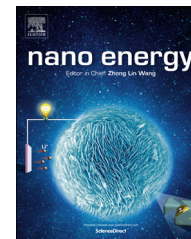


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## RAPID COMMUNICATION

# Palladium-iridium nanocrystals for enhancement of electrocatalytic activity toward oxygen reduction reaction

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**Abstract**

Exploiting nanomaterials with high electrocatalytic activity toward oxygen reduction reaction (ORR) and desirable durability in acid media has been recently one of the most significant tasks for developing electrochemical devices. Pd based nanostructures have received considerable interest owing to their Pt analogous surface and ever increasing catalytic performance. We herein report a series of Pd-Ir bimetallic nanoparticles with wire or dendritic shapes in a wide composition range, which were synthesized through a facile hydrothermal strategy. Such nanostructures featured with large electrochemical active surface area (EASA), show comparable catalytic activities to that of commercial Pt catalyst. More importantly, the catalysts display much high durability, as an example, Pd<sub>1</sub>Ir<sub>2</sub> losses 6% in EASA and 12% in mass activity after 10,000 potential sweeps, in contrast to respective losses of 42% and 58% for commercial Pt/C counterparts. The remarkable durability was also revealed in actual fuel cells supplied with hydrogen and air. The work demonstrates that these Pd-Ir nanostructures with enhanced performance are promising for practical electrocatalytic applications.

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**Introduction**

Developing nanomaterials as highly efficient electrocatalysts toward oxygen reduction reaction (ORR) is still challenging in catalysis research due to the sluggish kinetics process and the severity originating from the high corrosive

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(oxidizing) environment. Pt based nanomaterials have been recognized as the most effective ORR electrocatalysts due to their high catalytic performance and remarkable durability [1-4], while high cost and extreme scarcity restrict their practical applications. Great efforts have been dedicated to substituting Pt with less noble metals without compromising the catalytic activity [5]. Recently, Pd nanocrystals have attracted great interest as alternatives for Pt owing to their Pt analogous surface and improved catalytic activity [6-11]. For instance, Pd (100) showed three times of activity as high as that of Pt (110) [6]. An order of magnitude improvement in the catalytic activity was achieved by changing the Pd surface from (111) to (100) [7-8]. The specific activity of Pd nanorods were found to be ten times higher than that of Pd nanoparticles and comparable to that of bulk Pt [9]. Although precise control on nanocrystals' surface structure and morphologies could enhance the catalytic activity, a more diversified and efficient strategy is alloying with transition metals [12]. The Pd-Pd bond distance could be modified by alloying with transition metals so that the resulting adsorption/desorption behaviors were more preferable for catalyzing ORR. [13-14] Accordingly, significant progress has been made in the Pd based bimetallic nanocrystals, such as PdFe, PdCo and PdCu [13-19]. However, the inherent poor durability associating with the low redox-potentials of Pd and the alloyed transition metals limits their actual application. Compared with Fe, Co and Cu, Ir is more stable ( $\text{Ir}^{3+}/\text{Ir}$  1.16 V), and has been successfully used to improve the durability of Pd based catalysts [20-22]. In these catalysts, Ir tends to exist in the subsurface layers and substantially alters the surface electronic structure. The electron structure alternation lowers the activation barriers of O/OH hydrogenation and protects the alloyed elements from dissolving loss, while eventually enhance the catalytic activities and durability greatly [20]. Pd-Ir bimetallic nanoparticles have spurred growing attention due to their excellent catalysis for hydroconversion [23-26] and electrochemical reactions [27-29]. However, little work has been devoted to the ORR catalytic activity of Pd-Ir nanocrystals. In addition, the reported Pd-Ir bimetallic nanoparticles are commonly irregularly spherical shapes with very small size [23-25,30-33].

The catalytic ORR is well-documented to be highly structural dependent because the whole reaction involves both the surface adsorption/desorption behaviors and the interface catalyzing process. Morphologies, i.e., exposing facets and surface structures, are therefore very significant in tuning the surface chemical and physical properties, which accounts for the critical catalytic activity [2]. Among the identified solid nanocrystals with a variety of shapes, nanowire and nanodendrites structures are fascinating in catalysis field owing to their intrinsically structural advantages, i.e., high structural stability and preferential exposure of active crystal facets.[34-44] In this regard, the successful fabrication of Pd-Ir nanocrystals with nanowire or nanodendritic shapes might herald a new class of electrocatalysts with more accessible active surface and high stability against the degradation under electrochemical conditions, and in turn the more enhanced catalytic performance.

In this report, we demonstrate a facile synthesis for Pd-Ir bimetallic nanocrystals, which involves the coreduction of

$\text{PdCl}_2$  and  $(\text{NH}_4)_3\text{IrCl}_6$  with the use of 2,7-dihydroxynaphthalene (2,7-DHN) as reducing agent in an aqueous solution consisting of polyvinylpyrrolidone (PVP,  $M_w=40,000$ ) as the morphology stabilizer and NaI as the complexant. By simply varying the ratio of  $\text{PdCl}_2$  and  $(\text{NH}_4)_3\text{IrCl}_6$ , the nanostructures changed from nanowires to nanodendrites in a wide composition range. Characterizations of the Pd-Ir nanocrystals by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning TEM (STEM), as well as an investigation of their electro-catalytic activity toward ORR are presented. The work demonstrates that the Pd-Ir alloy nanostructures reported herein are superior ORR electrocatalysts with enhanced performances.

## Experimental

### Materials

All the reagents were used as received without further treatment. Palladium (II) chloride ( $\text{PdCl}_2$ ), ammonium hexachloroiridate (IV) ( $(\text{NH}_4)_2\text{IrCl}_6$ ), polyvinylpyrrolidone (PVP,  $M_w=40,000$ ) and sodium iodide (NaI) were purchased from Sinopharm Chemical Reagent Co. Ltd. 2,7-dihydroxynaphthalene (2,7-DHN) was purchased from Aladdin Industrial Corporation.

### Synthesis of Pd-Ir nanostructure

Pd-Ir nanodendrites were prepared via a hydrothermal method. Typically,  $\text{PdCl}_2$  (5.3 mg, 0.03 mmol),  $(\text{NH}_4)_2\text{IrCl}_6$  (26.5 mg, 0.06 mmol), NaI (300.0 mg) and PVP (800.0 mg) were dispersed in 12.0 mL of deionized water and stirred at 50 °C for 3 h. The mixture became a homogeneous dark red solution. 9 mg of 2,7-DHN was dissolved in 3.0 mL of deionized water and quickly added into the above mixture with stirring. The mixture was transferred into a 25 mL Teflon-lined stainless-steel autoclave and sealed. The autoclave was heated at 210 °C for 2 h and cooled to room temperature. The products were precipitated by isopropanol, washed with ethanol and centrifuged for at least five times. Pd-Ir nanodendrites with different Pt:Ir atomic ratio were obtained by varying the amount of  $\text{PdCl}_2$  and  $(\text{NH}_4)_2\text{IrCl}_6$  without changing the total amount of 0.09 mmol.

### Characterization

Transmission electron microscopy (TEM) was performed on a JEM-2100 TEM equipped with EDXA. Scanning transmission electron microscopy (STEM) images were taken on a Tecnai G2 F30 S-TWIN, equipped with high-angle annular dark-field (HAADF) detector. The metal compositions were determined by a Bruker ICP-MS (M90) system. The catalysts loading amount on carbon black were measured by TGA on a STA449F3 (METZSCH).

### Preparation of the catalysts suspension solution and working electrode

A mixed solution of 5 mL of ethanol and 5 mL of methanol consisting of 2 mg of Pd-Ir catalyst and 8 mg of carbon black

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