Supporting Information

Hydrogen generation from toxic formaldehyde catalyzed by lowcost Pd-Sn alloy driven by visible light

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Materials

All chemicals were commercial purchased and used without further purification. Graphite powder (Sinopharm Chemical Reagent Co., Ltd., CP), phosphorus pentoxide (P₂O₅, Kelong Chemical Reagent Factory, AR), sulfuric acid (H₂SO₄, Liangyou Reagent Co., Ltd, AR), sodium persulfate (K₂S₂O₈, Xilong Chemical Industry Co., Ltd., AR), potassium permanganate (KMnO₄, J&K Scientific Ltd., AR), hydrogen peroxide (H₂O₂, Hongyan Chemical Reagent Factory, AR), sodium nitrate (NaNO₃, J&K Scientific Ltd., AR), sodium borohydride (NaBH₄, Sinopharm Chemical Reagent Co., Ltd., AR), hydrochloric acid (HCl, Liangyou Reagent Co., Ltd., AR), palladium chloride (PdCl₂, Tianjin Kemiou Chemical Reagent Co., Ltd., AR), Tin (IV) chloride anhydrous(Xilong Chemical Co., Ltd., AR), sodium hydroxide (NaOH, Xilong Chemical Co., Ltd., AR), formaldehyde (HCHO, Xilong Chemical Co., Ltd., AR). Deionized water was used in all synthesis and reaction.

Experimental Procedures

Preparation of the oxide graphene

Graphene oxide (GO) was prepared from natural graphite by using a modified Hummers method (see Supporting information)[1, 2]. Typically, graphite powder (100 g) was added to an 80 °C mixture solution of concentrated H_2SO_4 (150 mL), P_2O_5 (50 g), and $K_2S_2O_8$ (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 NaNO₃ (10 g) were added to cold concentrated H₂SO₄ (0 °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.

Preparation of the RGO

Aqueous dispersions of RGO (2 mg mL⁻¹) were prepared by reducing GO with sodium borohydride (NaBH₄) as a reductant (see in Supporting information). In a typical synthetic procedure, 500 mg of graphene oxide powder was dispersed into 250 mL of distilled water with the ultrasound treatment (25 kHz, 250W) until the solution become clear. 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, 2g of NaBH₄ was added to the aqueous dispersions, and the reduction reaction was maintained at this temperature for 10 h, over which the color of the solution gradually changed into dark black, indicating the reduction of GO. After the reaction, the obtained dispersions was filtered, washed with water several times, and finally redispersed in water with ultrasonic treatment prior to use.

Photocatalytic activities measurement

Photocatalytic experiments were performed at room temperature in a sealed Pyrex flask (195 mL) with a flat window and a silicone rubber septum for sampling. 6.6 mg catalysts (66mg/mL) and 35 mg Eosin Y (EY) were added to 100 ml NaOH (pH=14) solution in the reactor. A calculated amount of formaldehyde was added to the mixture. The Xenon lamp (HSX-UV 300, NBeT) with a 420 nm cut-off filter was used as a light source to trigger the photocatalytic reaction. The amount of hydrogen evolution was measured using gas chromatograph (Agilent 6820, TCD, 13 X columns, Ar carrier). A continuous magnetic stirrer was applied in order to keep the catalyst in suspension status during the experiment. The recycling test of catalyst was removed from the mixture by centrifugation and was added to the reactor again. New cycle of reaction was carried out according to the procedure mentioned above.

Isotope tracer experiments

In order to identify the hydrogen formation mechanism, the isotopes tracer experiments were performed using D_2O instead of H_2O . The gas mixture in the container was measured by GC-MS (Aglient, 5975c, Triple-Axis Detector) or a Quadrupole Mass Spectrometer (LC-D200M).

Characterizations

The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis were performed on a Tecnai-G2-F30 field emission transmission electron microscope with a 300 kV accelerating voltage. The X-ray diffraction (XRD) patterns of the as-prepared catalysts were obtained on a Rigaku B/Max-RB X-ray diffractometer with a nickel-filtrated Cu K a radiation operated at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Scientific ESCALAB 210-XPS photoelectron spectrometer with a Mg Kα X-ray resource.

DFT

The adsorption energy of HCHO and H_2O on different alloy catalyst surface was studied using the Dmol3 program package in Materials Studio code based on DFT within the generalized gradient approximation (GGA) and Perdew-Wang (PW91) functional as implemented in the Materials studio 5.5 Package [31, 32]. A complete linear synchronous transit (LST) and quadratic synchronous transit (QST) search algorithm were used to identify the transition state of a reaction [33]. **Electrochemical performance**

All the electrochemical measurements were measured on an electrochemical

analyzer (CHI660E) in a home-made standard three-electrode quartz cell consisting of an organic glass enclosure with a quartz window and a 1.2 cm diameter opening window opposite to the work electrode. The working electrode was prepared by drop-coating sample suspension directly onto the pre-cleaned indium tin oxide glass (ITO glass) surface. Pt plate was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was 0.5 M aqueous H_2SO_4 solution without any additives. The visible light irradiation source was a 300 W Xe arc lamp system equipped with a 420 nm cut-off filter.



Fig. S1. The adsorption configuration of formaldehyde on different catalyst surface.



Fig. S2. The adsorption configuration of water on different catalyst surface.



Fig. S3. Effect of EY concentrations on hydrogen evolution rate under visible light irradiation.



Fig. S4. Effect of cocatalysts concentrations on hydrogen evolution rate under visible light irradiation



Fig. S5. (a) UV-Vis absorption spectra of EY-sensitized Pd/RGO, Pd3Sn1/RGO, Pd1Sn1/RGO,

Pd1Sn3/RGO catalyst; (b) UV-Vis absorption spectra of Pd/RGO, Pd3Sn1/RGO, Pd1Sn1/RGO, Pd1Sn3/RGO catalyst



Fig. S6. Photocatalytic activities for hydrogen evolution over Pd₁Sn₁/RGO catalyst under different conditions.



Fig. S7. Reaction order for (a) H₂O₂, (b) HCHO, determined from the method of chemical kinetics.

Table S1. Comparison of photocatalytic hydrogen evolution performance from HCHO of the

EY-Pd1Sn1/RGO catalyst with reference results

Photocatalyst	H ₂ evolution rate	Reference
Pt/TiO ₂	1.50 μmol·mg ⁻¹ ·h ⁻¹	[20]
Pt/TiO ₂	$0.50 \ \mu mol \cdot mg^{-1} \cdot h^{-1}$	[21]
Pt/TiO ₂	$0.65 \ \mu mol \cdot mg^{-1} \cdot h^{-1}$	[22]
PdO/LaCoO ₃	$1.26 \ \mu mol \cdot mg^{-1} \cdot h^{-1}$	[23]
Cu/LaCoO ₃	1.13 μ mol·mg ⁻¹ ·h ⁻¹	[24]
ZnO	8.15 μmol·mg ⁻¹ ·h ⁻¹	[25]
LaNiO ₃	0.03 µmol·mg ⁻¹ ·h ⁻¹	[26]
EY-Pd ₁ Sn ₁ /RGO	56.36 µmol·mg ⁻¹ ·h ⁻¹	This work

Table S2. The geometric structures of IS, TS and FS in the stepwise dissociation of O_2 on the Pd-

Catalyst	IS	TS	FS
Pd catalyst	Top-view side-view	Top-view side-view	Top-view Top-view side-view
Pd ₃ Sn ₁ catalyst	Top-view side-view	Top-view Side-view Control of the side-view	Top-view Top-view Side-view
Pd ₁ Sn ₁ catalyat	Top-view Top-view Side-view	Top-view Constraints Constrain	Top-view Top-view Side-view

Sn alloy catalysts.



References

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