

## Supporting Information

### **$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Hollow Meso-microspheres Grown on Graphene sheets and Effect on promising Counter Electrode in Dye-Sensitized Solar Cells**

Guomin Zhao \*, Guangji Xu and Shuang jin

School of Energy and Safety Engineering, Tianjin Chengjian University, Tianjin 300384, China. E-mail: guominzhao@163.com

#### *Synthesis of GO Nanosheets*

Graphene oxide (GO) nanosheets were made by a modified Hummers method. In detail, graphite powder (2 g) put into 100ml of cooled (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub>, followed by slow addition of KMnO<sub>4</sub> (6 g), a slight exotherm may be produced in this process. The suspension was then allowed to stir at 35 °C for 3 days. Afterwards, 200 ml of distilled water was added and the temperature was kept at 98 °C for 2 h. When the temperature was reduced to 60 °C, 10 ml of H<sub>2</sub>O<sub>2</sub> (30 %, 10 ml) was injected into the suspension to completely react with the excess KMnO<sub>4</sub> and a bright yellow mixture was obtained. The solid product was separated by centrifugation, and then washed with HCl (5%) for several times and with water until the pH value of the supernatant was nearly 6, and the graphite oxide was obtained. The collected precipitate was dispersed in water, then sonicated and subsequently concentration to obtain GO suspension.

#### **Fabrication of DSSCs**

CE materials slurry was made in ethanol by mixing 0.1g CE materials powder with 0.025 g PEG20000 which was used as dispersant as well as binder and stirred continuously. Then a film was made through using a doctor-blade to wipe CE materials

slurry on FTO conductive glass (LOF, TEC-15, 15 W per square). After the film was steady, the conductive glass with film was heated at 400 °C for 1 h under the protection of argon, and the counter electrode was gotten.

A commercial TiO<sub>2</sub> sol (Solaronix, Ti-Nanoxide T/SP) was used to prepare the TiO<sub>2</sub> film on FTO also through the doctor-blade method, and the film was soaked in an N719 dye solution (in ethanol) for 24 h to obtain dye-sensitized TiO<sub>2</sub> electrodes. DSSCs were assembled by injecting the electrolyte into the aperture between the dye-sensitized TiO<sub>2</sub> electrode and the counter electrode. The liquid electrolyte composed of 0.05 M I<sub>2</sub>, 0.1 M LiI, 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M 4-tert-butyl pyridine 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 the sealant to prevent the electrolyte solution from leaking. The effective cell area was 0.25 cm<sup>2</sup>. The standard sputtered Pt CE was purchased from Dalian Heptachroma Solar Tech Co., Ltd.

### **Characterization of CEs and DSSCs**

All the electrochemical measurements were measured with the Zahner IM6 electrochemical workstation. Photocurrent–voltage curves were conducted in simulated AM 1.5 illumination (100 mW cm<sup>-2</sup>, Trusttech CHF-XM-500W) with a Keithley digital source meter (Keithley 2410, USA). Electrochemical impedance spectra (*EIS*) analysis was conducted at zero bias potential and the impedance data covered a frequency range of 0.1 Hz–1 MHz. The amplitude of the sinusoidal AC voltage signal was 5 mV. The analyses of the resulting impedance spectra were conducted using the software Zview 2.0. Tafel–polarization measurements were employed in a symmetrical dummy cell which was used in the EIS experiments. The electrolyte was as the same of the electrolyte of DSSC. The scan rate was 20 mV s<sup>-1</sup>,

and the voltage range is -1.0 to 1.0 V. Cyclic voltammetry (CV) was recorded with a three electrode system on the electrochemical workstation. Pt was used as the counter electrode, and Ag/AgCl was used as the reference electrode. An solution of 10.0 mM LiI, 1.0 mM I<sub>2</sub>, and 0.1 M LiClO<sub>4</sub> in acetonitrile served as the electrolyte.

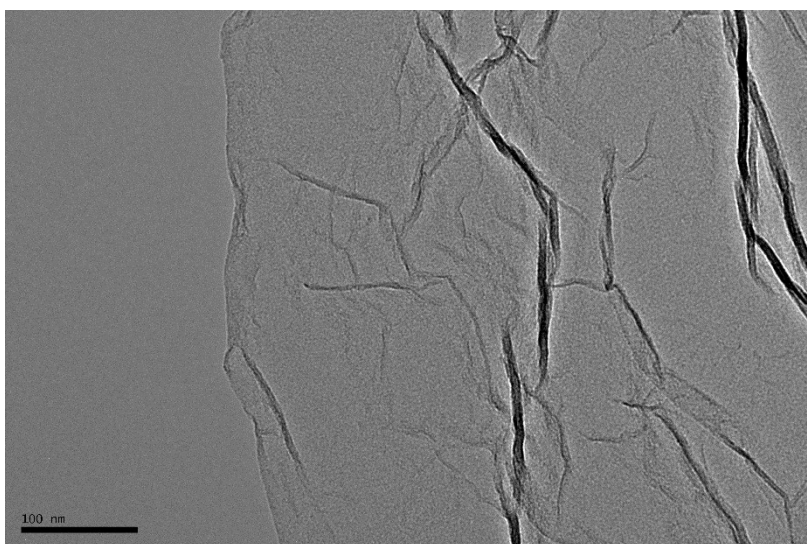


Figure S1. TEM images of graphene.

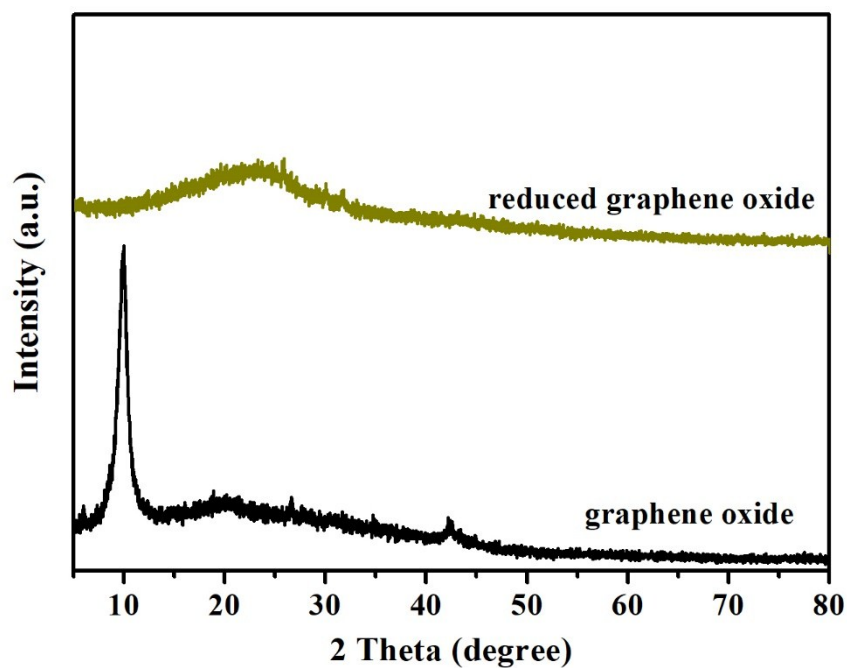


Figure S2. XRD patterns of graphene oxide and reduced graphene oxide.