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# Oxygen reduction reaction and hydrogen evolution reaction catalyzed by carbon-supported molybdenum-coated palladium nanocubes

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## ABSTRACT

Oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) are two important processes for electrochemical energy storage and conversion. Herein, we describe the preparation of carbon-supported Pd nanocubes@Mo core@shell nanostructures as efficient dual catalysts for both ORR and HER. The core@shell structure was manifested by high-resolution transmission electron microscopy measurements, including high angle-angular dark field-scanning transmission electron microscopy and elemental mapping analysis. Further structural insights were obtained in X-ray diffraction and X-ray photoelectron spectroscopy measurements. The nanostructures exhibited apparent electrocatalytic activity toward both ORR and HER, and the performances were markedly higher than those without the deposition of a Mo overlayer. In ORR, the activity was even better than that of commercial Pt/C within the context of onset potential, specific and mass activities; whereas in HER, the performance of Pd nanocubes@Mo core@shell nanostructures remained subpar as compared to that of Pt/C in terms of the overpotential to reach the current density of 10 mA cm<sup>-2</sup>, the Tafel slope was comparable and the stability was excellent. The excellent electrocatalytic performance can be attributed to the Pd-Mo synergistic effects imparted from the core-shell structure.

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## Introduction

Oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) are two important processes in the development of sustainable and green energy technologies for electrochemical energy conversion and storage [1–4]. Because of their complicated reaction pathways and sluggish electron-transfer kinetics, development of low-cost, high-performance catalysts is needed. Currently, Pt-based materials are the state-of-art catalysts for both ORR and HER [5–7]. However, the low natural abundance and high costs of Pt have significantly hindered the widespread commercialization of such technologies. In addition, Pt-based electrocatalysts typically exhibit insufficient long-term durability during the electrocatalytic operations, mainly due to Ostwald ripening and deactivation by adsorption of CO-like poisonous intermediates on the catalyst surface [8–10]. Therefore, substantial research efforts have been devoted to the design and development of non-Pt catalysts for both ORR and HER [11–15].

In fact, palladium has been recognized as a viable alternative, mainly due to its relatively low cost, desirable electrocatalytic performance and well-established techniques toward industrial applications [16–18]. For instance, the abundance of Pd in the Earth's crust is 0.015 ppm by weight, which is 3 times higher than that of Pt (0.005 ppm) [19]. Advanced Pd-based catalysts have been widely employed in the electrocatalysis of ORR and HER. For instance, Huang et al. developed a simple process based on controlled pyrolysis for the synthesis of palladium-cobalt nanoparticles supported on carbon nanotubes and observed apparent ORR and HER activity [20]. In another study, Liu and co-workers reported the preparation of porous Pd nanoparticle assemblies, which exhibited a small Tafel slope of  $30 \text{ mV s}^{-1}$ , and an exceptional low overpotential ( $\eta_{100}$ ) of 80 mV to reach the current density of  $100 \text{ mA cm}^{-2}$  for HER in 0.5 M  $\text{H}_2\text{SO}_4$ , as well as a half-wave potential of 0.837 V and an onset potential of 0.926 V at 1600 rpm with a scan rate of  $5 \text{ mV s}^{-1}$  for ORR in 0.1 M KOH [21].

The catalytic activity of Pd may be further enhanced by a range of structural engineering [22–25], such as surface modification [26], manipulation of composition and morphology [27,28], and alloying with transition metals [29]. For instance, in a recent study [30], Lee and Kwon deposited Pd nanoparticles (ca. 7 nm) on  $\text{MoS}_2$  surfaces by a one-step sonochemical method and observed enhanced electrocatalytic activity towards ORR in alkaline media. This was ascribed to the tensile strain produced at the Pd/ $\text{MoS}_2$  interface and the charge-transfer from Pd to  $\text{MoS}_2$  that raised the Pd d-band center. Note that a range of molybdenum-based compounds, such as  $\text{MoS}_2$  [31],  $\text{MoO}_3$  [32],  $\text{Mo}_2\text{C}$  [33], and  $\text{MoNi}_4$  [34], are also active in HER electrocatalysis. Thus, it will be of fundamental and technological significance to examine the dual activity of the resulting composites towards both ORR and HER. This is the primary motivation of the present study.

In this study, we report a facile approach to the preparation of carbon-supported palladium nanocubes that were decorated with a thin layer of molybdenum compounds as dual functional electrocatalysts for both ORR and HER.

Transmission electron microscopic measurements and elemental mapping analysis showed the formation of well-defined Pd nanocubes@Mo core-shell structures. In electrochemical tests, the nanostructures demonstrated superior activity and markedly higher long-term stability than Pt/C for ORR. In addition, in HER tests, the sample also displayed a remarkable performance that was comparable to that of Pt/C, with exceedingly enhanced durability. This was largely ascribed to the lattice strain at the Pd/Mo interface that manipulated the electronic interactions with reaction intermediates hence enhanced the catalytic activity.

## Materials and methods

### Chemicals

Poly(vinyl pyrrolidone) (PVP, MW = 55,000), L-ascorbic acid (99%), potassium bromide (KBr, 99%), sodium tetrachloropalladate(II) ( $\text{Na}_2\text{PdCl}_4$ , 99.95%), acetic acid glacial (99.5%), ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , 99%), and carbon black (Vulcan XC-72, Cabot) were purchased from Energy Chemicals. All aqueous solutions were prepared using de-ionized (DI) water with a resistivity of  $18.3 \text{ M}\Omega \text{ cm}$ .

### Synthesis of Pd nanocubes

Pd nanocubes were synthesized by adopting a literature protocol [35]. In a typical procedure, 8 mL of an aqueous solution containing PVP (105 mg), ascorbic acid (60 mg), and KBr (600 mg) was heated at  $80 \text{ }^\circ\text{C}$  under magnetic stirring at 800 rpm for 10 min. Then 3 mL of an aqueous solution containing 0.2 mmol  $\text{Na}_2\text{PdCl}_4$  was added quickly. The mixture was heated at  $80 \text{ }^\circ\text{C}$  in air under magnetic stirring for 3 h and then cooled down to room temperature. Pd nanocubes were collected by centrifugation and washed three times with a water/acetone mixture to remove excess PVP.

### Preparation of Pd nanocubes@Mo core@frame nanostructure

For the synthesis of Mo-coated Pd nanocubes [35], in a typical process, 2 mg of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and 12 mg of ascorbic acid were added into 10 mL of the aqueous suspension of Pd nanocubes obtained above ( $1 \text{ mg mL}^{-1}$ ). After heating at  $80 \text{ }^\circ\text{C}$  under magnetic stirring for 2 h, the reaction solution was cooled down to room temperature, affording Pd nanocubes@Mo core@frame nanostructures that were collected by centrifugation and washed three times with water.

### Preparation of carbon-supported Pd nanocubes and Pd nanocubes@Mo nanostructures

To prepare carbon-supported Pd nanocubes (denoted as Pd nanocubes/C), Pd nanocubes were collected by centrifugation and re-dispersed in 10 mL of ethanol. A specific amount of carbon black (Vulcan XC-72, Cabot) was added into the suspension, and the loading of Pd was controlled at 20 wt %. The mixture was then stirred and sonicated for 6 h. The resultant Pd nanocubes/C composites were collected by centrifugation.

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