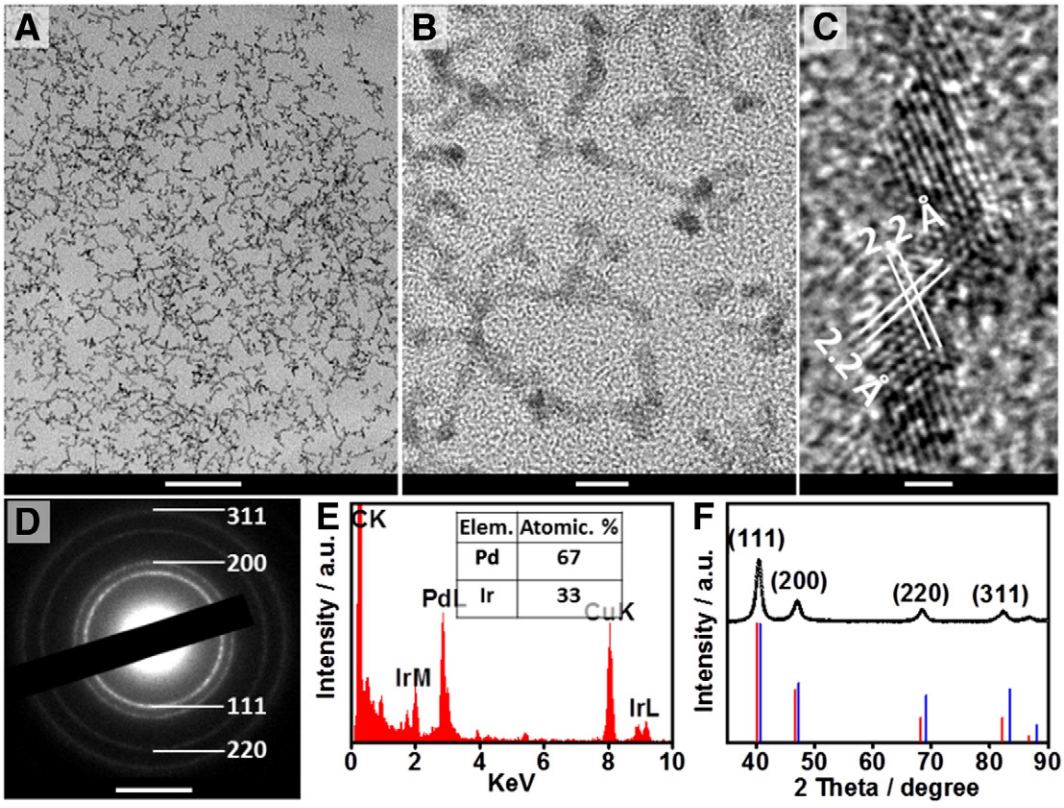

Fig. 1. (A) and (B) TEM images of the as-made product at different magnifications. (C) HRTEM image of the nanowire. The corresponding (D) SAED, (E) TEM-EDS and (F) XRD pattern. The scale bars in (A), (B) and (C) are 50 nm, 5 nm and 1 nm, respectively.