

Electronic Supplementary Information

Robust Pt-Sn Alloy Decorated Graphene Nanohybrid Cocatalyst for Photocatalytic Hydrogen Evolution

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Experimental section

Preparation of graphite oxide (GO)

All the reagents were of analytical grade and were used without further purification. Graphite powder (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.

Preparation of aqueous dispersions of graphene

Aqueous dispersions of graphene (3 mg/mL) were prepared by reducing graphene oxide with hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) 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 and the pH value of the reaction solution was adjusted to 10 by addition appreciated amount of ammonia solution. The obtained yellow-brown dispersions of graphene oxide were then heated to 95 °C in an oil bath under magnetic stirring. After stirring for few minutes, 2 mL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (85%) was added to the aqueous dispersions, and the reaction was maintained at this temperature for 2 h. When the color of the solution changed into dark black indicate 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.

Synthesis of catalysts and measurements of the photocatalytic H_2 evolution activity and AQYs

Synthesis of catalysts and measurements of the photocatalytic H_2 evolution activity were performed in a sealed Pyrex flask (150mL) with a flat window (an efficient irradiation area of 10.2 cm^2) and a silicone rubber septum for sampling. The amount

of hydrogen evolution was measured using gas chromatography (Agilent 6820, TCD, 13×column, Ar carrier). The apparent quantum efficiencies (AQEs) were measured under the same photocatalytic reaction conditions with irradiation light through a band-pass filter (430, 460, 490, 520, or 550nm). Photon flux of the incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum, 400-700 nm; sensitivity, 10-50 $\mu\text{V } \mu\text{mol}^{-1}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$). The reaction solutions were irradiated for 1 h with bandpass filters for AQEs tests on the H_2 production. The following equation was used to calculate the AQE.

$$AQEs = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\%$$

Synthesis of catalysts details and measurements of photocatalytic H_2 evolution activity were described as follows (The pH of 10 v/v% TEOA aqueous solution was adjusted to 7 by adding the concentrated hydrochloric acid):

(1) Pt-Sn/Graphene (Pt-Sn/G): 2mL of above graphene suspensions (3 mg/mL) was dispersed into 80mL of triethanolamine (TEOA)- H_2O solution (v/v=10%, pH=7) with the ultrasound treatment (25 kHz, 250 W) about 10 minutes, the calculated amount of aqueous K_2PtCl_6 (5mg/mL) and aqueous SnCl_4 (0.3mol/mL) were added and followed by magnetic stirring for 30 min, 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 synthesis of catalysts and measurements of the photocatalytic H_2 evolution activity. The irradiation times were 90 min. The light source was a 300-W Xenon lamp, which equipped with a 420 nm cutoff filter.

(2) Pt-Sn: 600 μL of aqueous K_2PtCl_6 (5mg/mL) and 200 μL of 0.3 mol/L SnCl_4 were added into 80mL of TEOA- H_2O solution by magnetic stirring for 30 min, and then Eosin Y ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) was added. The photoreaction conditions were the same with that of Pt-Sn/G.

(3) Pt/Graphene (Pt/G): 2mL of graphene suspensions (3 mg/mL) was dispersed into 80mL of TEOA- H_2O solution with the ultrasound treatment (25 kHz, 250 W)

about 10 minutes, 600 μL of aqueous K_2PtCl_6 (5mg/mL) was added and followed by magnetic stirring for 30 min, and then Eosin Y ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) was added. The photoreaction conditions were the same with that of Pt-Sn/G.

(4) Pt: 600 μL of aqueous K_2PtCl_6 (5mg/mL) was added into 80mL of TEOA- H_2O solution (v/v=10%, pH=7) by magnetic stirring for 30 min, and then Eosin Y ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) was added. The photoreaction conditions were the same with that of Pt-Sn/G.

(5) Sn/Graphene (Sn/G): 2mL of graphene suspensions (3 mg/mL) was dispersed into 80mL of TEOA- H_2O solution (v/v=10%, pH=7) with the ultrasound treatment (25 kHz, 250 W) about 10 minutes, 200 μL of aqueous SnCl_4 (0.3mol/mL) were added and followed by magnetic stirring for 30 min, and then Eosin Y ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) was added. The photoreaction conditions were the same with that of Pt-Sn/G.

(6) SnO_2/G : 5 mg of GO was dispersed into 80mL of TEOA solution (10%, v/v, pH=10) with the ultrasound treatment (25 kHz, 250 W) about 10 min, 450 μL 0.3mol/L SnCl_4 was added and followed by magnetic stirring for 30 min, 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 synthesis of catalysts. The irradiation times were three hours. The light source was a 300-W Xenon lamp, which equipped with a 420 nm cutoff filter. The product was collected and washed with deionized water until the filtrate was neutral. SnO_2/G was dispersed into 80mL of TEOA solution (10%, v/v, pH=7) with the ultrasound treatment about 10 minutes, and then Eosin Y ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) was added. The photoreaction conditions were the same with that of Pt-Sn/G.

(7) Graphene (G): 2mL of graphene suspensions (3 mg/mL) was dispersed into 80mL of triethanolamine (TEOA)- H_2O solution (v/v=10%, pH=7) with the ultrasound treatment (25 kHz, 250 W) about 10 minutes, and then Eosin Y ($1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) was added. The photoreaction conditions were the same with that of Pt-Sn/G.

(8) Measurements of AQYs: Pt-Sn/G nanohybrid (precursor: 6 mg graphene, 200 μL 0.3mol/L SnCl_4 and 600 μL 5mg/mL K_2PtCl_6) was dispersed in 80 mL of 10% (v/v) TEOA aqueous solution at 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 a 300-W Xe lamp with a cutoff filter of 420 nm and a bandpass filter for AQEs tests on the H₂ production. Irradiation time: 1 h.

(9) SnO₂: The pH of 100 mL 0.3mol/L SnCl₄ solution was adjusted to 10 by the addition of 3 mol/L NaOH drop by drop. The precipitate was filtrated and dried at 80 °C for 4 h. The product was washed, filtered repeatedly with deionized water until the filtrate was neutral, and then calcined at 300 °C for 4 h.

(10) Pt/SnO₂: 40 mg SnO₂ was dispersed into 80mL of TEOA solution (10%, v/v, pH=7) with the ultrasound treatment about 10 minutes, 600 μL K₂PtCl₆ (Pt: 2mg/mL) was added and followed by magnetic stirring for 30 min, and then Eosin Y (1 × 10⁻³ mol·L⁻¹) was added. The reactant mixture was degassed by bubbling Ar gas for 40 min, and then was irradiated by visible light for synthesis of catalysts and measurements of the photocatalytic H₂ evolution activity. The irradiation times were 90 min. The light source was a 300-W Xenon lamp, which equipped with a 420 nm cutoff filter.

Samples characterization

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping images were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtrated Cu K α radiation operated at 40 kV and 40mA. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific ESCALAB210-XPS photoelectron spectrometer with an Mg K α X-ray resource. UV-vis absorption spectra were obtained with a Hewlett-Packard 8453 spectrophotometer.

Electrochemical measurements

The electrochemical measurements were measured on an electrochemical analyzer (CHI660A) in a standard three-electrode cell. Platinum foil was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrodes were prepared by drop-coating sample suspensions directly onto the precleaned glassy carbon electrode (GCE) surface (The sample prepared by the above method were dispersed in 2 mL of alcohol, and 40 μL of suspensions was coated on the surface of GCE). The supporting electrolyte was 10% (v/v) TEOA mixed with 0.1 mol/L Na_2SO_4 aqueous solution. The scan rate was $50 \text{ mV}\cdot\text{s}^{-1}$.

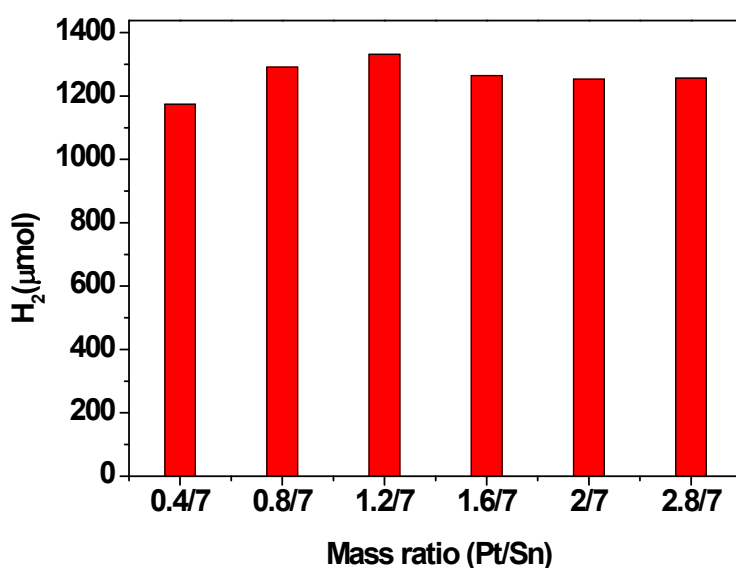


Fig. S1 Comparison of the photocatalytic activity of Pt-Sn/G with different weight ratio of Pt to Sn (The weights of graphene and Sn were 6 and 7 mg respectively) for H_2 production under visible light irradiation ($\lambda \geq 420 \text{ nm}$) for 90 min.

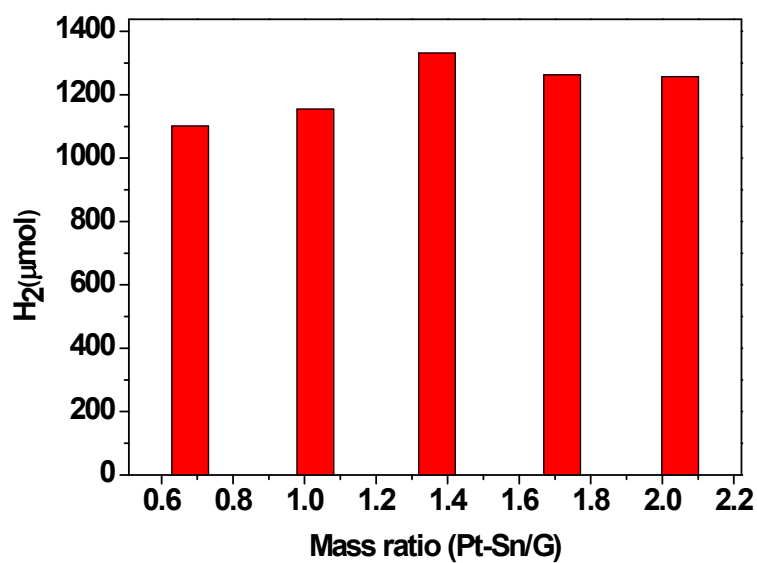


Fig. S2 Comparison of the photocatalytic activity of Pt-Sn/G with different weight ratio of Pt-Sn to graphene (Graphene: 6 mg, the weight ratio of Pt to Sn was 1.2/7) for H₂ production at the same conditions.

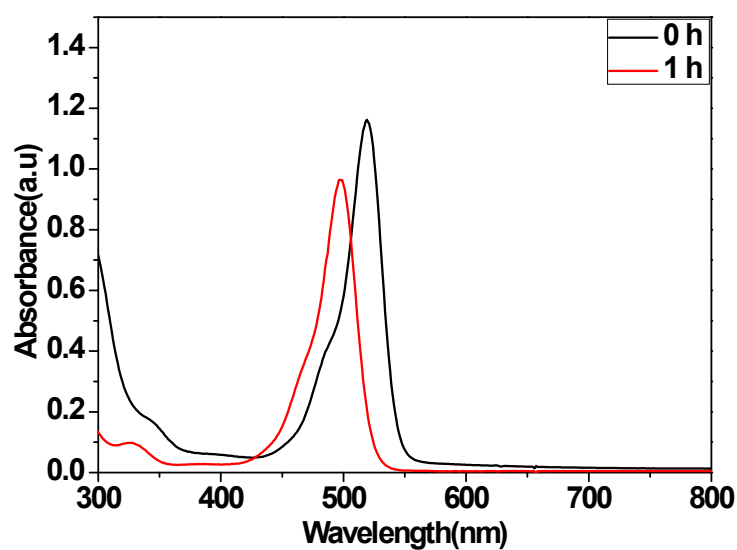


Fig. S3 Absorption spectra of Eosin Y (1×10^{-3} mol/L⁻¹) with different reaction times

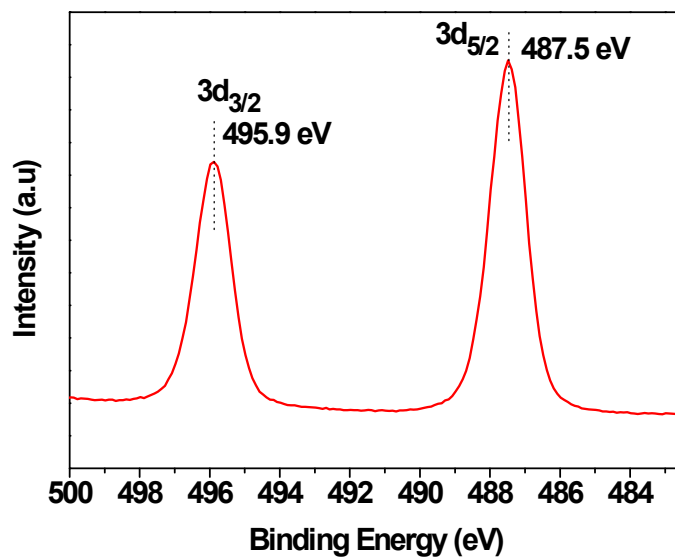
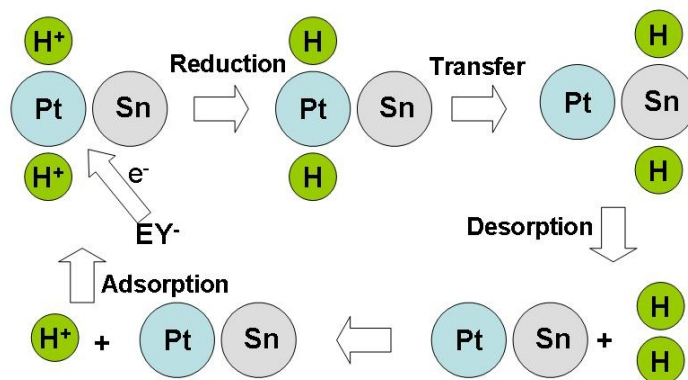


Fig. S4 Sn 3d scan spectra of the recycled Pt-Sn/G after stability test.



Scheme S1 Proposed mechanism for hydrogen evolution over Pt-Sn alloy