Electronic supplementary information

Facilitating charge transfer by giant magnetoresistance effect for high-efficiency photocatalytic hydrogen production

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Experiment section

Preparation of graphite oxide (GO)

All the reagents were of analytical grade and were used without further purification. Graphite powder (5 g) and NaNO₃ (2.5 g) were added to 200 mL cold concentrated H₂SO₄ (0 °C). KMnO₄ (15 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 (200 mL) was slowly added to the mixture, followed by stirring for 15 min. The reaction was terminated by adding distilled water (2 L) and then 30% H₂O₂ solution (12.5 mL). The product was then dialyzed until the solution showed neutral, and then dried in a vacuum oven at 60 °C.

Preparation of G aqueous dispersions

Aqueous dispersions of graphene (3 mg·mL⁻¹) were prepared by reducing graphene oxide with hydrazine hydrate (N₂H₄·H₂O) as a reductant. In a typical procedure, graphite oxide powder (500 mg) 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, 1.8 mL of N₂H₄·H₂O (85%) was added to the aboved 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 were filtered, washed with water several times, and finally redispersed in water with ultrasonication treatment prior to use.

Photocatalysts preparation and hydrogen evolution tests

Photocatalysts preparation and photocatalytic hydrogen evolution experiments were carried out in a home-made reactor with a volume of 200 mL, and the efficient irradiation area is 10 cm². The amount of hydrogen was measured using gas chromatography (Aglient 7820A, TCD, 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 550 nm). 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 μ V· μ mol⁻¹·m⁻²·s⁻¹). The reactions were irradiated for 30 min with bandpass filters for AQEs tests. The following equation was used to calculate the AQE.

$\frac{\text{the amount of hydrogen}}{\text{AQE=2} \times \text{the number of incident photons}}$

Synthesis of catalysts details and measurements of photocatalytic H₂ production activity were described as follows: (the pH of 10 v/v% TEOA aqueous solution) Pt@CoCu/G, CoCu/G, Co/G, Cu/G, Pt/G: in a type process, 2 mL aboved G suspensions (3 mg·mL⁻¹) was dispersed into 100 mL of triethanolamine (TEOA)-H₂O solution (v/v=10%, pH=11) with the ultrasound treatment (25 kHz, 250 W) about 10 min, the 100 μ L aqueous K₂PtCl₆ (5mg·mL⁻¹) were first added and followed by magnetic stirring for 30 min, then the calculated amount CoCl₂ and CuCl₂ were added in sequence. Eosin Y (EY, 1×10⁻³ mol·L⁻¹) was finally added. The reactant mixture was degassed by bubbling Ar gas for 20 min, and then was irradiated by visible light for synthesis of catalysts and measurements of the photocatalytic H₂ evolution activity. The irradiation times were 180 min. The light source was a 300-W Xenon lamp, which equipped with a 420 nm cutoff filter. The preparation process of CoCu/G, Co/G, Cu/G and Pt/G is similar except the amount of added raw. The hydrogen evolution activity results of Fig. 1a are achieved under followed condition: the addition amount of CoCu, Co, Cu and Pt is same as Pt@CoCu mass.

Characterization

Magnetic hysteresis curves of photocatalysts were collected by vibrating sample magnetometer with a type of BHV-50HTI. Hall Effects were detected in a variable magnetic field Hall Effect instrument. 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-F20 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 Shimadzu 2550 spectrophotometer. Raman spectra were recorded in confocal Raman spectroscopy with a type of LabRAM HR Evolution.



Fig. S1 Photocatalytic hydrogen production activity with the same amount of additional Pt in Pt@CoCu and Pt/G system, the added Pt amount is 0.2 mg.



Fig. S2 The XPS fine spectra of (a) C 1s and (b) O 1s.



Fig. S3 The photocatalytic hydrogen production activity of Pt@CoCu/G in different pH reaction solution.



Fig. S4 The hydrogen production AQE of Pt@CoCu/G system.



Fig. S5 The UV-vis spectra of EY sensitized photocatalyst.



Fig. S6 The photocatalytic hydrogen production stability of Pt@CoCu/G system.



Scheme S1 The preparation schematic diagram of Pt@CoCu/G photocatalyst.

Systems	Lifetime(ns)	Pre-exponential factors A/%	Average lifetime<τ>/ns	χ^2
Pt/G	τ_1 =0.33; τ_2 =1.52	A ₁ =36.5; A ₂ =63.5	1.39	1.02
CoCu/G	τ_1 =0.88; τ_2 =1.55	A ₁ =56.1; A ₂ =43.9	1.27	1.01
Pt@CoCu/G	τ_1 =0.92; τ_2 =1.99	A ₁ =57.8; A ₂ =42.2	1.58	1.03

Tab. S1 Decay parameter of EY $(1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ in different catalytic systems.