# Facile synthesis of palladium–graphene nanocomposites and their catalysis for electro-oxidation of methanol and ethanol

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## ARTICLE INFO

## ABSTRACT

Well-dispersed Pd nanoparticles (PdNPs) supported on graphene sheets were successfully prepared by a simple one-pot process, in which the reduction of Poly Vingl Pyrrolidone-functionalized graphite oxide and Pd precursor was carried out simultaneously using ascorbic acid as a soft reductant. The Pd nanoparticles decorated graphene composite (PdNPs/PVP-graphene) was characterized by X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy. Morphology and structure characterizations directly showed that Pd nanoparticles with crystallite size of about 8.5 nm were evenly formed on graphene. Catalysis activity as in fuel cells was investigated by further electrochemical experiments including cyclic voltammograms and chronoamperometric measurements. Compared to the commercial Vulcan XC-72 supported Pd nanoparticles, PdNPs/PVP-graphene exhibits superior electrocatalytic activity and stability toward electro-oxidation of alcohols, showing its potential use as new electrode material for direct alcohol fuel cells (DAFCs).

## 1. Introduction

Due to the continuous consumption of fossil fuels and the ever-increasing environmental problems, there has been increasing interest in the development of fuel cell systems, especially the direct alcohol fuel cells (DAFCs). As a new generation of power sources with characteristics of high energy conversion efficiency, low pollutant emission and low operating temperature, fuel cell systems show great potential in portable devices [1–3]. In recent years, Pt-based catalysts have been widely studied as the anode catalysts for alcohols electro-oxidation in an acid medium. However, the poisoning by CO-like intermediates and the high price of Pt hamper their extensive use in DAFC in the commercial market [4–6]. Therefore, Pd-based catalysts have become a hot topic of interest in view of the superior activity, greater resistance to CO-like formation and lower cost. In order to further maximize the catalytic activity and utilization efficiency of Pd, an alternative way is to load highly dispersed Pd nanostructures with controlled size and morphology on supporting materials having a large specific surface area [7–10].

As supports for catalysts in DAFC, various carbon materials have been investigated. The structure and properties of the carbon supports have significant effects on the activity and stability of the catalysts, such as active surface area, surface functional groups and the degree of graphitizing [11,12]. Graphene, the two dimensional carbon nanomaterial with an extremely large specific surface area, superior electronic conductivity, the best mechanical strength and highest stability among carbon materials, is expected to be the best candidate as the support material [13,14]. And graphene supported metal or metal oxide nanoparticles have demonstrated high efficiencies for fuel cell applications [2,15]. Therefore, the approaches of combining the graphene and Pd nanoparticles have been studied intensively due to their applicability to the catalysis of alcohol electro-oxidation. Fundamentally, graphene and metal nanoparticles were prepared separately and then mixed in assistant of polymer or bridging agent [16,17]. But the complex stepwise procedures and use of bridging agents might decrease the catalysis ability of Pd. Although the reduction of metal ions and graphite oxide (GO) could be performed simultaneously by some chemical reductants, such as hydrazine and $NaBH_4$, the toxicity of the chemical reagents and somewhat structural damage to the graphene support were still a challenge [18,19].

In our previous report, it was possible to synthesize Pt nanoparticles on the graphene substrate just *via* reducing the platinum precursor by ascorbic acid, which showed satisfying attachment and high catalysis performance for the methanol oxidation [19].

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It was demonstrated that ascorbic acid could reduce the oxygen-containing groups, such as carboxylic and epoxy groups on the surface of graphite oxide in recent reports [20–23]. The outstanding advantage for using ascorbic acid is due to its moderate reducibility and environment-friendly nature compared with vigorous and poison reductants, e.g. hydrazine and sodium borohydride.

In this study, the one-pot process using ascorbic acid as reductant was extended to prepare Pd nanoparticles loaded graphene composite materials, considering the similar properties of Pd and Pt. It was hoped to combine the advantages of graphene and Pd nanoparticles by using this simple, green but powerful technique to make a new kind of carbon composite materials for the catalyst of fuel cell. This method offers the possibility of making different noble-metal nanoparticles loaded graphene composite and also provides a new carbon nanocomposite material for DAFC application. The morphology and structure of Pd nanoparticles loaded graphene composite materials (PdNPs/PVP-graphene) were systematically characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). With the adding of Poly Vingl Pyrrolidone, Pd nanoparticles can firmly attach to the surface of graphene and hardly aggregate after reduction. Further electrochemical experiments revealed excellent electrocatalytic activity and stability of the PdNPs/PVP-graphene toward alcohols oxidation compared with Pd nanoparticles modified X-Vulcan materials, showing potential applications of PdNPs/PVP-graphene in the direct alcohol fuel cells.

## 2. Experimental

### 2.1. Chemicals

Graphite was obtained from Alfa Aesar. Vulcan XC-72 was purchased from Cabot CorP. $K_2PdCl_4$ was obtained from Aldrich Chem Co. 5% nafion was purchased from DuPont. Ascorbic acid, sulfuric acid, N,N-dimethylformamide (DMF), Poly Vingl Pyrrolidone (PVP), $KMnO_4$, $K_2S_2O_8$ and $P_2O_5$ were purchased from Sinopharm Chemical Reagent Co. The pure water for solution preparation was from a Kertone Ultrapure Water System P60-CY (Kertone Water Treatment Co., Ltd., resistivity > 18 MΩ cm).

### 2.2. Apparatus

The morphology and structure of the as-synthesized samples were characterized with transmission electron microscopy (TEM; FEI TECNAI20, USA). X-ray diffraction (XRD) analysis was carried out using a D/Max-3C diffractometer (Japan) with Cu Kα radiation source ($\lambda$ = 0.15418 nm). X-ray photoelectron spectra (XPS) were recorded by a SPeCS system (PHOIBOS 150, Germany) with Al Kα radiation ($h\nu$ = 1486.6 eV). Thermogravimetric analysis (TGA) was taken with a thermogravimetric analyzer (Perkin-Elmer TGA-7, USA). All electrochemical measurements were performed with a 550 electrochemical workstation (Gaoss Union Instrument Company, China). The conventional three-electrode system was used with a modified glassy carbon (GC) working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode. For TEM characterization, Pd nanoparticles/graphene was first dispersed into ethanol with sonication for several minutes, and was then casted on a copper mesh and dried in ambient condition, and then transferred into the microscope for observation.

### 2.3. Procedures of preparing PdNPs/PVP-graphene, PdNPs/graphene and PdNPs/Vulcan composites

The graphite oxide powders were prepared from graphite using the modified Hummers' method [24]. Our novel route to
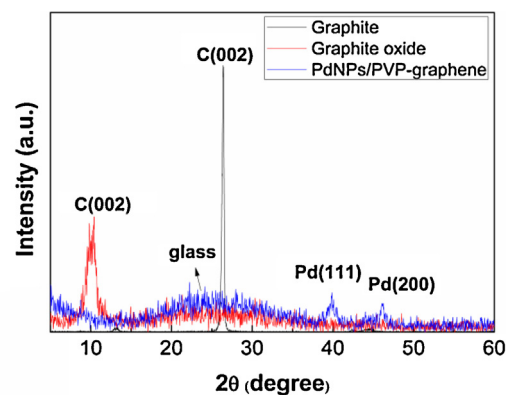


**Fig. 1.** XRD patterns of graphite (black line), graphite oxide (red line), and PdNPs/graphene (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

prepare palladium–graphene nanocomposites is as follows: 12.5 mg graphite oxide was dissolved in 25 mL water and exfoliated by ultrasonic treatment for 1 h, and then 200 mg PVP and 24 mL water were added while stirring for another 1 h. After that, 2 mL 0.01 M $K_2PdCl_4$ and 250 mg ascorbic acid were added into the above solution under stirring. The mixture was kept stirring for 12 h at a temperature of 85 °C with the reflux condition. Finally, the collected solid sample, denoted as PdNPs/PVP-graphene, was separated by centrifugation and then thoroughly washed with ethanol and water and then dried in a vacuum oven at 50 °C. For comparison, Pd nanoparticles attached on graphene (without adding of Poly Vingl Pyrrolidone) and Vulcan XC-72 were prepared by the same procedure as described above and the composites were denoted as PdNPs/graphene and PdNPs/Vulcan, respectively. By thermogravimetric analysis (TGA), the Pd loading amounts were calculated to be 31.76% in PdNPs/PVP-graphene, 73.8% in PdNPs/graphene and 57.15% in PdNPs/Vulcan, respectively.

### 2.4. Fabrication of PdNPs/PVP-graphene, PdNPs/graphene and PdNPs/Vulcan working electrodes

The PdNPs/PVP-graphene working electrode was manufactured as follows. 6 mg PdNPs/PVP-graphene composites were well dispersed in 1 mL DMF by ultrasonic treatment to form a homogeneous black suspension. Then, 5 μL of the resulting suspension was carefully pipetted onto the surface of glassy carbon disk (diameter 3 mm) which had been polished with slurry of 1, 0.3 and 0.05 μm alumina and rinsed with pure water. After being dried at room temperature for hours, the catalyst formed. Finally, 10 μL 5% nafion was transferred evenly onto the surface of the dried PdNPs/PVP-graphene to form a layer protecting catalyst particles from detaching. The working electrode was kept at room temperature in vacuum furnace until dry. PdNPs/graphene and PdNPs/Vulcan working electrodes were prepared with the same procedure described above.

## 3. Results and discussion

### 3.1. The characterization of morphology and structure of PdNPs/PVP-graphene composites

Crystalline structure of the as-prepared PdNPs/PVP-graphene composites was characterized by XRD, and the typical spectrum is shown in Fig. 1 together with the spectra of original graphite powders and graphite oxide. For the spectrum of graphite, the diffraction peak centered at $2\theta$ of 26.2° is attributed to the (0 0 2) plane reflection of hexagonal crystalline graphite [25],