



# Controllable synthesis of palladium nanocubes/reduced graphene oxide composites and their enhanced electrocatalytic performance



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## HIGHLIGHTS

- Pd nanocubes/reduced graphene oxide was synthesized within one-step process.
- Environment friendly ascorbic acid was chosen as the reductant.
- Experimental factors have been systematically studied for the formation mechanism.
- The PdNCs/G exhibits superior activity and stability towards ethanol oxidation.

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## ABSTRACT

Homogeneous distribution of cube-shaped Pd nanocrystals on the surface of reduced graphene oxide is obtained via a facile one-step method by employing AA and KBr as the reductant and capping agent, respectively. The experimental factors affecting the morphology and structure of Pd nanoparticles have been systematically investigated to explore the formation mechanism of Pd nanocubes (PdNCs). It is revealed that PdNCs enclosed by active {100} facets with an average side length of 15 nm were successfully synthesized on the surface of reduced graphene oxide. KBr plays the role for facet selection by surface passivation and AA controls the reduction speed of Pd precursors, both of which govern the morphology changes of palladium nanoparticles. In the further electrochemical evaluations, the Pd nanocubes/reduced graphene oxide composites show better electrocatalytic activity and stability towards the electro-oxidation of ethanol than both reduced graphene oxide supported Pd nanoparticles and free-standing PdNCs. It could be attributed to the high electrocatalytic activity of the dominated active {100} crystal facets of Pd nanocubes and the enhanced electron transfer of graphene. The developed approach provide a versatile way for shape-controlled preparation of noble metal nanoparticles, which can work as novel electrocatalysts in the application of direct alcohols fuel cells.

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## 1. Introduction

Novel electronic, thermal, optical, magnetic and catalytical properties of nanocrystals are proved to be much dependent on their shape and structure. Therefore, extensive interest in past decades have been devoted to controllable synthesis of metal nanocrystals with different shapes and facet orientations, which is

a powerful means to tune the properties of nanomaterials for various applications [1–3]. As an extremely important nanomaterial in catalysis, Pd nanocrystals exhibit efficient electrocatalytic activities in fuel cell applications [4–7]. In this regard, controlling the shape and facets of Pd nanocrystals is an effective way to enhance the performance in catalytic reactions. Among the Pd nanomaterials, Pd nanocubes have gained exceptional attention for their superior catalytic ability resulting from the relatively high surface energy of the surrounding {100} facets among low index facets. Notably, Zhang et al. applied a one-pot method to fabricate the cubic Pd nanocrystals with {100} facets showing a higher activity than the {110}-facet-enclosed Pd rhombic dodecahedral in

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electro-oxidation of ethanol [8]. Moreover, Shao et al. and Yin et al. demonstrated that the {100}-facet-enclosed Pd nanocrystals also showed a higher activity than the other types of Pd nanocrystals towards the methanol electro-oxidation [9,10].

In order to further maximize the catalytic activity of Pd nanocrystals and minimize the use of precious Pd metal, a combination of Pd nanocrystals with carbon materials, such as carbon black, carbon nanotubes and carbon nanofibers, has been considered an effective way [11,12]. These carbon materials supports can enhance the dispersity of Pd nanocrystals and increase the utilization and efficiency of Pd-based electrocatalysts [11]. Among the carbon materials, graphene, with distinctive 2-dimensional sheet structure consisting of a few layers of  $sp^2$ -hybridized carbon lattice [13,14], has received great attention due to its outstanding physicochemical properties, such as large specific surface area, superior electrical conductivity and good mechanical strength [12,15–18]. Thus, it is expected to be the best candidate for the combination with Pd nanocrystals to design novel catalyst for direct alcohols fuel cells (DAFCs) [19–22]. So far, Pd nanostructures supported on graphene are mostly nanospheres [20,21,23], nanoclusters [24], and nanodendrites [11,25]. The study about the preparation of cube-shaped Pd nanocrystals attached graphene composites and their application in the electro-oxidation of alcohols is rarely reported. A complete understanding about the details of the formation mechanism of PdNCs on the surface of RGO is also lacking, including the influencing of substrate and experimental factors, and the relationship between structure and properties. In anticipation of fascinating electrochemical properties of Pd nanocubes attached graphene, it is desirable to develop a facile chemical method for the synthesis of Pd nanocubes anchoring on graphene and further investigate their electrocatalytical performance towards ethanol oxidation.

In the present work, we attempt to synthesize the cube-shaped Pd nanocrystals/reduced graphene oxide composites *via* a facile one-step method, in which the reduction of graphite oxide and metal precursor was carried out simultaneously by employing ascorbic acid (AA) and potassium bromide (KBr) as the soft reducing and capping agents, respectively [23,26,27]. Herein, the experimental factors affecting the morphology and structure of Pd nanoparticles on the graphene, such as the role of reduced graphene oxide, concentrations of KBr and AA, the reduction time and reaction temperature, have been systematically investigated to explore the formation mechanism of Pd nanocubes. The morphology and structure of Pd nanocubes/reduced graphene oxide (PdNCs/G) composites were characterized by transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Further electrochemical experiments including cyclic voltammograms and chronoamperometry were performed toward the electro-oxidation of ethanol. The results revealed superior electrocatalytic activity and stability of the PdNCs/G as compared with both reduced graphene oxide supported Pd nanoparticles (PdNPs/G) and free-standing PdNCs, showing a great potential as new anode catalysts in DAFCs.

## 2. Experimental section

### 2.1. Chemicals and materials

Potassium tetrachloropalladate (II) ( $K_2PdCl_4$ ) was purchased from Aldrich Chem Co. Graphite was obtained from Alfa Aesar and 5wt% nafion was purchased from DuPont. Ascorbic acid (AA), Potassium Bromide (KBr), sulfuric Acid,  $KMnO_4$ ,  $K_2S_2O_8$  and  $P_2O_5$  were purchased from Sinopharm Chemical Reagent Co and used without further purification. All chemicals were analytically pure

and used as received without further purification. The deionized water for solution preparation was from a Kertone Ultrapure Water System P60-CY (Kertone Water Treatment Co. Ltd, resistivity  $>18 M\Omega cm$ ).

### 2.2. Synthesis of PdNCs/G, PdNPs/G composites and PdNCs

The graphite oxide (GO) powder were prepared from graphite powder *via* a modified Hummers' method [28]. 12.5 mg GO was first dissolved in 40 mL pure water and exfoliated using ultrasonic treatment for 1 h to achieve well dispersion. Then, 1 mL of 0.035 M  $K_2PdCl_4$  and 1 mL of 0.03 mM KBr were mixed with 48 mL pure water. Next, the resulting solution was mixed with the above GO dispersed solution, following the addition of 200 mg AA as the reductant. The mixture was kept stirring for 1 h at a temperature of 85 °C under reflux conditions. Finally, solid powders were collected *via* centrifugation, sequentially washed with double-distilled water and ethanol for several cycles, and dried at 60 °C in a vacuum oven for 12 h. The PdNCs/G composite was then obtained. Similarly, Pd nanoparticles attached reduced graphene oxide (PdNPs/G) and free standing Pd nanocubes (PdNCs) were prepared by the same procedure in the above description without the capping agent and supporting materials, respectively.

### 2.3. Electrochemical characterizations of PdNCs/G

The working electrodes were independently fabricated as follows. First, a glassy carbon (GC) disk (diameter = 3 mm) electrode was polished with slurry of 1, 0.3 and 0.05  $\mu m$  alumina to mirror finish, rinsed with pure water and dried at room temperature in a vacuum oven for hours. Then, 2 mg of PdNCs/G composite was dispersed in the mixture of 0.9 mL  $H_2O$  and 0.1 mL 5 wt% Nafion using ultrasonic treatment to form a homogeneous black suspension. Finally, 5  $\mu L$  of the catalyst suspension was carefully pipetted onto the surface of the GC disc and dried at room temperature to form a layer that prevented the catalyst particles from detaching. The as-prepared PdNCs/G working electrodes were for electrochemical evaluations. PdNPs/G and PdNCs working electrodes were prepared using the same procedure described above.

All electrochemical measurements including cyclic voltammograms (CV) and chronoamperometry (CA) were conducted using a 550 electrochemical workstation (Gaoss Union Instrument Company, China) at room temperature in a conventional three-electrode cell, with PdNCs/G, PdNPs/G or PdNCs modified glassy carbon electrode as the working electrode, a Pt wire as the counter electrode and a Ag/AgCl electrode saturated with KCl as the reference electrode. Before each experiment,  $N_2$  gas (99.999%) was used to remove the dissolved oxygen in the solution to preserve an inert atmosphere.

### 2.4. Physicochemical characterizations of PdNCs/G

Pd nanocubes/reduced graphene oxide composites were characterized by XRD using a D8-Advance diffractometer (Bruker, Germany) with Cu  $K\alpha$  radiation source ( $\lambda = 0.15418 nm$ ) and glass plates as a substrate. The morphology and structure of the samples were characterized using TEM (FEI TECNAI 20, USA, and JEOL 2100F with an image-corrector, Japan) and FE-SEM (JSM-7100F, Japan). EDS analysis of chemical composition was taken by the analyzer coupled to the FE-SEM. XPS were recorded by a SPECS system (PHOIBOS 150, Germany) with Al  $K\alpha$  radiation ( $h\nu = 1486.6 eV$ ), and the vacuum in the analysis chamber was maintained at about  $10^{-9}$  mbar. By EDS, the Pd loading amounts were calculated to be 43.2% in PdNCs/G and 48.2% in PdNPs/G.

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