Rhodium Tin Composite Oxides Co-catalyst for High Efficient Photocatalytic Hydrogen Evolution

Zhen Li^{a,b}, Chao Kong^{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.

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.

Keywords: Photocatalysis, Visible light, Hydrogen evolution, Co-catalyst, RhSn_xO_y, Eosin Y Sensitization.

1. 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 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 ($\lambda \geq 420\text{nm}$). 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.

2. Experimental section

2.1 Photocatalytic Hydrogen Evolution Activity and AQY Measurements.

Preparation of co-catalysts was performed in a sealed Pyrex flask (170mL) 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 ($\lambda \geq 420\text{nm}$) 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 100ml of triethanolamine (TEOA)- H_2O solution (10%, v/v) by magnetic stirring. Then, 1.32 ml SnCl_4 aqueous solution (0.3mol/L) was added in the same way. After stirring ten minutes, 70mg 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, $10\sim 50\mu\text{V } \mu\text{mol}^{-1}\text{ m}^{-2}\text{ S}^{-1}$). A magnetic stirrer was used to keep the catalyst in suspension. The amount of hydrogen evolution was detected by gas chromatography (Aglient 6820, TCD, column: 13 X, Ar as carrier gas). The following equation was used to calculate the AQEs.

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

2.2 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 filtrated Cu K α 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 Mg K α X-ray resource.

3. 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 μmol 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 μmol 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 μmol in 60 min, 8.3 times higher than hydrogen evolution amount over Rh) when the atomic ratio of Sn and Rh was 10: 1. But further increasing the atomic ratio of Sn and Rh exhibited the weak effect on the hydrogen generation activity over RhSn $_x$ O $_y$ co-catalyst. Rh $_2$ O $_3$ co-catalyst showed 321.6 $\mu\text{mol/h}$ hydrogen but is was much lower than RhSn $_x$ O $_y$ co-catalyst.

Fig. 2 shows the time course of hydrogen evolution catalyzed by the dye-sensitized RhSn_xO_y photocatalytic system at pH 7 under visible light irradiation ($\lambda \geq 420$ nm). It was clear that the amount of hydrogen evolution increased quickly with the increase of RhSn_xO_y amount, and the hydrogen evolution rate reached the highest point ($1280.3 \mu\text{mol}\cdot\text{h}^{-1}$) when the added amount of RhSn_xO_y co-catalyst was $20 \mu\text{mol}$. The optimized the atomic ratio of Sn and Rh was 10: 1. The optimal RhSn_xO_y co-catalyst dosage was $20 \mu\text{mol}$ in reaction system.

The effect of pH on activity of RhSn_xO_y sensitized by EY was shown in Fig. 3 (A), the activity of RhSn_xO_y was highly dependent on the pH of reaction system. The optimum pH was around 7, corresponding the rate of hydrogen evolution was $1280.3 \mu\text{mol}\cdot\text{h}^{-1}$. No hydrogen evolution was observed at pH 2 and 4, which was likely due to the protonation of TEOA and EY in acidic solution. That protonation process would impact the electron-donating properties of TEOA [17] and the absorption performance of EY in the visible light region. In alkaline solution, the hydrogen evolution activity of RhSn_xO_y dropped rapidly with the increase of pH, only $85.9 \mu\text{mol}$ of hydrogen was produced in 60 min at pH 12. It might result from the decreasing of H^+ concentration. Apparent quantum efficiencies (AQEs) of EY- RhSn_xO_y system were measured from 430 to 550 nm, and the results were shown in Fig. 3 (B). Under optimized conditions, the highest AQE reached 21.0% at 430 nm, due to the high photon energy. The AQE was about 12% at 518 nm which corresponded to the highest absorption peak of EY [9-10].

Since the structure of RhSn_xO_y co-catalysts might be also affected by the atomic ratios of Sn and Rh, which could determine the affinity of hydrogen atom on the co-catalyst surface, RhSn_xO_y co-catalyst with the different atomic ratios of Sn and Rh were investigated by XRD. As shown in Fig. 4, the typical diffraction peaks of SnO_2 centered at 26.6 , 33.7 , 51.6 and 65.7° were observed in RhSn_xO_y co-catalysts. Those peaks could be attributed to (110), (101), (211) and (301) facets of tetragonal SnO_2 (JCPDS#88-0287), respectively. However, the typical peaks for (111) facet shifted from 26.58° (low Rh loading sample, Sn: Rh=1: 1) to 26.25° (high Rh sample, Sn: Rh=15: 1), which implied the structure of SnO_2 could be adjusted by Rh atoms. In addition, no other typical diffraction peaks were observed in RhSn_xO_y samples with the different

atomic ratios of Sn and Rh, which implied that Rh was highly dispersed in all RhSn_xO_y co-catalysts samples. The calculated particle size of RhSn_xO_y co-catalysts by the Scherrer formula was 5.8 nm.

Transmission electron microscopy (TEM) image of the typical RhSn_xO_y was given in Fig. 5. As shown in Fig. 5 (A), RhSn_xO_y nanoparticles are distributed uniformly and their size are all less than 10 nm. According to the distribution of particle size shown in Fig. 5(D), the average size was 5.3 ± 0.7 nm, with sizes ranging from 4.9 to 6.0 nm. This result was in good agreement with the result of XRD (5.8nm). The high-resolution TEM (HRTEM) image (Sn: Rh= 10: 1) (Fig. 5 B) showed that the co-catalysts were well crystalized. The lattice spacing of 0.34 nm could be assigned to (110) facet of SnO_2 (JCPDS#77-0452) and the lattice spacing of 0.27 nm could be attributed to (121) facet of Rh_2O_3 (JCPDS#76-0148). Simultaneously, the element composition of co-catalyst was also detected and the results were presented in Fig. 5(C), which indicated that the Rh, Sn and O were highly and homogeneously dispersed in RhSn_xO_y co-catalyst.

The surface chemical state of Sn and Rh might be affected by the value of Sn: Rh, which in turn determined the affinity of hydrogen atom on the co-catalyst surface. The XPS characterization results of RhSn_xO_y co-catalysts were shown in Fig. 6 (A). The binding energy of Sn $3d_{5/2}$ shifted from 486.7 eV (high Rh loading sample, Sn: Rh=1: 1) to 487.3 eV (low Rh sample, Sn: Rh=15: 1). These results indicated that the chemical state of Sn could be partially adjusted by the addition of Rh because the arrangement of Sn atoms on the surface of SnO_2 could be changed by Rh atoms. The XPS results further indicated that the chemical environment of Sn changed to more negative value when the amount of Rh increased. It implied that the charge transfer tendency from Rh atom to Sn atom in RhSn_xO_y co-catalyst, and those charge transfer tendency could be controlled by Rh atom arrangement on the co-catalyst surface. This interaction was also strongly supported by Rh $3d_{5/2}$ XPS results. As shown in Fig. 6 (B), the binding energy of Rh $3d_{5/2}$ shifted from 309.2 eV (high Rh loading sample, Sn: Rh=1: 1) to 309.9 eV (low Rh loading sample, Sn: Rh=15: 1). These results reflected that charge transfer tendency from Rh atom to Sn atom became stronger when the concentration of Sn increased. In these samples, Rh site was more positively charged, which might lead to more effective

charge separation in photo-induced hydrogen generation.

Generally, hydrogen evolution reaction involves the five processes: (1) H^+ chemisorption; (2) chemisorbed H^+ was reduced by excited electron to form H atom; (3) freshly formed H atom diffusion from H atom formation site to neighbor active site; (4) forming fresh hydrogen molecule by H-H recombination; (5) hydrogen desorption. Among them, the chemisorbed H recombination might be the rate-determining step [18-19]. Therefore, it is reasonable to suppose that the recombination of chemisorbed H is determined by the distance between adjacent chemisorbed sites located on the co-catalyst surface. The surface geometry became important in the formation of fresh hydrogen. When the distance of neighbor chemisorbed site for H is within a reasonable distance ($d_{H-H} < 1.8 \text{ \AA}$) [20], the chemisorbed H recombination probably becomes easy. All the geometry models of hydrogen molecular chemisorption on neighboring Rh sites were shown in Fig. 7 (A), the recombination of chemisorbed H may undergo in three possible surface transit states: $\angle HRhRh > 90^\circ$, $\angle HRhRh = 90^\circ$ and $0^\circ < \angle HRhRh < 90^\circ$. Since the bond lengths of r_{Rh-H} and d_{H-H} are $1.43 \text{ \AA}$ [21] and $1.8 \text{ \AA}$, respectively, the r_{Rh-Rh} must be less than $4.66 \text{ \AA}$ for the chemisorbed H recombination. In the typical Rh crystal, only the types of $r_{Rh2-Rh1}$ ($2.69 \text{ \AA}$), $r_{Rh2-Rh3}$ ($3.80 \text{ \AA}$) and $r_{Rh1-Rh12}$ ($2.69 \text{ \AA}$) were suitable. In this case, because of too strong interaction between chemisorbed H and Rh atom, the chemisorbed H diffusion between Rh atoms was inhibited in some extent. So it is difficult to reach the suitable sites for H-H recombination, which might lead to low activity. However, when neighbor Sn atom was created, as shown in Fig. 7 (B), the chemisorbed H recombination followed different three models. Because of the bond lengths of r_{Sn-H} ($1.94 \text{ \AA}$) [22] and d_{H-H} ($< 1.8 \text{ \AA}$), so the r_{Sn-Sn} must be less than $5.68 \text{ \AA}$ for the chemisorbed H recombination, and in the SnO_2 cell, the types of $r_{Sn1-Sn2}$ ($4.74 \text{ \AA}$), $r_{Sn1-Sn4}$ ($3.19 \text{ \AA}$) and $r_{Sn1-Sn9}$ ($3.71 \text{ \AA}$) were possible surface transit states. However, for chemisorbed H recombination, SnO_2 showed weak ability than Rh, due to its weak H^+ chemisorption ability, so it is hard to form reduced H atom, leading to low activity for hydrogen generation. For $RhSn_xO_y$ co-catalyst, H^+ was first chemisorbed on Rh sites, then was reduced to form fresh H, and migrated to Sn atoms for recombination to form hydrogen molecules. Then hydrogen molecules desorption finished over Sn sites. If the

hydrogen formation follows this process, the distribution of Rh atom in RhSn_xO_y co-catalyst will determine the activity of hydrogen evolution. As the results shown in Fig. 7 (C), the spacing of Rh atoms increased as the Sn amount increase, the TON showed very good linear dependence on $d_{\text{Rh-Rh}}$ in different RhSn_xO_y co-catalysts. The TONs of hydrogen evolution dependence on Sn-Rh ratio were also given in Table 1. The TON of RhSn_xO_y co-catalyst increased with the amount of Sn specie. And the highest value (64.0) was achieved at 10: 1 of the atomic ratio (Sn: Rh).

The hydrogen evolution stability of RhSn_xO_y was tested as shown in Fig. 8. The results indicated that the RhSn_xO_y co-catalyst showed the high stability for hydrogen evolution reaction. In the first run, the RhSn_xO_y co-catalyst showed excellent activity. However, the activity gradually reduced in the next two runs, due to the consumption of TEOA and EY. In the fifth run, RhSn_xO_y co-catalyst was collected from the reaction mixture by centrifuging, after adding fresh EY and TEOA, the activity was renewed and its activity was 1.4 times higher than that of the first run. The lower activity in the first run might due to the induction period.

The reaction mechanism of hydrogen evolution was proposed in scheme 1. During the reaction process, EY absorbed photons to form singlet excited state EY^{1*} , and then produced the lowest-lying triplet excited state EY^{3*} via an efficient intersystem crossing. EY^{3*} could be reductively quenched by TEOA and produce $\text{EY}^{\bullet}$ and oxidative donor (TEOA^+). By collision, The electron of $\text{EY}^{\bullet}$ species was transferred to RhSn_xO_y co-catalyst to reduce the H^+ adsorbed on the Rh atom, and then the H atoms migrated to Sn atoms to form hydrogen molecules. At last, the hydrogen molecules desorption finished over Sn sites.

4. Conclusions

A novel and stable RhSn_xO_y composite oxides co-catalyst was synthesized by *in situ* chemical deposition via Eosin Y photosensitizer under visible light irradiation at pH 7. The reactive sites were adjusted by different Sn and Rh ration, which led to excellent photocatalytic performance and stability for hydrogen evolution. When the atomic ratio

of Sn to Rh was 10/1, the hydrogen evolution rate over RhSn_xO_y co-catalyst in 60 min was 1280.3 $\mu\text{mol}\cdot\text{h}^{-1}$ (corresponding TON 64), which was 8.3 times than that of Rh sample without the Sn, and the highest apparent quantum efficiency (AQE) reached 21.0% at 430 nm. Based on the XRD and XPS characterizations, the Rh atom arrangement on the RhSn_xO_y co-catalyst surface were achieved to future adjust the interaction between Rh and Sn. By adjusting this interaction, more efficient the excited charge separation and transfer from Rh atom to Sn atom was fulfilled, leading to more effective photo-induced hydrogen generation.

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Scheme and Figure Captions

Fig.1 Hydrogen evolution from EY (1.0×10^{-3} 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 ($\text{pH} = 7$) under visible light irradiation ($\lambda \geq 420 \text{ nm}$).

Fig.2 Hydrogen evolution from EY (1.0×10^{-3} mol/L) photosensitized systems catalyzed by different quantity of RhSn_xO_y co-catalyst (the atomic ratio of Sn: Rh is 10: 1) in 100 ml of 10% (v/v) triethanolamine (TEOA) aqueous solution ($\text{pH} = 7$) under visible light irradiation ($\lambda \geq 420 \text{ nm}$).

Fig.3 (A) Effect of pH on photocatalytic activity of RhSn_xO_y co-catalyst for hydrogen evolution; (B) AQEs of hydrogen evolution for EY (1.0×10⁻³mol/L) photosensitized systems catalyzed by the RhSn_xO_y co-catalyst. The system was irradiated by a 300 W Xe lamp with a cutoff filter of 420 nm and a band-pass filter.

Fig.4 Representative XRD patterns: (1) Rh; (2) SnO₂; (3), (4), (5), (6) RhSn_xO_y co-catalyst with different atomic ratio of Sn and Rh (1:1, 5:1, 10:1, 15:1, respectively).

Fig.5 (A) TEM image and (B) HRTEM image for Rh-Sn co-catalyst; (C) HAADF-STEM (high-angle annular dark field scanning transmission electron microscopy) image and elemental mapping images of RhSn_xO_y co-catalyst; (D) the distribution of RhSn_xO_y (Sn: Rh= 10: 1)particle size.

Fig.6 (A) Sn 3d XPS spectra of RhSn_xO_y co-catalyst (1, 2, 3 and 4 represented the atomic ratios Sn: Rh were 1: 1, 5:1, 10: 1 and 15: 1, respectively). (B) Rh 3d XPS spectra of Rh-Sn co-catalyst (1, 2, 3 4 and 5 represented the atomic ratios of Sn: Rh were 1: 0, 1: 1, 5: 1, 10: 1 and 15: 1, respectively).

Fig.7 Schematic diagram of chemisorbed H recombination over Rh atoms (A), Sn atoms (B) and the relation between TON and the distance of Rh-Rh(C).

Table.1 The TON of RhSn_xO_y co-catalyst in different atomic ratio (Sn: Rh).

Fig.8 Stability test of hydrogen evolution over EY-sensitized RhSn_xO_y composite oxides. The reaction was continued for 360 min, with evacuation every 60 min: (1) first run; (2) second run; (3) third run; (4) fourth run;(5) RhSn_xO_y co-catalyst was collected by centrifuging from the reaction mixture. The recycled RhSn_xO_y co-catalyst was mixed with TEOA solution and fresh EY, and evacuation; (6) sixth run (the black line represent

RhSn_xO_y co-catalyst, the red line represent the system without the specie of Sn).

Scheme.1 Proposed photocatalytic mechanism for hydrogen evolution over RhSn_xO_y co-catalyst under visible light irradiation.

Fig. 1

Fig. 2

Fig. 3 (A)

Fig. 3 (B)

Fig. 4

Fig. 5 (A)

Fig. 5 (B)

Fig. 5 (C)

Fig. 5 (D)

Fig. 6 (A)

Fig. 6 (B)

(A)

Rh

Fig. 7 (A)

Fig. 7 (B)

Fig. 7 (C)

Table 1

The atomic ratio (Sn:Rh)	TON
1:0	0.01
0:1	7.8
1:1	43.0
5:1	49.8
10:1	64.0
15:1	61.5
20:1	61.6

Fig. 8

Scheme 1

Graphic Abstract.

Novel and stable rhodium tin composite oxides (RhSn_xO_y) photocatalyst exhibited higher hydrogen evolution activity than Rh alone. In this work, we studied the modification of surface active site of RhSn_xO_y composite oxides co-catalyst by Sn addition for high efficient photocatalytic hydrogen evolution under visible light irradiation in detail. After sensitized by Eosin Y (EY) dye, the photocatalyst exhibited the apparent quantum efficiency (AQE) of 21.0% at 430 nm for hydrogen generation. Under optimized conditions, the highest hydrogen evolution rate of $1280.3 \mu\text{mol}\cdot\text{h}^{-1}$ (corresponding TON 64) was achieved, which was 8.3 times higher than that of Rh co-catalyst alone. The significant activity promotion was accomplished by the adjustment of Rh sites *via* Sn addition. Based on the XRD and XPS characterizations, the Rh atom arrangement on the RhSn_xO_y co-catalyst surface were achieved. By adjusting this interaction, more efficient the excited charge separation and transfer from Rh atom to Sn atom was fulfilled, leading to more effective photo-induced hydrogen generation.