



Graphene nanomaterials supported palladium nanoparticles as nanocatalysts for electro-oxidation of methanol



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ABSTRACT

We herein report a facile hydrothermal approach to prepare well-dispersed nitrogen-doped graphene quantum dots-supported Pd (N-GQDs/Pd) nanocomposites of a narrow size distribution with diameter of 4.8 ± 0.2 nm. The N-GQDs/Pd nanocomposite demonstrates an excellent electrocatalytic activity for the methanol oxidation reaction in an alkaline medium when compared with the graphene sheets-supported Pd nanocomposites (GS/Pd), graphene quantum dots supported Pd nanocomposites (GQDs/Pd) and commercial palladium catalyst (Pd/C). The N-GQDs/Pd of good dispersion and, small and narrow size distribution offers superior electrical conductivity and remarkable cycling stability. In addition, it offers promising and attractive practical opportunities for electronic materials which possess high catalytic activity and stability, yet the noble metal usage is reduced. This study demonstrated the potential use of N-GQDs/Pd as new electrocatalytic nanomaterials for direct methanol fuel cells.

1. Introduction

Palladium nanoparticles (Pd NPs) have been proven to be marvelous metallic heterogeneous catalysts for a wide range of chemical reactions. Preparation of palladium nanocrystals (Pd NCs) of well-defined size and shape is one of the most challenging goals in developing highly active Pd-based catalysts. The support is one of the most crucial factors because it can improve some of the desirable properties of the resulting catalyst, such as mechanical strength, stability, activity, and selectivity. Pd nanoparticles supported by carbon-based, including active carbon, carbon fibers, nanotubes, copolymer and graphene, are promising for a variety of applications ranging from catalysis, chemical and bio-sensing, to fuel cells and other renewable energy-related areas [1–5]. Effective control in morphology and size of Pd nanostructures allows the enhancement of their catalytic properties and activity on a mass or specific basis [6]. Despite significant work related to carbon-supported Pd nanoparticles have been reported, tailoring the properties of the support for catalysis remains a challenge.

Compared with conventional carbon supports, nitrogen-doped carbon materials can (i) increase the electric conductivity and surface area; (ii) enhance the affinity between the catalysts and supports through electrostatic and coordinative action; and (iii) avoid the migration and aggregation of nanocatalysts, and thus improve the

durability of catalysts [7,8]. It is recognized that nitrogen doping offers active sites for deposition of metal particles on the support with better dispersion, smaller particle size, and more active surface area of electrocatalyst [9]. Higher doping amount of nitrogen favors a stronger adhesion of the Pd to the support [10]. The Pd nanoparticle-decorated nitrogen-doped graphene (Pd/NG) catalyst exhibited excellent electrocatalytic activity towards the ORR in alkaline media [11]. In contrast to two dimensional graphene nanosheets and one dimensional nanoribbons, zero-dimensional graphene quantum dots (GQDs) possess strong quantum confinement and edge effects when their sizes are as small as ~ 10 nm, at which unique physical properties are induced [12]. For the nitrogen-doped graphene quantum dots (N-GQDs), the chemically bonded N atoms could drastically produce new phenomena and unexpected properties, for example, altering the electronic characteristics and providing high number of anchoring sites for the adsorption of metal ions [13]. At the same time, N-GQDs possess many oxygen-containing functional groups that can make it more hydrophilic and also easier to form a stable chemical bond with other materials. Therefore, N-GQDs could provide high electrical conductivity which gives Pd nanoparticles supported on N-GQDs the superior auxiliary catalytic activity [14]. Herein, we employed a simple and direct approach to prepare novel spherical Pd nanoparticles supported on nitrogen-doped GQDs (N-GQDs/Pd). The covalent interaction between

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the Pd particles and N-GQDs was supported by infrared (IR) spectroscopy, which provides important insights regarding the possible mechanisms of carbon-supported Pd particles. The electrocatalytic activity of the as-prepared N-GQDs/Pd nanomaterials for methanol oxidation was investigated and compared with GS/Pd, GQDs/Pd and commercial catalyst Pd/C for oxidation of methanol in alkaline solution. We demonstrated that N-GQDs/Pd possesses a superior electrocatalytic performance and remarkable cycling stability.

2. Experimental section

2.1. Materials and reagents

$(\text{NH}_4)_2\text{PdCl}_4$ the graphite powder; 5% Nafion methanol solution and Pd/C catalyst (containing 10 wt% Pd); and Hydrazine hydrate solution 78–82% (acidimetric) were purchased from Sigma-Aldrich Co. LLC (USA) and rod glassy carbon electrodes (3-mm, GC) were from Shanghai Chenghua Co. Ltd. (China). All other reagents were of analytical grade and used upon purchase without further purification. The pure water for solution preparation was from a Millipore Autopure WR600A system (USA).

2.2. Apparatus

Morphologies of Pd NPs and other nanocomposites observed by TEM and HRTEM were performed on a JEM-2100 transmission electron microscopy with an acceleration voltage of 200 kV. All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on a copper grid coated with carbon film. X-ray powder diffraction (XRD) patterns were obtained with a Rigaku D/max-2500 using Cu K_α radiation. Electronic binding energies of C_{1s} , N_{1s} and Pd_{3d} were measured by XPS analysis which was performed on a PHI Quantum 2000 Scanning ESCA Microprobe with a monochromatised microfocused Al X-ray source. All the binding energies were calibrated by using C_{1s} as reference energy ($\text{C}_{1s} = 284.6 \text{ eV}$). Fourier Transform Infra-Red (FTIR) spectra were recorded by Nicolet Magna 550 Series II FTIR spectrometer. Thermogravimetric analysis (TGA) of sample was performed on a Pyris Diamond TG/DTA thermogravimetric analyzer (Perkin-Elmer Thermal Analysis). Sample was heated from 30 to 800 °C at the rate of $5 \text{ }^\circ\text{C min}^{-1}$ under nitrogen flow (20 mL min^{-1}).

All electrochemical studies were conducted on a CH Instrument CV 600E electrochemical workstation (CH Instruments, Inc. USA) using a standard three-electrode configuration. A Pt wire (1-mm diameter, Chenghua) was employed as the counter electrode and an Ag/AgCl electrode was the reference electrode. The working electrode was the GS/Pd GQDs/Pd Pd/C and N-GQDs/Pd nanocomposites modified GC electrode. The N_2 were introduced into 0.50 M H_2SO_4 and 1.0 M NaOH solution at a flow rate of 100 mL min^{-1} for 15–30 min. Electrochemical methods including cyclic voltammetry (CV), a scan rate of 0.05 V s^{-1} was used. Linear sweep voltammetry and chronoamperometry were used to study the electrochemical behaviors of bare GC, bare Pd and the N-GQDs/Pd modified GC electrodes towards methanol oxidation in 1.0 M NaOH at ambient conditions.

2.3. Preparation of GQD/Pd and N-GQDs/Pd

Graphene oxide (GO) was prepared by chemical oxidization of graphite powder according to the modified Hummers method as reported [15]. Graphene sheets (GSs) were obtained by reduction of GO sheets with NaBH_4 at 85 °C for 12 h. The graphene sheets (0.05 g) were then oxidized in concentrated H_2SO_4 (10 mL) and HNO_3 (30 mL) for 15–20 h under mild sonication (500 W, 40 kHz) [16]. The oxidized graphene sheets (OGSs) were diluted and purified with microporous membrane and then redispersed in deionized water. Homogeneous OGSs water dispersion (5 mL) was mixed with 3.0 mL of ammonia solution (28 wt% in water) and 5 mL of deionized water in a glass vial.

After stirring for 30 min, the mixture was transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (50 mL) and heated at 180 °C for 12 h. After cooling to room temperature, the insoluble precipitates were filtered out using a microporous membrane to obtain a brown filtrate. To remove large graphene nanoparticles, the colloidal solution was dialyzed in a dialysis kit (retained molecular weight 3500 Da) for 5 days. The N-GQDs was found to be stable for more than 3 months.

$(\text{NH}_4)_2\text{PdCl}_4$ weighing 28.4 mg (0.10 mM) was dissolved in 20 mL of aqueous solution under vigorous stirring. An appropriate concentration, determined by the desired $\text{Pd}^{2+}/\text{N-GQDs}$ weight ratio, of 10 mL of N-GQDs colloidal solution was added into the $(\text{NH}_4)_2\text{PdCl}_4$ solution to obtain a dispersion mixture. After 12 h of stirring, a 5.0 mL aqueous solution of NaBH_4 (37 mg, 1.0 mM) was added dropwisely and stirred until the mixture turned black, indicating the formation of Pd NPs. The black mixture was stirred for further 30 min. The sample was isolated from the solvent by centrifugation at 13000 rpm.

GQDs/Pd was obtained by the same procedure except that 3.0 mL of ammonia solution (28 wt% in water) was replaced with 3.0 mL of 1.0 M NaOH solution. GS/Pd was prepared by one step method by mixing the homogeneous OGSs water dispersion (5 mL) with 10 mL of the 0.1 M $(\text{NH}_4)_2\text{PdCl}_4$ solution. After 12 h of stirring, a 10.0 mL of 78–82% hydrazine hydrate solution was added dropwisely and stirred until the mixture turned black, indicating the formation of Pd NPs. The sample was isolated from the solvent by centrifugation at 13000 rpm.

3. Results and discussion

The nitrogen-doped graphene quantum dots-supported Pd (N-GQDs/Pd), graphene quantum dots supported Pd (GQDs/Pd) and graphene sheets supported Pd (GS/Pd) nanocomposites were prepared from oxidized graphene sheets (OGSs) without organic additives (Fig. 1). Facile hydrothermal method was applied to synthesize both N-GQDs/Pd and GQDs/Pd. The morphology of these as-prepared nanocomposites was examined by transmission electron microscopy (TEM). In obvious contrast to GQDs/Pd and GS/Pd composites, the N-GQDs/Pd exhibited the highest dispersion of the spherical Pd nanoparticles (Pd NPs) and having a narrow size distribution with diameter ranging from 3.8 to 6.2 nm, the mean size is $4.8 \pm 0.2 \text{ nm}$ as determined from about 100 particles. This highlights the crucial role of nitrogen doping in size and morphology controlling of Pd NPs that grew on the graphene-based supporting materials. TEM images and thermogravimetric analysis (TGA) of these composites are shown in Fig. 2. The average size of Pd NPs on GQDs/Pd and GS/Pd composites was about 9.8 nm and 12.0 nm with aggregation. The Pd content estimated from TGA is 40%, 42% and 11% respectively in GS/Pd, GQDs/Pd and N-GQDs/Pd nanocomposites. Considering the fact that N-GQDs/Pd nanocomposite consists of only a quarter of Pd content compared with GS/Pd and GQDs/Pd, attributing to the fact that N-GQDs can provide chemical binding sites resulting in smaller particles of better dispersed palladium nanoparticles, N-GQDs/Pd nanocomposite can reduce promisingly usage of the noble metal in electronic materials. Fig. S1a and S1b showed high resolution TEM image of the N-GQDs/Pd composite and single N-GQDs respectively. It was revealed that ultra-fine spherical Pd NPs were well-dispersed on the surface of N-GQDs. Meanwhile, energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) displayed in Fig. S1c and S1d additionally confirmed the presence of Pd nanoparticles supported on N-GQDs. The XRD of N-GQDs/Pd exhibited diffraction peaks at 40.0, 46.7 and 68.3° which were assigned to the (111), (200) and (220) planes, respectively, of Pd from the $Fm\bar{3}m$ space group of the face-centered cubic (fcc) structure [17–19].

X-ray photoelectron spectroscopy (XPS) measurement was applied to investigate the structural composition of the as-prepared N-GQDs and N-GQDs/Pd. The characteristic peaks were compared in their corresponding XPS spectra (Fig. 3a and b). The core level binding energies (BEs) and the full-width at half maximum (fwhm) of the diffraction peaks were measured with particular attention to the Pd 3d spin-orbit

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