



# Palladium litchi-like nanoclusters for remarkably elevating methanol electrocatalytic activity

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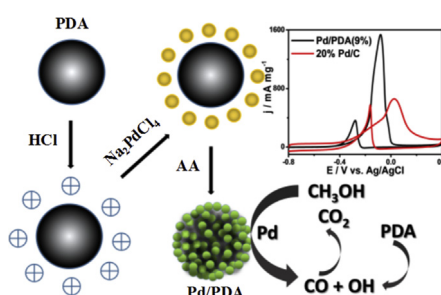
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## HIGHLIGHTS

- Well dispersive litchi-like Pd nanoclusters is made using optimal amount of polydopamine.
- Such Pd@PDA with many exposure active sites has superior catalysis for methane oxidation.
- Pd@PDA existing many OH groups shows a good capability against CO species poison.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

The Palladium/polydopamine (Pd/PDA) litchi-like nanoclusters are synthesized via a two-step route. The resultant product is characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and the electrochemical properties were evaluated by cyclic voltammetry (CV) and chronoamperometry. Notably, the as-prepared litchi-like Pd/PDA nanoclusters show superior catalytic properties for methanol electro-oxidation in an alkaline medium due to unique Pd dots adhered at PDA surface providing a large electrochemically active surface area (ECSA). Additionally, the high concentration of oxygen functional groups on PDA is essential to the removal of carbonaceous species from the adjacent at the Pd sites. This PDA-based straightforward synthesis strategy offers a new pathway for developing highly active electrocatalysts with aid of special organic polymer.

## 1. Introduction

Design and synthesis of excellent electrocatalysts is of crucial importance for the development of fuel cell [1–3]. Pd-based nanomaterials have emerged as attractive candidates to replace the widely used scarce Pt-based nanomaterials because Pd is relatively abundance and highly reasonable activity for the oxidation of a large variety of substrates especially in an alkaline medium [4–6]. However, for large scale

commercial applications, it is still necessary to lower the usage of Pd [7]. Therefore, construction of highly efficient Pd-based catalysts is urgently needed in optimal methods. It is reported that the catalytic performance of nanoparticles highly contingents on the morphology, dimensions and compositions [8,9]. Catalytic properties of nanocatalysts are always determined by their morphologies due to different types of exposed facets on the surfaces [10,11]. Accordingly, for developing sustainable Pd-based catalysts, myriad methodologies of

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controlled-synthesis of Pd-based nanomaterials for further improvement of the utilization and catalysis activity of Pd have been extensively studied, such as core-shell [12], hexameric octahedral [13], dandelion-like [14], and hyperbranched [15]. Significantly, mesoporous or flower-shaped three-dimensional nanomaterials of noble metals have shown promising structures for implementing superior catalytic activity thanks to their advantages of larger surface area and more exposure active sites [16,17]. Beyond that, another problem with Pd-based anodic catalysts is that Pd catalysts are susceptible to CO-like carbonaceous intermediates poisoning [18,19], which needs to be overcome by exploring new strategies.

Polydopamine (PDA), easily produced via the self-polymerization of dopamine at alkaline environments, contains catechol and amine functional groups, which not only provides an effective platform for connection of metal nanoparticles, but also can be employed for surface modification [20–22]. In addition, the PDA encompassing many –OH groups could be expected to facilitate the oxidation removal of carbonaceous intermediate, which is expected to improve the CO tolerance of Pd catalyst and enhance the activity and stability of catalyst.

In this work, we reported a facile and efficient two-step strategy to prepare palladium nanoclusters dotted PDA with open structure (Denoted as litchi-like Pd/PDA NCs). First, PDA nanospheres were obtained via the spontaneously oxidative polymerization of dopamine under alkaline conditions. Second, Pd/PDA NCs were prepared by the in-situ reduction process of  $\text{PdCl}_4^{2-}$  at the surface of PDA nanospheres by using reductive reagent. For the methanol oxidation reaction, the as-synthesized litchi-like Pd/PDA NCs catalyst exhibited beyond 2-fold of mass activity, compared with the state-of-the-art commercial Pd/C catalyst as well as strong resistance to CO poisoning. Therefore, individual Pd nanoclusters together with massive OH groups at the PDA surface will hopefully become the importantly catalytic platform for fuel cell application.

## 2. Experimental section

### 2.1. Materials

Tris(hydroxymethyl) aminomethane hydrochloride (Tris, 99%) and dopamine hydrochloride (DA, 98%) were purchased from Aladdin (Shanghai, China). Sodium tetrachloropalladate (II) ( $\text{Na}_2\text{PdCl}_4$ , 99.995%) and *L*-ascorbic acid (AA, > 99%) were obtained from Sigma-Aldrich. 20%Pd/C (20% Pd loading, nominally 50% water wet) was commercially available from Alfa Aesar. Methanol ( $\text{CH}_3\text{OH}$ , AR), Potassium hydroxide (KOH, AR) and Potassium chloride (KCl, AR) were bought from Shanghai Richjoint Chemical Reagents Co. Ltd. Deionized (DI) water (18.2 M $\Omega$  cm) was used throughout the experiment.

### 2.2. Characterization

The morphologies of the as-prepared samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100 operating at 200 kV). The crystalline structure was analyzed by X-ray powder diffraction (XRD, Rigacu D/Max-2000, monochromatic Cu K $\alpha$

radiation). The electronic structure was investigated X-ray photoelectron spectroscopy (XPS, PHI5000 Versa Probe; all of the binding energies were corrected with reference to the C 1s peak at 284.8 eV). The amount of metal (Pd) was determined with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Varian VISTA-MPX).

### 2.3. Preparation of litchi-like Pd/PDA NCs

#### 2.3.1. Preparation of PDA spheres

PDA spheres were prepared via the self-polymerization of dopamine. In detail, DA (50 mg) was dissolved in Tris-HCl buffer (10 mM, pH = 8.5) with magnetic stirring. Then, ethanol (100 mL) was added and magnetic stirred for 24 h at room temperature. After the reaction, the product was collected by centrifugation and washed with water several times and finally dried in vacuum at 40 °C, and finally dispersed in 2 mL of DI water (0.4 g/L).

#### 2.3.2. Preparation of Pd/PDA nanoclusters catalysts

50  $\mu\text{L}$  PDA suspension was added into 5.0 mL of DI water and the mixture was ultrasonicated for 10 min. Subsequently, the pH was appropriately adjusted to about 3.0 by adding HCl solution (0.4 M) dropwise. Then  $\text{Na}_2\text{PdCl}_4$  (10 mM, 400  $\mu\text{L}$ ) solution was put into under vigorously stirring. The mixed solution was stirred and heated to 80 °C and 1.0 mL of 0.1 M AA (freshly made) was injected dropwise. After 30 min, the finally solution was centrifuged and washed with water for several times and the nanoparticles were dispersed in DI water.

### 2.4. Electrochemical experiments

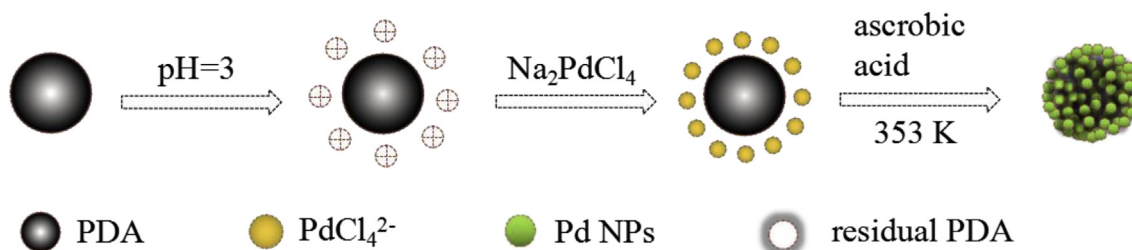
The electrochemical measurements were conducted on an electrochemical workstation (CHI 660E) coupled with a three-electrode system. A Pt wire and a Ag/AgCl electrode filled with 3 M KCl aqueous solution were used as the counter and reference electrodes, respectively. The grassy electrodes modified by Pd NPs, Pd/PDA NCs, or commercial Pd/C were used as the working electrode, respectively. The modified electrodes were obtained by dropping 10  $\mu\text{L}$  of the catalysts with Pd loading of 1.25  $\mu\text{g}$  onto the polished and cleaned glassy carbon electrode (GCE, 3 mm in diameter) surface and dried at room temperature.

Cyclic voltammetric (CV) experiments were carried out in an aqueous solution containing 0.5 M KOH and 1.0 M methanol at a scan rate of 50  $\text{mV s}^{-1}$ .

CO stripping experiments were performed in a 0.5 M KOH solution from –0.8 to 0.4 V vs. Ag/AgCl, with a scan rate of 50  $\text{mV s}^{-1}$ . In advance, the solutions were deaerated by bubbling ultrapure  $\text{N}_2$  for 30 min. Then CO was bubbled for 30 min to allow the complete adsorption of CO on the catalyst surface and the working electrode was hold at a potential of 0.1 V vs. Ag/AgCl. After that, the excess CO dissolved in solution was further purged out with  $\text{N}_2$  for 15 min.

Chronoamperometry curves were obtained in a solution containing 0.5 M KOH and 1.0 M  $\text{CH}_3\text{OH}$  for 10000 s at –0.1 V applied potential.

All electrochemical experiments were carried out at room temperature.



**Scheme 1.** The synthetic procedure of Pd/PDA NCs.

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