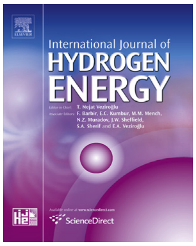
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 5824–5830

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



The dual functional roles of Ru as co-catalyst and stabilizer of dye for photocatalytic hydrogen evolution

Chao Kong [a,b], Zhen Li [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

ARTICLE INFO

Article history:
Received 5 January 2015
Received in revised form
3 March 2015
Accepted 5 March 2015
Available online 29 March 2015

Keywords:
Ruthenium
Eosin Y
Cocatalyst
Stabilizer
Visible light
Hydrogen evolution

ABSTRACT

In this work, a highly efficient and relatively stable photocatalyst, Eosin Y (EY)-sensitized metal Ru for hydrogen generation under visible light irradiation, was developed. Ru-EY photcatalyst showed 4.9 times higher hydrogen generation activity than Pt-EY under the same conditions. The highest apparent quantum efficiency (AQE) of Ru-EY photocatalyst was found to be 46.3% at the wavelength of 520 nm. XPS and TEM characterization results and fluorescence decay experiments indicated that there was a strong interaction between Ru and EY. This interaction could enhance the utilization of photogenerated electron and reduce the degradation rate of EY under visible light irradiation, thereby enhancing the photocatalytic performance of Ru-EY system.

Introduction

Dye-sensitized photocatalytic hydrogen production driven by free and sustainable solar energy is one of the most promising routes in developing renewable and clean energy [1–13]. Dye (EY)-sensitized photocatalytic hydrogen production systems have shown high efficiency under visible light irradiation, in which noble metal such as Pt and graphene-supported transition metal compound (Co/G, CoS_x/G, NiS_x/G, MoS_2/G) co-catalysts showed the excellent activities for photocatalytic hydrogen generation [3,14,15]. However, the degradation of dyes under irradiation is a major drawback of EY-sensitized hydrogen production system, which leads to the decrease of absorption ability and catalytic performances [3,14]. Therefore, the improvement of EY stability under visible light irradiation becomes a critical factor in enhancing the hydrogen evolution efficiency of EY-sensitized photocatalyst. In addition, the strong contact of co-catalyst and sensitizer is key factor in promoting the transfer of photogenerated electron and enhancing the utilization of photogenerated electron. For example, co-catalysts (Pt, PtO or

---

* *Corresponding author*. Tel./fax: +86 931 4968 178.
E-mail address: gxlu@lzb.ac.cn (G. Lu).

http://dx.doi.org/10.1016/j.ijhydene.2015.03.014

MoS_2) loaded on the surface of semiconductor nanoparticles such as TiO_2 and CdS could improve the photocatalytic hydrogen generation performances of semiconductor [16–18]. The weak interaction between dye and co-catalyst might result in the low utilization of photogenerated electron [19,20].

In this paper, Ru was used as the stabilizer of EY and hydrogen evolution co-catalyst to develop EY sensitized photocatalytic hydrogen evolution system. The developed Ru-EY system showed much higher efficiency and stability than Pt-EY system for photocatalytic hydrogen evolution under irradiation longer than 420 nm. The characterization results indicated that there existed a strong interaction between Ru and EY in Ru-EY system. This interaction made Ru function as the dual functional roles of co-catalyst and dye stabilizer in Ru-EY system.

Experimental section

Co-catalysts synthesis, photocatalytic H_2 evolution activity and AQE measurements

Co-catalysts were prepared by in-situ photoreduction reaction. Co-catalysts synthesis and photocatalytic H_2 evolution activity measurements were performed in a sealed Pyrex flask (150 mL) with a flat window (an efficient irradiation area of 10.2 cm^2) and a silicone rubber septum for sampling. Construction details of photocatalytic hydrogen evolution system were described as follows. 600 μL of aqueous $RuCl_3$ (Ru: 2 mg/mL) and 600 μL of aqueous K_2PtCl_6 (Pt: 2 mg/mL) were dispersed into 80 mL of triethanolamine (TEOA) aqueous solution (v/v = 10%, pH = 7) respectively. Subsequently, Eosin Y (1×10^{-3} mol L^{-1}) was added to obtain the precursor mixture of Ru-EY and Pt-EY system. The reactant mixtures were degassed by bubbling Ar gas for 40 min to ensure an anaerobic condition, and then were irradiated under visible light for the measurements of H_2 evolution activity. Ru^{3+} and $PtCl_6^{2-}$ were firstly reduced to form Ru and Pt under visible light irradiation. A 300-W Xenon lamp was used as light source, and equipped with a 420 nm cut-off filter for obtaining visible light. The amount of hydrogen evolution was measured using gas chromatograph (Aglient 6820, TCD, 13X column, Ar carrier). The apparent quantum efficiency (AQE) was measured under the same photocatalytic conditions with irradiation light through a band-pass filter (430, 460, 490, 520, or 550 nm). The photon flux of incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum, 400–700 nm; sensitivity, 10–50 μV μmol^{-1} m^{-2} s^{-1}). The reactant mixture of EY and Ru nanoparticle was irradiated for 30 min by a 300-W Xe lamp equipped simultaneously with a cut-off filter of 420 nm and a band-pass filter for the AQE measurements. The following equation (1) was used to calculate the AQEs.

$$\text{AQEs} = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\% \quad (1)$$

Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were taken with a Tecnai-G2-F30 field emission transmission electron microscope operating at an accelerating voltage of 300 kV. The X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtrated Cu Kα radiation operated at 40 kV and 40 mA. UV–vis absorption spectra were obtained with a Hewlett–Packard 8453 spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific ESCALAB210-XPS photoelectron spectrometer with an Mg Kα X-ray resource. The fluorescence decay time were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulses at 460 nm with 1 MHz repetition rate was used as an excitation source. After the photocatalytic reaction, co-catalysts were centrifuged and washed with water several times until the supernatant was colorless, and finally dispersed in ethanol. The dispersions of co-catalyst were dropped onto glass substrates, copper grids and Si wafers to prepare samples for XRD, TEM, and XPS characterizations, respectively. 500 μL of Pt and Ru aqueous dispersions were added into EY aqueous solution (1×10^{-6} mol L^{-1}) for fluorescence decay experiments, respectively. Ru and Pt centrifuged from reaction solutions were directly dried in a vacuum oven at 40 °C for 24 h as Ru-EY and Pt-EY sample for XPS characterizations.

Results and discussion

Aqueous $RuCl_3$ and solid-state EY as precursors were added into triethanolamine (TEOA) aqueous solution to build Ru-EY system under visible light irradiation. This system showed

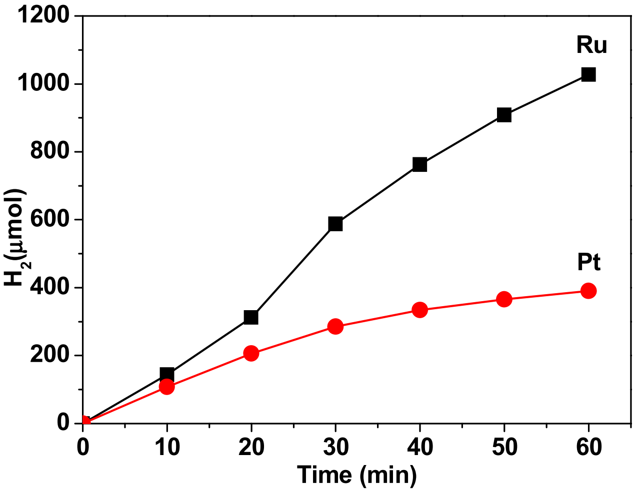


Fig. 1 – H_2 evolution from EY-sensitized (EY:1.0 × 10^{-3} mol/L) systems catalyzed by Ru and Pt in 80 mL of 10% (v/v) TEOA aqueous solution (pH = 7) under visible light irradiation (λ ≥ 420 nm).