

Invited feature article

Gathered sensitizer on the surface of catalyst by sodium polyacrylate for highly efficient photocatalytic hydrogen evolution



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ABSTRACT

In this paper, sodium polyacrylate (PAAS) was used as an assistant to markedly enhance the hydrogen generation efficiency of Eosin Y (EY) sensitized Pt photocatalyst. The molecule chain of polyacrylic acid ion adsorbed on Pt could gather EY on the surface of Pt nanoparticles, thereby enhancing the contact of EY and Pt and the utilization of photo-generated electrons generated by EY under visible light irradiation. Therefore, sodium polyacrylate stabilized Pt nanoparticles showed 3.25 times higher hydrogen generation activity than Pt-EY under the same conditions. The highest AQE of EY-PAAS₁ ($m_w > 30$ million)-Pt system was 34.3% at 520 nm. This result provided a new approach for improving the hydrogen evolution efficiency of photocatalytic system.

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1. Introduction

Solar energy is clean and pollution-free. Hydrogen energy has high energy density, and its combustion product is water. Therefore, storing solar energy in the form of hydrogen is the most ideal way to solve the energy problem [1–17].

In photocatalytic hydrogen generation system, the excellent co-catalyst with high catalytic activity and the high separation efficiency of electron-hole pairs were considered the two most important factors for enhancing the efficiency of hydrogen evolution. A series of excellent co-catalysts were used to build high efficient photocatalytic hydrogen evolution systems, such as NiS [3], Co [18], CoS [18], Co₂P [19], Mo₂S [20], Pt-Sn [21], etc. Graphene [3,18,21], graphene sponge [22], C₃N₄ [23,24] and TiO₂ [25,26], these conductors and semiconductors materials were successfully introduced into photocatalytic systems to reduce the recombination of current carrier. Therefore, searching a simple and low-cost method to enhance the hydrogen evolution activity of photocatalytic system is still an interesting and challenging research work.

Sodium polyacrylate (PAAS), a cheap macromolecule material, was used as a capping agent to prepare Pt nanoparticles with different exposed facets due to its strong interaction with Pt, and its polymer backbone could aggregate molecule or group on surface of catalyst, thereby enhancing the catalytic efficiency of

catalyst [27–29]. In this paper, sodium polyacrylate was introduced into Eosin Y (EY) sensitized Pt photocatalyst to increase significantly its photocatalytic performance by gathering EY on the surface of Pt. Sodium polyacrylate stabilized Pt nanoparticles co-catalyst showed high hydrogen evolution performance. The amount of H₂ evolution was 1335.8 μmol over EY-PAAS₁@Pt photocatalyst in 120 min, which was 3.25 times higher than that of EY-Pt at the same conditions. Comparing with graphene, sodium polyacrylate showed the comparative advantage in enhancing the hydrogen generation efficiency of EY-Pt system. In this system, more EY molecule were gathered on the surface of Pt by the polymer backbone of polyacrylic acid ion adsorbed on Pt, which might be beneficial to promote the directly transfer of photo-electrons and enhanced the photocatalytic activity. This research work might provide a new approach for improving the hydrogen evolution efficiency of photocatalytic system.

2. Experimental section

2.1. Hydrogen evolution system construction and photocatalytic H₂ evolution activity measurements

All the reagents were of analytical grade and were used without further purification. Co-catalyst was synthesized by one-step photoreduction. The reactor for measuring photocatalytic H₂ evolution activity was a sealed Pyrex flask (188 mL) with a flat window of 12.0 cm² and a silicone rubber septum for sampling. Construction details of photocatalytic system were described as follows. 1 mL of aqueous K₂PtCl₆ (Pt: 2 mg/mL) and 500 μL of

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aqueous H_2AuCl_4 (Au: 4 mg/mL) were respectively dispersed into 100 mL of triethanolamine (TEOA) aqueous solution ($v/v=10\%$, $\text{pH}=7$) with the ultrasound treatment (25 kHz, 250 W) about 10 min, the different volume of 0.1 mol/L PAAS_1 ($M_w > 30$ million) or 1 mL of 0.1 mol/L other polymers (PAAS_2 : $M_w \approx 5100$; polyvinyl pyrrolidone (PVP_1): $M_w \approx 10000$, PVP_2 : 29000, PVP_3 : 40000) were added and followed by magnetic stirring for 30 min, and then Eosin Y ($1 \times 10^{-3} \text{ mol L}^{-1}$) was added. The reactant mixture was degassed by bubbling Ar gas for 30 min, and then was irradiated by visible light for the synthesis of co-catalysts and the measurements of photocatalytic activity. The light source was a 300-W Xenon lamp, which equipped with a 420 nm cutoff filter. The amount of hydrogen evolution was measured using gas chromatograph (Agilent 6820, TCD, 13Xcolumn, Ar carrier). The apparent quantum efficiencies (AQEs) were measured under the same conditions with irradiation light through a band-pass filter (430, 460, 490, 520, or 550 nm) and a cut-off filter of 420 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, $10\text{--}50 \mu\text{V} \mu\text{mol}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$). The reactant mixture including EY ($1 \times 10^{-3} \text{ mol/L}$), 1 mL 0.1 mol/L PA_i , and K_2PtCl_6 (Pt: 2 mg/mL) was irradiated for 30 min by a 300-W Xe lamp equipped with a cut-off filter of 420 nm. After evacuation, the above system was irradiated for 60 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 Eq. (1) was used to calculate the AQEs.

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

2.2. Photoelectrochemical measurements

The photoelectrochemical measurement was determined on an electrochemical analyzer (CHI660A) in a homemade standard three-electrode cell with a quartz window and a 1.2 cm diameter opening opposite the window to which the work electrode was clamped. A saturated calomel electrode (SCE) was used as the reference electrode and Platinum foil as the counter electrode. PAAS_1 @Pt and Pt were collected, and then dispersed into Eosin Y aqueous solution ($1 \times 10^{-5} \text{ mol L}^{-1}$), respectively. Subsequently, PAAS_1 @Pt and Pt were collected, and then dropped onto the conductive surface of the cleaned indium tin oxide glass (ITO glass) surface (ca. 1.96 cm^2) to prepare the working electrodes. The supporting electrolyte was the mixture of TEOA ($v/v=10\%$) and Na_2SO_4 aqueous solution (0.1 mol/L). The surface area of the working electrode was about 1.6 cm^2 exposed to the electrolyte. A 300-W Xe lamp equipped with an optical cutoff filter of 420 nm was used as the light source.

2.3. 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 scanning electron microscope (SEM) images were obtained with a JEOL JSM 6701F electron microscope. FT-IR spectra were measured on a Nexus 870 FT-IR spectrometer from KBr pellets as the sample matrix. 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. UV-vis absorption spectra were obtained with a Hewlett-Packard 8453 spectrophotometer. After activity measurement,

Pt co-catalyst was centrifuged and then washed with deionized water until the supernatant was colorless, and finally dispersed in ethanol. The dispersion of Pt was dropped onto copper grids to prepare samples for TEM characterization. 10 μL of 0.1 mol/L PAAS_1 was added into 10 mL EY aqueous solution ($1 \times 10^{-6} \text{ mol L}^{-1}$) with the ultrasound treatment (25 kHz, 250 W) about 10 min for photoluminescence and fluorescence decay experiments.

3. Results and discussion

The hydrogen evolution activity tests of EY- PAAS_1 @Pt and EY-Pt systems are shown in Fig. 1. As shown in Fig. 1, EY- PAAS_1 @Pt system had excellent photocatalytic hydrogen evolution performance under visible light irradiation using triethanolamine (TEOA) as sacrificial donor. The hydrogen production over EY- PAAS_1 @Pt photocatalyst in 120 min was 1335.8 μmol , which was 3.26 times higher than that of EY-Pt (410.4 μmol). This result indicated that the photocatalytic hydrogen generation performance of EY-Pt system could be significantly enhanced by the addition of sodium polyacrylate ($M_w > 30$ million), and the function of sodium polyacrylate for enhancing photocatalytic hydrogen evolution was comparative with that of graphene [21].

After completion of photocatalytic reaction, photogenerated Pt co-catalysts were collected, washed, and then subjected to TEM and HRTEM characterizations, as shown in Fig. 2. Pt co-catalyst collected from EY- PAAS_1 @Pt system reveals a rice-candy shape nanoparticle of $\sim 50 \text{ nm}$, which was composed of small Pt nanoparticles twined by the molecule skeleton of sodium polyacrylate (Fig. 2A and C). Pt nanoparticles collected from EY-Pt system scattered at random (Fig. 2B and D). The diameters of Pt nanoparticles from these two systems were not significantly different. The HRTEM images showed that these Pt samples had the lattice spacing of 0.23 nm which belonged to the (111) planes of cubic Pt (Fig. 2E and F). Comparing with Fig. 2(F), the lattice fringes of Pt nanoparticles in Fig. 2(E) was obscure, which might be due to that the plentiful polyacrylic acid ion existed on the surface of Pt nanoparticles. In Pt sample from EY- PAAS_1 @Pt, polyacrylic acid ion on Pt intertwined, resulting in the formation of swelled-rice-candy shape Pt nanoparticles. These results indicated that zero-valent Pt existed in these two systems, and the surface of Pt nanoparticles from EY- PAAS_1 @Pt adsorbed a large number of polyacrylic acid ion. Pt and PAAS_1 @Pt were measured by Fourier-transform infrared spectroscopy (FT-IR). As shown in Fig. 3, PAAS_1 @Pt had the stronger absorption peaks than Pt, which indicated that the surface of Pt nanoparticles adsorbed a large amount of polyacrylic acid ion. In the FT-IR spectra of PAAS_1 @Pt, the absorptions at 3412 cm^{-1} and

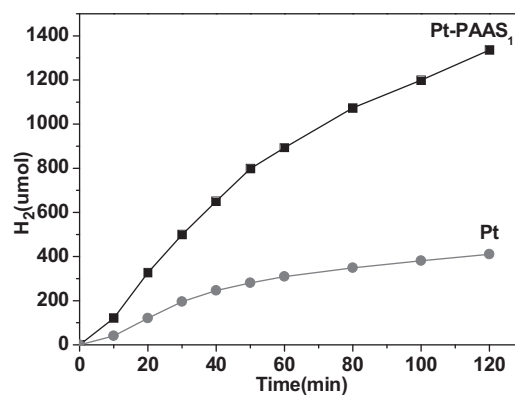


Fig. 1. H_2 evolution from EY ($1.0 \times 10^{-3} \text{ mol/L}$) sensitized Pt and PAAS_1 @Pt photocatalyst in 100 mL of 10% (v/v) TEOA aqueous solution ($\text{pH}=7$) under visible light irradiation ($\lambda \geq 420 \text{ nm}$).

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