



Water-soluble Microwave-exfoliated Graphene Nanosheet/Platinum Nanoparticle Composite and Its Application in Dye-Sensitized Solar Cells



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ABSTRACT

In this paper, a facile and scalable aqueous process including mild oxidative intercalation, microwave exfoliation, ultrasonication, drying and Ar-annealing is developed to synthesize the water-soluble microwave-exfoliated graphene (MEG)/platinum nanoparticles (PtNPs) composite, which has a relative low defect level and can be readily dispersed in deionized water without adding surfactants. This low cost synthesis method is applicable in many systems, such as supercapacitors, thermal storage, lithium battery and Dye-sensitized solar cells (DSSCs). An efficiency of 6.69% for the MEG/PtNPs composite deposited on ITO PEN as flexible counter electrode (CE) for DSSCs has been obtained, higher than the control device made by PVP-Pt as flexible CE.

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1. Introduction

Graphene-based composite materials, such as graphene-polymer or graphene-nanoparticle composites, have attracted global attention due to their unique combination of thermal, mechanical, chemical and electronic properties [1–4]. The manufacturing of such composites requires the graphene sheets dispersed in a media that is compatible with polymers or nanoparticles. Chemical vapor deposition (CVD) is a method to produce the graphene with continuous areas of pristine monolayer, but not cost-effective for mass production [5,6]. Hummers method is the most common used aqueous approach for preparation of reduced graphene oxide (RGO) [7–9]. It uses the strong oxidizer ($\text{H}_2\text{SO}_4/\text{KMnO}_4$) to intercalate graphite layers followed by chemical reduction (NaBH_4 or hydrazine) [10–12]. Then, a good exfoliation performance of RGO can be obtained in high polarity solvents, such as N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) [13–16]. However, the harsh oxidization process would damage the pristine sp^2 carbon-bonded structure to induce many

structural defects, and the use of organic solvent causes the process complexity, high cost, and organic contamination. Therefore, from a practical application point of view, the “green” water dispersion of graphene materials is preferred [17–19]. Generally, the graphene materials are intrinsic hydrophobic, which are difficult to be dispersed in water. Surfactant has been commonly used to keep stable exfoliated graphene sheets in water, but the formation of covalent bond or the presence of the polymeric covering on graphene surface may be undesirable for the further surface modification and functionalization to form the graphene-based composite materials. Even though many other diazonium salt methods have been developed to synthesize water-soluble graphene which can be dispersed in water without the use of surfactant stabilizers, the employment of organic solvents influences the solution stability leading to a phase separation when the concentration of graphene increases [20]. Therefore, a facile and cost-effective aqueous method to prepare low-defect graphene-based materials directly stabilizing in water remains highly desirable.

Carbonaceous materials are of great interest since they possess excellent electrical conductivity and low material cost, as well as high specific surface areas, good chemical stability and fair electrocatalytic activity, enabling them to serve as promising candidates in fabrication of flexible CEs in DSSCs. Graphene [21,22], carbon

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nanoparticles [23] and CNTs [24] have been studied to replace Pt-based flexible CEs. Up to now, the moderate electrocatalytic activities of the flexible carbon-based CEs still cannot match up to those of Pt, showing a relative low energy conversion efficiency (<5%) and thus limiting their further applications.

This paper therefore presents an aqueous process to prepare the low-defect and water-soluble microwave exfoliated graphene nanosheet/platinum nanoparticles (MEG/PtNPs) composite by mild oxidative intercalation, microwave exfoliation, ultrasonication, drying and Ar-annealing. The composite can be directly dispersed in water without adding surfactants. Here, platinum nanoparticles were chosen because platinum is an inert metal and its suspension is readily prepared without additional purification. A wide array of nanoparticle materials can also be used. This low cost synthesis method is applicable in many systems, such as supercapacitors, thermal storage, lithium battery and Dye-sensitized solar cells (DSSCs). We demonstrate this potential in the flexible counter electrode (CE) for DSSCs.

2. Experimental

2.1. Preparation of water-soluble MEG/PtNPs composite:

45 ml of concentrated H_2SO_4 (96%, Sigma Aldrich) and 5 ml of hydrogen peroxide (30%, Prolabo) were mixed as a mild oxidizer. 1 g of natural graphite flakes (Sigma Aldrich) were added into 50 ml $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ mixture and then stirred for 120 min at room temperature. The powders were rinsed several times with deionized water until the pH value reached around 7. After filtering and drying, the acid-intercalated graphite flakes were irradiated in microwave oven (700 W) for 60s to obtain MEG nanosheets. 0.3 mg/ml as-made MEG nanosheets and 0.3 mg/ml sodium dodecyl sulfonate (SDS, Fluka) were added into 30 ml of dilute PVP-PtNPs solution (250 ppm) followed by 2 hrs probe sonication (750 W) to fragment MEG flakes to MEG nanosheets. The PVP-PtNPs solution with MEG nanosheets were dried out on hot plate followed by annealing in tube furnace under Ar atmosphere at 450°C for 30 min to obtain MEG/PtNPs composite powders. The composite powders were then readily re-dispersed into deionized (DI) water by ultrasonication for 15 min to form stable suspension.

2.2. Fabrication of flexible MEG/PtNPs CE:

After centrifugation at 12000 rpm for 20 min to remove large-size particles, the homogeneous suspension was vacuum-filtered through the porous cellulose filter membrane (0.22 μm pore size, Whatman) to form a MEG/PtNPs composite layer. The composite layer was weighted pressed and transferred onto ITO PEN (15 Ω/\square) by using isopropanol to remove the trapped air at contact interface. The cellulose filter membrane was then dissolved by acetone vapor bath. Lastly, the sample was immersed in acetone liquid bath to remove the residuals. The thickness of obtained MEG/Pt NPs composite film is about 4.80 μm . For the comparison, the MEG/PtNPs suspension was diluted by DI water to achieve 3.8 and 1.42 μm films.

2.3. Fabrication of flexible MEG CE:

0.3 mg/ml as-made MEG nanosheets and 0.3 mg/ml SDS were added into 30 ml deionized water followed by 4 hrs probe sonication (750 W) to fragment MEG flakes to MEG nanosheets. Then, MEG layer was transferred onto ITO PEN as DSSCs CE by using the abovementioned procedure.

2.4. Fabrication of flexible PtNPs CE:

A two-step dip-coating process was utilized to prepare PtNPs CE. ITO PEN was first immersed in 1% cationic conditioner (ML 371, OM Group) for 5 min at 60°C and then was immersed in PVP-PtNPs suspension (750 ppm) for 10 min at 40°C . After each step, the ITO PEN was rinsed with deionized water, dried in open air, and finally treated by UV (275 W, TK-110-H01, Kingo) for 10 min to decompose the capped PVP.

2.4.1. DSSCs cell assembly and characterization:

The TiO_2 photoanode for DSSC was prepared as follows: FTO glass (10 Ω/\square , 3.1 mm thick, Nippon Sheet Glass) was immersed in a 2% PK-LCG545 (Parker Corp.) at 50°C for 30 min with sonication to clean the surface followed by deionized water rinse. Then, the nano- TiO_2 paste (particle size 20 nm, product, Eternal) was screen-printed on FTO glass repeatedly until the film thickness reached 10 μm . Finally, a 4 μm light scattering film (PST400, CCIC) was screen-printed on nano- TiO_2 film. The bilayer film was then sintered at 450°C for 30 min in furnace. Dye impregnation was done by immersing the TiO_2 photoanode in a 0.4 mM N719 (D719, Everlight Chemical Industrial Corp.) ethanol solution at room temperature for 12 h. The effective area of the TiO_2 photoanode is 0.16 cm^2 . The dye-adsorbed TiO_2 photoanode and the flexible CE (PtNPs, MEG or MEG/PtNPs) were stacked face-to-face and sealed with a 30 μm -thick thermal-plastic Surlyn spacer (SX1170-25, Solaronix). A proper amount of liquid electrolyte (0.6 M PMII, 0.05 M I2, 0.1 M LiI, 0.5 M TBP in AN/VN) was injected into the gap between the two electrodes. EIS was measured by scanning the symmetric dummy cell (CE/electrolyte/CE) with a potentialstat (CHI 660E) from 100 kHz to 0.1 Hz with 5 mV amplitude at open-circuit condition. The current-voltage (IV) curve of DSSC cell was measured with a computer-controlled digital source meter (Keithley 2400) under exposure of a standard solar simulator (PEC-L01, Pecell) under 1 sun illumination (AM 1.5G, 100 $\text{mW}\cdot\text{cm}^{-2}$).

3. Results and discussions

Figure 1a is a process flow diagram showing the fabrication of a water-soluble composite of MEG/PtNPs. The detail processing conditions are given in the Experimental Section. Figure 1b is a photograph showing that hydrophobic MEG nanosheets would float on the deionized water while the water-soluble MEG/PtNPs composite can be dispersed well in the deionized water without surfactants. Figure 1c displays MEG/PtNPs composite layer coated on ITO PEN under bending deformation. There is no obvious peeling or cracks occurring after bending, manifesting the strong interfacial adhesion. Here, we use $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ [25] as a mild oxidative to intercalate the graphite flakes with no need for chemical reduction, which can avoid structural defects and excessive oxygen containing functionalities (epoxide, hydroxyl, carbonyl and carboxyl groups). The microwave rapid heating was then used to exfoliate the intercalated graphite to obtain MEG nanosheets [26]. As seen in Figure 2a, the graphite powders are dramatically expanded yielding a black and fluffy worm-like MEG nanosheets. The conjugated structure in the graphitic basal plane prefers to form crumpled and curved graphite sheets closely interconnected with each other to reach a thermodynamic stability [27]. The as-made MEG nanosheets are hydrophobic so that sodium dodecyl sulfonate (SDS) is added as a surfactant stabilizer to well disperse MEG nanosheets in an aqueous PVP-PtNPs solution [28]. Subsequently, ultrasonication process is used to fragment the loose-packed MEG nanosheets in the PVP-PtNPs solution. Similarly, the stable graphene suspension was obtained by ultrasonating MEG nanosheets in deionized water with SDS. Figure 3a is TEM

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