Electronic Supplementary Information

A Novel Amorphous CoSn_xO_y Decorated Graphene Nanohybrid Cocatalyst for High-Efficient Photocatalytic Hydrogen Evolution

Chao Kong^{a,b}, Shixiong Min^{a,b}, Gongxuan Lu^{a*}

^a State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute

of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, China

^b University of Chinese Academy of Science, Beijing 10080, China.

*Corresponding author: E-mail: gxlu@lzb.ac.cn.

Tel.: +86-931-4968 178.

1

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 ^{S1,S2}. Briefly, graphite powder (100 g) was added to an 80 °C mixture solution of concentrated H₂SO₄ (150 mL), K₂S₂O₈ (50 g), and P₂O₅ (50 g). The resultant mixture was isolated and allowed to cool down to room temperature. Then the mixture was diluted with distill 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 NaNO₃ (10 g) were added to cold concentrated H₂SO₄ (0 $^{\circ}$ C, 460 mL). KMnO₄ (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 H₂O₂ solution (50 mL, 30%). The product was filtered, washed repeatedly with HCl (1:10, v/v) until sulfate could not be detected with BaCl₂, and then dried in a vacuum oven at 40 °C for 24 h.

2. Synthesis of catalysts and measurements of the photocatalytic H₂ evolution activity and AQY.

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 cm²) and a silicone rubber septum for sampling. The amount of hydrogen evolution was measured using gas chromatography (Aglient 6820, TCD, 13×column, Ar carrier). The apparent quantum efficiency (AQE) was measured under the same photocatalytic reaction conditions with irradiation light through a band-pass filter (430, 460, 490, 520, or 550nm). CoSn_xO_y/G nanohybrid (precursor: 5 mg GO, 450 μ L 0.3mol/L CoSO₄ and 450 μ L 0.3mol/L SnCl₄) was dispersed in 80 mL of 10% (v/v) TEOA aqueous solution (pH=10), 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 a 300-W Xe lamp with a cutoff filter of 420 nm and a bandpass filter for AQEs tests on the H₂ production. The irradiation time was 1 h. 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 µmol⁻¹·m⁻²·s⁻¹). The following equation was used to calculate the AQE.

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

Synthesis of catalysts details and measurements of photocatalytic H₂ evolution activity were described as follows:

(1) Graphene (G): 5 mg of GO was dispersed into 80mL of triethanolamine (TEOA)-H₂O solution (10%, v/v, pH=10) 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 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 three hours. The light source was a 300-W Xenon lamp, which equipped with a 420 nm cutoff filter.

(2) SnO₂/Graphene (SnO₂/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 μ L 0.3mol/L SnCl₄ was added and followed by magnetic stirring for 30 min, and then Eosin Y (1×10⁻³ mol·L⁻¹) was added. The photoreaction conditions were the same with that of G.

(3) Cobalt/SnO₂ (Co/SnO₂): 20 mg 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.) was dispersed into 80mL of TEOA solution (10%, v/v, pH=10) with the ultrasound treatment about 10 minutes, 450 µL 0.3 mol/L CoSO₄ was added and followed by magnetic stirring for 30 min, and then Eosin Y (1×10⁻³ mol·L⁻¹) was added. The photoreaction conditions were the same with that of G.

(4) Cobalt (Co): 450 μ L 0.3mol/L CoSO₄ was added into 80mL of TEOA solution (10%, v/v, pH=10), and then Eosin Y (1×10⁻³ mol·L⁻¹) was added. The photoreaction conditions were the same with that of G.

(5) $CoSn_xO_y$: 450 µL 0.3mol/L CoSO₄ and 450 µL 0.3mol/L SnCl₄ were added into 80mL of TEOA solution (10%, v/v, pH=10) simultaneously, and then Eosin Y (1×10⁻³ mol·L⁻¹) was added. The photoreaction conditions were the same with that of G. (6) Cobalt/Graphene (Co/G): 5 mg of GO was dispersed into 80mL of TEOA solution (10%, v/v, pH=10) with the ultrasound treatment about 10 minutes, 450 μ L 0.3mol/L CoSO₄ was added and followed by magnetic stirring for 30 min, and then Eosin Y (1×10⁻³ mol·L⁻¹) was added. The photoreaction conditions were the same with that of G.

(7) Platinum/Graphene (Pt/G): 5 mg of GO was dispersed into 80mL of TEOA solution (10%, v/v, pH=10) with the ultrasound treatment about 10 minutes, 140 mg $H_2PtCl_6\cdot 6H_2O$ (Pt mole numbers were equal to the total mole numbers of Co and Sn in $CoSn_xO_y$) was added and followed by magnetic stirring for 30 min, and then Eosin Y (1×10⁻³ mol·L⁻¹) was added. The photoreaction conditions were the same with that of G.

(8) Amorphous $CoSn_xO_y/Graphene$ ($CoSn_xO_y/G$): 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 minutes, the different volume of 0.3mol/L CoSO₄ and 0.3mol/L SnCl₄ were added simultaneously and followed by magnetic stirring for 30 min, and then Eosin Y (1×10⁻³ mol·L⁻¹) was added. The photoreaction conditions were the same with that of G.

(9) Crystalline $CoSn_xO_y/G$: 25 mg of GO was dispersed into 20mL of water with the ultrasound treatment (25 kHz, 250 W) about 30 minutes, then 3.75 mL of 0.3mol/L CoSO₄ and 3.75 mL of 0.3mol/L SnCl₄ were added simultaneously and followed by magnetic stirring for 60 min. The pH value of the mixture was adjusted to 10 by the addition of NH₃·H₂O, and then the mixture solution was transferred into a 50 mL

Teflon-lined autoclave and heated in an oven at 180 °C for 2 h. The products were collected by filtration under vacuum, washed carefully with water, and finally dispersed into 5 mL of water. 1 mL of $CoSn_xO_y/G$ dispersion was dispersed into 80mL of triethanolamine (TEOA)-H₂O solution (10%, v/v, pH=10) with the ultrasound treatment (25 kHz, 250 W) about 10 minutes, 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 measurements of the photocatalytic H₂ evolution activity. The irradiation times were three hours. The light source was a 300-W Xenon lamp, which equipped with a 420 nm cutoff filter.

3. Photoelectrochemical measurements

The photoelectrochemical measurements were measured on an electrochemical analyzer (CHI660A) in a homemade standard three-electrode cell. The working electrodes were prepared by drop-coating sample suspensions directly onto the precleaned indium tin oxide glass (ITO glass) surface, and then 500 μ L of EY aqueous solution (1.0 × 10⁻³ mol/L) was added onto the above catalyst film electrode surface and then dried. Platinum foil was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The supporting electrolyte was 10% (v/v) TEOA mixed with 0.1mol/L Na₂SO₄ aqueous solution. The surface area of the working electrode exposed to the electrolyte was about 0.95 cm². A 300-W Xe lamp equipped with an optical cutoff filter of 420 nm was used for excitation.

4. 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 300 kV. Xray 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.



Fig.S1 X-ray diffraction (XRD) patterns of crystalline CoSn_xO_v/G prepared by hydrothermal

method



Fig.S2 Comparison of the photocatalytic activity of amorphous CoSn_xO_y/G (1) and

crystalline $CoSn_xO_y/G$ (2)



Fig.S3 Comparison of the photocatalytic activity of $CoSn_xO_y/G$ (precursor: 5 mg GO, the number of moles of Co and Sn was the same) with different weight ratio of $CoSn_xO_y$ to graphene for the H₂ production photosensitized by EY (1.0×10⁻³ mol/L) in 10% (v/v) TEOA aqueous solution (pH =10) under visible light irradiation ($\lambda \ge 420$



Fig.S4 Comparison of the photocatalytic activity of $CoSn_xO_y/G$ with different molar ratio of $CoSO_4$ to $SnCl_4$ in precursor (GO: 5 mg, total volume of 0.3mol/L $CoSO_4$ and 0.3mol/L $SnCl_4$ was 0.75 mL) for the H₂ production photosensitized by EY (1.0×10^{-3} mol/L) in 10% (v/v) TEOA aqueous solution (pH =10) under visible light irradiation ($\lambda \ge 420$ nm) for 3 h.



Fig. S5 Absorption spectra of Eosin Y sensitized $CoSn_xO_y/G$ hydrogen evolution system with different reaction times in 10 % (v/v) TEOA aqueous solution at pH 10 upon visible light irradiation ($\lambda \ge 420$ nm). The EY-CoSn_xO_y/G system was diluted 100 times for measurement.

References

- S1 W.S Hummers, R.E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339-1339.
- S2 N.I.Kovtyukhova, P.J. Ollivier, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva,
- A.D. Gorchinskiy, Chem. Mater., 1999, 11, 771-778.