

Supporting Information for

Dye-sensitized NiS_x Catalyst Decorated on Graphene for

Highly Efficient Reduction of Water to Hydrogen under

Visible Light Irradiation

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1. Preparation of graphite oxide (GO)

All the reagents were of analytical grade and were used without further purification. Graphite oxide (GO) was prepared from natural graphite using a modified Hummers method. Briefly, graphite powder (100 g) was added to an 80 °C mixture solution of concentrated H_2SO_4 (150 mL), $\text{K}_2\text{S}_2\text{O}_8$ (50 g), and P_2O_5 (50 g). The resultant mixture was isolated and allowed to cool down to room temperature. Then the mixture was diluted with distilled water (7.5 L) and the product was filtered, washed with distilled water until the filtrate pH become neutral. The product was dried in air at room temperature for 24 h. Subsequently, the preoxidized graphite (20 g) and NaNO_3 (10 g) were added to cold concentrated H_2SO_4 (0 °C, 460 mL). KMnO_4 (60 g) was then added gradually with stirring and cooling so that the temperature of the mixture was kept below 20 °C. The mixture was then stirred at 35 °C for 2 h. Distilled water (920 mL) was slowly added to the mixture, followed by stirring for 15 min. The reaction was terminated by adding distilled water (2.8 L) and then H_2O_2 solution (50 mL, 30%). The product was filtered, washed repeatedly with HCl (1:10, v/v) until sulfate could not be detected with BaCl_2 , and then dried in a vacuum oven at 40 °C for 24 h.

2. Preparation of Aqueous Dispersions of graphene.

Aqueous dispersions of graphene ($3 \text{ mg}\cdot\text{mL}^{-1}$) were prepared by reducing graphene oxide with sodium borohydride (NaBH_4) as a reductant. In a typical synthetic procedure, 500 mg of graphite oxide powder was dispersed into 250 mL of distilled water with the ultrasound treatment (25 kHz, 250 W) until the solution become clear. The pH of graphene oxide dispersions was adjusted to 10 by adding

$\text{NH}_3 \cdot \text{H}_2\text{O}$, and then the dispersions was heated to $95\text{ }^\circ\text{C}$ in an oil bath under magnetic stirring. After stirring for few minutes, 2 g of NaBH_4 was added to the aqueous dispersions, and the reaction was maintained at this temperature for 10 h. When the color of the solution changed into dark black indicated the completion of graphite oxide reduction reaction. After the reaction, the obtained dispersions was filtered, washed with water several times, and finally redispersed in water with ultrasonication treatment prior to use. The graphene dispersions were characterized using TEM (Tecnai-G2-F30 field emission transmission electron microscope) and XPS (VG Scientific ESCALAB210-XPS photoelectron spectrometer). The result showed that graphene had same structural characterizations as reported in our previous results (Figure. S1).

3. Measurements of the photocatalytic H_2 evolution activity and AQE of EY-Pt.

560 μL of aqueous H_2PtCl_6 (Pt: 5mg/mL) was added into 100mL of triethanolamine (TEOA)- H_2O solution (v/v=10%, pH=7), and then Eosin Y ($1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) was added. The reactant mixture was degassed by bubbling Ar gas for 40 min, and then was irradiated by visible light for measurements of the photocatalytic H_2 evolution activity and the apparent quantum efficiency (AQE). The photoreaction conditions were the same with that of NiS_x/G .

4. Preparation of Samples for XRD, TEM, and XPS Characterizations

2mL of graphene suspensions ($3 \text{ mg} \cdot \text{mL}^{-1}$) was dispersed into 100mL of triethanolamine (TEOA)- H_2O solution (10%, v/v) with the ultrasound treatment (25 kHz, 250 W) about 10 minutes, 310 μL of 0.1 mol/L aqueous $\text{Ni}(\text{NO}_3)_2$, 310 μL of 0.1

mol/L aqueous Na₂S, and 70 mg of Eosin Y were added in proper sequence under stirring conditions and each addition was followed by magnetic stirring for 30 min. The reaction solutions were irradiated under $\lambda \geq 420$ nm for 30 min. After the reaction, the catalyst was centrifuged, washed with water several times, and finally dispersed in water. NiS_x was prepared in the absence of graphene by the same method. The dispersion of catalyst was dropped onto glass substrates, copper grids and Si wafers to prepare samples for XRD, TEM, and XPS characterizations, respectively.

5. Electrochemical and photoelectrochemical measurements

All the electrochemical and photoelectrochemical measurements were determined on an electrochemical analyzer (CHI660A) in a homemade standard three-electrode cell with a quartz window and a 1.2 cm diameter opening opposite the window to which the work electrode was clamped. A saturated calomel electrode (SCE) was used as the reference electrode and Platinum foil as the counter electrode. The working electrodes were prepared using drop-coating sample suspensions onto the conductive surface of the cleaned indium tin oxide glass (ITO glass) surface (ca. 1.96 cm²) and dried. The supporting electrolyte was the mixture of TEOA (v/v =10%) and Na₂SO₄ aqueous solution (0.1mol/L). The surface area of the working electrode was about 1.6 cm² exposed to the electrolyte. The linear sweep voltammetry (LSV) technique was used to determine the cathodic polarization curves, and the scan rate was 1 mV·s⁻¹. 500 μ L of EY aqueous solution (1.0×10^{-3} mol/L) was added onto the above catalyst film electrode surface to prepare the working electrodes for photoelectrochemical measurements. A 300-W Xe lamp equipped with an optical

cutoff filter of 420 nm was used as the light source.

6. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a Tecnai-G2-F30 field emission transmission electron microscope operating, and the accelerating voltage was 300 kV. X-ray diffraction (XRD) patterns of samples were taken using a Rigaku B/Max-RB diffractometer with a nickel filtrated Cu K α radiation operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) analysis was recorded using a VG Scientific ESCALAB210-XPS photoelectron spectrometer with an Mg K α X-ray resource (see preparation details of catalysts sample for TEM, XRD and XPS characterizations in the Supporting Information). UV-vis absorption spectra were obtained using a Hewlett-Packard 8453 spectrophotometer. Photoluminescence spectra were determined by a Hitachi F-4500 spectrometer. The fluorescence decay times were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulses at 460 nm with 1 MHz repetition rate was used as an excitation source.

Figure Captions

Figure S1 TEM image of graphene.

Figure S2 UV-vis absorption spectra of EY and EY (1×10^{-5} mol/L) sensitized NiS_x, NiS_x/G in 10 % (v/v) TEOA aqueous solution at pH 7.

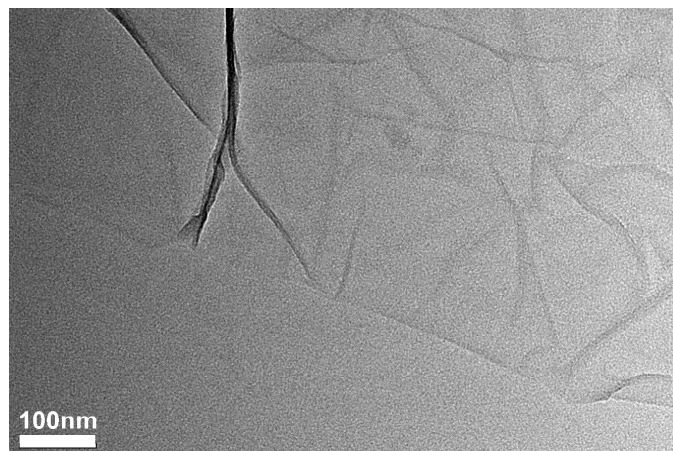


Figure S1

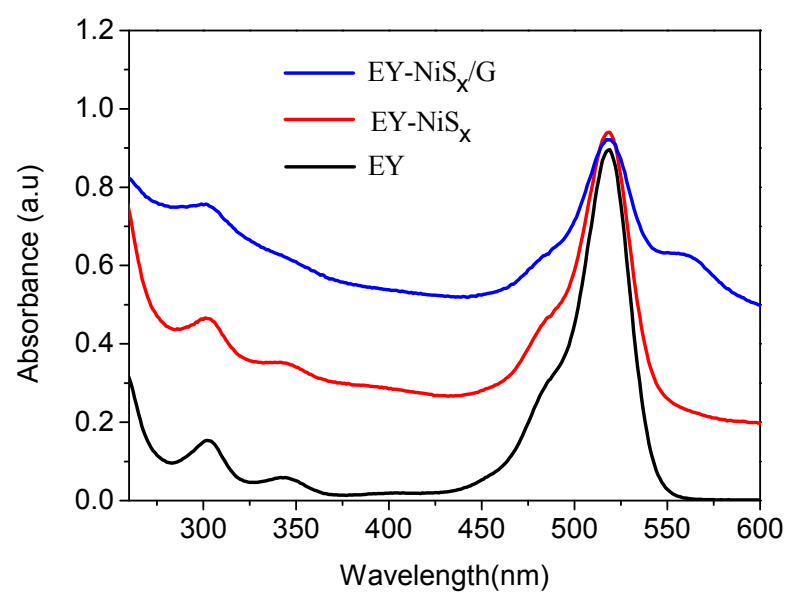


Figure S2