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Rhodium tin composite oxides co-catalyst for high efficient photocatalytic hydrogen evolution

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ABSTRACT

In this work, we studied the modification of surface active site of Rh in RhSn_xO_y composite oxide co-catalyst by the addition of Sn for high efficient photocatalytic hydrogen evolution under visible light irradiation. The significant activity promotion was accomplished by the adjustment of Rh sites via Sn addition. After sensitized by Eosin Y (EY) dye, the RhSn_xO_y co-catalyst exhibited the apparent quantum efficiency (AQE) of 21.0% at 430 nm for hydrogen generation. Under optimized conditions, the highest hydrogen evolution rate of 1280.3 μmol h⁻¹ (corresponding TON 64) over RhSn_xO_y co-catalyst was achieved, which was 8.3 times higher than that of Rh co-catalyst. Based on the XRD and XPS characterizations, Rh atom arrangement on the surface of RhSn_xO_y co-catalyst was confirmed. By adjusting Rh sites, it showed significantly different interaction between Rh atoms and Sn atoms, which led to more efficient excited charge separation and transfer from Rh atoms to Sn atoms with the amount of Sn increased, resulting in more effective photo-induced hydrogen generation.

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Introduction

Hydrogen is one of stable, clean and renewable energy carriers, which is considered as an ideal alternative energy carrier to solve the problems of fossil energy consumption and related environmental pollution problems. Many efforts have been devoted to find the methods for efficient hydrogen generation, such as alkanes reforming [1–5], biological fermentation [6] and photocatalysis [7]. Among them, using free and sustainable solar energy to produce hydrogen is a promising route because there is no net carbon dioxide emission in this process. In a typical photocatalytic hydrogen evolution

system, an electron donor, a proton reducing co-catalyst and a photosensitizer are usually necessary [8–10]. Among them, the co-catalyst plays a key role in hydrogen evolution reaction since it not only provides a proton reduction and hydrogen formation site, but also induces the excited electron to efficiently separate with hole to get a prolonged lifetime. Recently, several excellent co-catalysts have been reported, for example, the Pt nanoparticles immobilized on functionalized graphene, which can effectively enhance the separation of electrons and holes, and promote activity of catalyst under visible irradiation [11,12].

Nobel metals are frequently used as co-catalysts because of their highly activity and low overpotential for hydrogen

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evolution [13]. It is only recently known that the surface arrangement of those Pt or Rh atoms determines the separation, transfer and reaction of excited charges [11,12]. And those phenomena have been also observed in other non-noble metal co-catalysts, such as transition metal, transition metal oxides and transition metal sulfides [14]. Our previous works indicated that the surface arrangement of co-catalyst could be adjusted by Sn addition [15,16]. By modifying the surface active site of hydrogen evolution by Sn in Pt–Sn alloy, hydrogen atom migration from Pt to Sn was achieved, as a result, the enhancement of hydrogen molecules desorption over this catalyst was accomplished.

In our present work, the modification of surface active site of Rh and its effect on photocatalytic hydrogen evolution were studied in RhSn_xO_y co-catalyst. After sensitized by Eosin Y (EY), this photocatalyst exhibited highly activity of hydrogen evolution and excellent stability under visible light irradiation ($\lambda \geq 420$ nm). The results of XRD and XPS characterizations showed that the Rh sites on the surface of RhSn_xO_y co-catalyst could be adjusted by adding different amount of Sn. More efficient charge separation and transfer from Rh atom to Sn atom leads to more effective photo-induced hydrogen generation over optimized ratios of Rh and Sn in RhSn_xO_y co-catalysts.

Experimental section

Photocatalytic hydrogen evolution activity and AQY measurements

Preparation of co-catalysts was performed in a sealed Pyrex flask (170 ml) with a flat window (an efficient irradiation area of 10.2 cm^2) and a silicone rubber septum for sampling at room temperature. A series of other co-catalysts were prepared by *in situ* reaction under visible light irradiation ($\lambda \geq 420$ nm) using rhodium (III) chloride (RhCl_3) and tin (IV) chloride (SnCl_4) aqueous solution as precursors. Typically, 2 ml of RhCl_3 aqueous solution ($1.0 \times 10^{-2} \text{ mol/L}$) was added dropwise into 100 ml of triethanolamine (TEOA)- H_2O solution (10%, v/v) by magnetic stirring. Then, 1.32 ml SnCl_4 aqueous solution (0.3 mol/L) was added in the same way. After stirring ten minutes, 70 mg of Eosin Y (EY) was added and treated another two minutes to make the reactants fully dissolve by ultrasound. The pH values of the reaction solution were adjusted by addition of hydrochloric acid or sodium hydroxide. The reference Rh_2O_3 co-catalyst was also prepared by hydrothermal method. Calculated amount of RhCl_3 was dissolved in the mixture water and potassium citrate, then was heated at 95°C . The Rh content was about 0.4 mg/ml. Prior to irradiation, the reactant mixture was degassed by bubbling Ar gas for 30 min. The light source was a 300-W Xe lamp, equipped with either a 420 nm cut-off filter or various band-pass filters for AQEs tests. 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, $10\text{--}50 \mu\text{V} \mu\text{mol}^{-1} \text{ m}^{-2} \text{ s}^{-1}$). A magnetic stirrer was used to keep the catalyst in suspension. The amount of hydrogen evolution was detected by gas chromatography (Agilent 6820, TCD, column: $13 \times$, Ar as carrier gas). The following equation was used to calculate the AQEs.

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

Characterizations

TEM (Transmission electron microscopy), HRTEM (high-resolution Transmission electron microscopy), HAADF-STEM (high angle annular dark field scanning transmission electron microscopy) and elemental mapping images were performed with a Tecnai-G2-F30 field emission transmission electron microscope operating at an accelerating voltage of 300 kV. The XRD (X-ray diffraction) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtered $\text{Cu K}\alpha$ radiation. The accelerating voltage and current were 40 kV and 30 mA, respectively. XPS (X-ray photoelectron spectroscopy) analysis was taken using a VG Scientific ESCALAB210-XPS photoelectron spectrometer with an $\text{Mg K}\alpha$ X-ray resource.

Results and discussions

The time course of hydrogen evolution catalyzed by the dye-sensitized co-catalysts with different atomic ratio of Sn and Rh (0:1, 1:1, 5:1, 10:1, 15:1, 20:1 and 1:0) at pH 7 under visible light irradiation ($\lambda \geq 420$ nm) were shown in Fig. 1. A negligible amount of hydrogen evolution ($2.5 \mu\text{mol}$ in 60 min) was produced when Sn was used only. This result indicated that Sn specie was inactive for hydrogen evolution. Similarly, a little amount of hydrogen ($155.1 \mu\text{mol}$ in 60 min) was produced over Rh co-catalyst, indicating that the Rh specie had low activity for hydrogen evolution. But the hydrogen generation activity of Rh increased significantly with the addition of Sn, and the activity reached the highest point ($1280.3 \mu\text{mol}$ in 60 min, 8.3

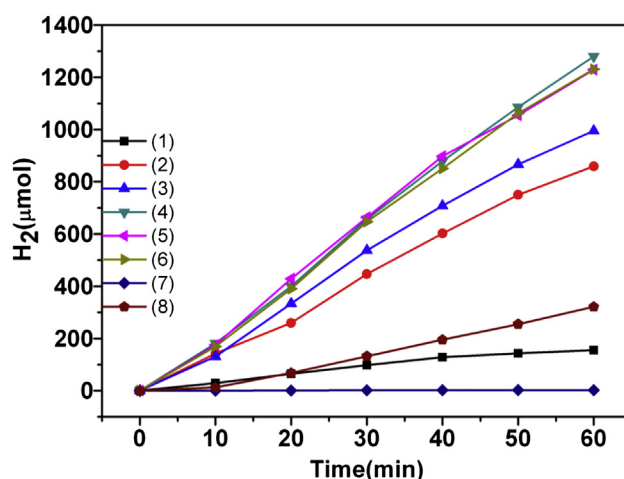


Fig. 1 – Hydrogen evolution from EY ($1.0 \times 10^{-3} \text{ mol/L}$) photosensitized systems catalyzed by different atomic ratios of Sn:Rh (the amount of Rh is constant, $20 \mu\text{mol}$): (1) 0:1, (2) 1:1, (3) 5:1, (4) 10:1, (5) 15:1, (6) 20:1, (7) 1:0, (8) Rh_2O_3 in 100 ml of 10% (v/v) triethanolamine (TEOA) aqueous solution (pH = 7) under visible light irradiation ($\lambda \geq 420$ nm).

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