Nickel Phosphide-embedded Graphene as Counter Electrode for

Dye-sensitized Solar Cells **

Y. Y. Dou, G. R. Li, J. Song, and X. P. Gao



Fig. S1. Raman spectra of the commercial graphene oxide (a), graphene (b), and graphene- $Ni_{12}P_5$ composite (c). Raman spectra contain both G band (1594-1603 cm⁻¹) and D band (1348-1359 cm⁻¹). The intensity ratio of D band and G band (I_D/I_G) is increased from 0.78 for the graphene oxide to 1.03 for the graphene- $Ni_{12}P_5$ composite due to the decrease in the average size of the sp² domains upon reduction of the exfoliated graphene oxide. ¹⁻²



Fig. S2. SEM image of the graphene- $Ni_{12}P_5$ composite with corresponding energy-dispersive X-ray spectroscopy (EDS) maps for carbon (b), phosphorus (c) and nickel (d).



Fig. S3. HRTEM images of the $Ni_{12}P_5$ (a), and graphene- $Ni_{12}P_5$ composite (b).



Fig. S4. SEM images of electrode films on FTO substrate (cross-section), showing the film thickness.



Fig. S5. The equivalent circuits of EIS from the symmetric cell for the Pt, graphene, $Ni_{12}P_5$, and graphene- $Ni_{12}P_5$.





Fig. S6. (a) Cyclic voltammograms of the graphene-Ni₁₂P₅, Ni₁₂P₅, graphene and Pt electrodes with a scan rate of 50 mV s⁻¹ in 10 mM LiI, 1 mM I₂ acetonitrile solution containing 0.1 M LiClO₄ as the supporting electrolyte. (b) Cyclic voltammograms of the graphene-Ni₁₂P₅ electrode in the potential range of -0.6 ~ 0.1 V (vs Ag/Ag⁺) with a scan rate of 50 mV s⁻¹. The inset shows the anodic and cathodic peak current densities vs. cycle times.

Preparation and characterization of the Ni₁₂P₅ and graphene-Ni₁₂P₅ composite. The commercial graphene oxide (Nanjing XFNANO Materials Tech Co., Ltd) was used to prepare graphene-Ni₁₂P₅ composite. In a typical synthesis process of the graphene-Ni₁₂P₅ composite, red phosphorus (Alfa, 195 mg) was added to a stirred solution of nickel chloride (243 mg) in a mixture of ethylene glycol/water (25 mL, volume ratio 9:16). The reaction mixture was stirred for 30 min, ultrasoniced for 30 min and then stirred for another 1 h. Subsequently, the graphene oxide (50 mg) was ultrasonically dispersed in distilled water (20 mL) and then was slowly added into the stirred reaction mixture. After the reaction mixture was stirred for 30 min, it was sealed in a Teflon lined stainless steel autoclave (60 mL) for the hydrothermal treatment at 180 °C for 12 h. The graphene- $Ni_{12}P_5$ composite was washed with distilled water and ethanol, respectively, and finally dried in a vacuum drying oven at 50 °C for 12 h. For comparison, Ni₁₂P₅ nanopaticles were synthesized by the same method as described above without graphene oxide. Graphene sheets were obtained by dispersing graphene oxide (50 mg) into a mixture of ethylene glycol/water (45 mL, volume ratio of 1:4) and following by the hydrothermal treatment under the same condition. The structure and morphology of the samples were detected using X-ray diffraction (XRD, Rigaku MiniFlex II), scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, FEI Tecnai F20).

Preparation of counter electrodes. The FTO/Pt electrode was obtained by thermal deposition a platinum layer on the surface of FTO (15Ω /sq, Nippon Sheet Glass) at 400°C for 30 min. The other counter electrodes were prepared by using the as-prepared samples, distilled water, and an organic binder (sodium carboxymethyl cellulose 800-1000, CMC-Na). After the as-prepared sample being ground using agate mortar for 30 min, CMC-Na solution (10 mg/mL) and distilled water were added to the ground sample. Subsequently, the mixture was ground for another 30 min to form a paste. The resulting paste was coated onto the cleaned FTO conductive glass by

doctor-blade method to obtain the counter electrode film, which was dried under a vacuum drying oven at 50 $^{\circ}\mathrm{C}$ for 24 h.

Preparation of dye-sensitized TiO₂ film photoanodes. A TiO₂ film was prepared by doctorblade method using a commercial TiO₂ sol (China National Academy of Nanotechnology & Engineering) onto the treated FTO conductive glass with TiCl₄ (0.02 mol/ml) solution. The film was calcined at 500 °C for 30 min in Muffle furnace at air and soaked in N-719 (3×10^{-4} M in ethanol) dye solution for 24 h to obtain dye-sensitized TiO₂ photoanodes. Dye-sensitized solar cells were fabricated by injecting the electrolyte into the aperture between the dye-sensitized TiO₂ electrode and the counter electrode. The liquid electrolyte composed of I₂ (0.05 M), LiI (0.1 M), 1, 2–dimethyl–3–propylimidazolium iodide (DMPII, 0.6 M), and 4-tert-butyl pyridine (TBP, 0.5 M) with acetonitrile as the solvent. Surlyn 1702 was used as the spacer between the two electrodes. The two electrodes were clipped together and solid paraffin was used as a sealant to prevent the electrolyte from leaking. The effective cell area was 0.20 cm².

Photoelectrochemical performance measurement. The DSSCs were illuminated by a solar simulator (Oriel® Sol2A, Newport Corporation) under 100 mW/cm² irradiation, which was calibrated by a standard silicon solar cell. Both the photocurrent-voltage (*J-V*) characteristic curves of the DSSCs under simulated sunlight and the electrochemical impedance spectra (EIS) of the counter electrodes were recorded using an IM6ex electrochemical workstation (Zahner). EIS spectra were measured in symmetric cell configuration with two identical counter electrodes, which was assembled with the similar procedure as described above. The frequency range was from 100 kHz to 100 mHz with an AC modulation signal of 10 mV and bias DC voltage of -0.60 V. The cyclic voltammetry (CV) was carried out using an Ag/Ag⁺ electrode as reference electrode, a large area Pt sheet as counter electrode. The apparent area of the working electrode is 0.25 cm². The data were collected using a LK 2005 electrochemical workstation with a scan rate of 50 mV s⁻¹ in an acetonitrile solution containing 0.1 M LiClO₄, 10 mM LiI and 1 mM I₂.

References

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