Efficient photocatalytic hydrogen production from water over Pt–Eosin Y catalyst: A systemic study of reaction parameters

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ABSTRACT

A high efficient homogeneous system for hydrogen production from water consisting of Eosin Y as a photosensitizer, methyl viologen (MV^{2+}) as an electron transfer mediator, triethanolamine (TEOA) as a sacrificial electron donor and colloid Pt as a catalyst, has been systemicly studied. The initial system pH and the concentration of Eosin Y have remarkable effects on the rate of hydrogen evolution. The optimal pH and concentration of Eosin Y are 9 and 7.2×10^{-5} M. Triethanolamine (TEOA) as an electron donor, can reductively quench the oxidized Eosin Y and the quenching is well modeled by the Stern–Volmer equation. The optimal concentration of TEOA and the concentration of MV^{2+} are 0.3 M and 3.1×10^{-4} M, respectively. In addition, the role of colloid Pt has been investigated.

1. Introduction

A great technological challenge facing our global future is the development of a secure, clean, and renewable energy source [1–4]. The photocatalytic production of hydrogen from water attracts great scientific interest due to its relevance to solar energy conversion and artificial photosynthesis [5]. Photoinduced hydrogen evolution systems, consisting of a photosensitizer, a quencher and electron transfer mediator, an electron donor, and a hydrogen evolution catalyst (e.g., colloidal Pt or biological enzymes such as hydrogenase), have been studied extensively [3,6–11].

The photosensitizer functions as both a light-harvesting complex for photoabsorption and the primary photoreductant and may be a metal complex or an organic compound. There have been many reports on metal complexes, such as metalloporphyrins and metal polypyridyl complexes, used to reduce water to hydrogen. However, compared with metal complexes, few organic dyes have been investigated for the hydrogen evolution from water [12–16], although they are usually less expensive and more readily available. Xanthene appears to be one of the more potential organic dyes used for the photoreduction [13–16]. Of particular interest is Eosin Y (2′, 4′, 5′, 7′-tetrabromofluorescein disodium salt, EY^{2-}), a well-known and extensively studied water soluble photosensitizer with a very high visible absorption band around 520 nm [17] and with relatively small $S_1 \leftrightarrow T_1$ gap [18].

The homogeneous system for hydrogen production from water consisting of Eosin Y as a photosensitizer, methyl viologen (MV^{2+}) as an electron transfer mediator, TEOA as a sacrificial electron donor and colloid Pt as a catalyst, has high efficiency and has been studied since 1983 [19]. However, the systemic study of reaction parameters of this high efficient photocatalytic system has not been reported. In the present study, the effects of parameters such as the initial system pH, the concentration of TEOA, the concentration of Eosin Y, the concentration of MV^{2+}, and the role of Pt were investigated.

2. Experimental

2.1. Chemical reagents

Commercially available Eosin Y dye (2′,4′,5′,7′-tetrabromofluorescein, bisodium salt) was used without further purification. Other chemicals used in our experiments were of analytic reagent.

2.2. Characterization

Photoluminescence (PL) spectra were recorded at room temperature on a fluorescence spectrophotometer (Hitachi F-7000, Japan) using Xenon lamps as a excitation source, all samples were excited using a wavelength of 450 nm.

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2.3. Preparation of the Polymer-Stabilized platinum colloids

The preparation of the Polymer-Stabilized Pt colloids was similar to the literature [20–23]. Typically, in a 100 ml flask equipped with a condenser, an oil bath, and a magnetic stirrer, we dissolved 0.222 g poly(vinyl-2-pyrrolidone) (PVP) (2.00×10^{-3} mol as monomeric unit) and 0.052 g $H_2PtCl_6 \cdot 6H_2O$ (1.00×10^{-4} mol) in a mixed solution of 30 mL methanol and 30 mL water, vigorous stirring was maintained all the time. The reaction mixture was refluxed for 3 h to give a homogeneous dark-brown solution of colloidal platinum. They were evaporated to dryness with rotated evaporator under reduced pressure below 60 °C. The resulting solid residues were redispersed in methanol with a definite concentration, giving a thoroughly homogeneous dispersion prior to the reaction.

2.4. Photocatalytic H_2 production under visible light irradiation

The photocatalytic reaction was conducted in a closed glass circulation system. A 300 W Xe lamp (Trusttech PLS-300UV, China) with a cutoff filter (kP420 nm), was used as the light source. The photocatalytic reaction was carried out in a top-irradiation glass vessel of about 250 mL with a flat quartz glass window. The reaction mixtures inside the vessel were maintained homogeneous by means of a magnetic stirrer. In a typical photocatalytic experiment, a certain amount of Eosin Y was added to a 100 ml aqueous solution of TEOA (with certain concentration). To facilitate the charge transfer, MV^{2+} was added to the reaction vessel. Colloidal Pt was added to act as a catalyst for the promotion of H_2 evolution. The whole reaction process was cooled between 4 °C and 9 °C. The amount of H_2 evolved was determined using an online thermal conductivity detector (TCD) gas chromatograph with Ar as the carrier gas.

To investigate the effect of pH value on the activity of hydrogen evolution, pH values of solution were adjusted by the addition of hydrochloric acid or sodium hydroxide as required.

3. Results and discussion

3.1. Effect of the concentration of TEOA on the hydrogen evolution

In this homogeneous hydrogen production system, the electron donor (TEOA in this work) plays an important role which may be viewed in light of its dual function since it could quench the oxidized form of the dye (Eosin Y) as a sensitizer regenerator or it could extend its lifetime in the photosensitized system providing long-term hydrogen generation [16]. The effect of TEOA working as the sensitizer regenerator was examined. Fig. 1a shows that Eosin Y undergoes reductive quenching by TEOA and the quenching of Eq. (1) was dynamic in nature and was well modeled by the Stern–Volmer equation [19] (Eq. (1)), where I_0 is the integrated Eosin Y emission intensity in the absence of quencher, τ_0 is the excited-state lifetime in the absence of quencher, I and τ are the corresponding values in the presence of quencher, k_q is the bimolecular quenching rate constant, and $[Q]$ is the quencher concentration. Linear plots of I_0/I vs $[Q]$ for the Eosin Y was 5.907 M^{-1}.

$$I_0/I = \tau_0/\tau = 1 + k_q \tau [Q] \tag{1}$$

The photocatalytic hydrogen production of the Eosin Y at various TEOA concentrations is shown in Fig. 2. The results show that there is no hydrogen production under visible light irradiation without added TEOA, thereby indicating the vital role of TEOA in the photocatalytic system. Moreover, the photocatalytic hydrogen production rate increases with increasing TEOA concentration. It reaches a maximum when TEOA concentration was at 0.3 M (about

302 turnover numbers of H_2 vs Eosin Y). Because the optimum TEOA concentration levels off, instead of increasing, the hydrogen production is decreased with further increase in TEOA concentration beyond the optimum value. One of the reasons is that a TEOA concentration of 0.3 M is sufficient for regenerating or quenching the oxidized sensitizer, as well as preventing electron excited sensitizer recombination [24]. The other reason is that TEOA can increase reaction pH value which is another predominant influence in hydrogen production. The pH values of reaction system with different TEOA concentration are 8 for 0.15 M, 9.3 for 0.3 M, 12 for 0.75 M and 14 for 1.25 M, respectively. There is an optimum pH value in this hydrogen production system (9 in this work showed below). Since the 0.3 M TEOA was experimentally verified to be the most suitable electron donor concentration for the investigated system, it was used as a base condition for further experiments.

3.2. Effect of pH on hydrogen evolution

As shown in Fig. 3, initial system pH has dramatic effects on the average rate of hydrogen evolution from an aqueous solution of TEOA. When pH values vary from 6 to 11, the maximum average rate of hydrogen evolution is achieved at pH 9. The corresponding hydrogen generation rate is 633 µmol h^{-1}. The rate of hydrogen evolution decreases as the three-quarter becomes either more acidic or more basic. The similar dependence on pH in H_2 photogeneration is commonly seen in many hydrogen production systems [25–27]. The following are the possible reasons for explaining this phenomenon.

For TEOA, the pH value of the solution might have effects on its form in aqueous solution. In strongly acidic solution, the ability of donating electrons would weaken, which is caused by the total protonation of the electron donor TEOA [28]. As a result, the lifetime of the excited Eosin Y and regeneration of Eosin Y might be affected, which results in the low rate of hydrogen evolution, even no hydrogen evolution when pH value was adjusted to less than 4 [27].

In addition, the pH value of the solution could affect the reactions of hydrogen evolution and TEOA oxidation. Since the reaction of hydrogen evolution involves the reduction of H^+, the rate of hydrogen evolution should depend on the concentration of H^+. The higher the concentration of H^+, the faster the reduction of H^+ would proceed. However, Kalyanasundaram et al. have reported that TEOA is oxidized by means of losing one of the unpair electron of the N atom [29], so the protonated forms of TEOA are difficult to oxidize. As a result, the photosensitized hydrogen evolution process should occur at an optimized pH. At pH 9, maximum turnovers were achieved numbering ∼310 after 10 h irradiation.

3.3. Effect of the concentration of Eosin Y on hydrogen evolution

The effect of Eosin Y concentration on photocatalytic hydrogen production is shown at conditions of 0.3 M TEOA, 6.0×10^{-5} M colloidal platinum and 3.1×10^{-4} M MV^{2+} (Fig. 4). It is found that the amount of hydrogen evolution increases with increasing Eosin Y concentration and reaches a maximum at 7.2×10^{-5} M (hydrogen generation amount about 2126 µmol) after 5 h irradiation. With further increase in Eosin Y concentration beyond the the optimum value (7.2×10^{-5} M), the amount of hydrogen evolution significantly decreases. The present observation was found to be comparable with previous reports [24,27]. It is thought that only the fraction of the Eosin Y sensitizer on an effectual collision with MV^{2+} is photocatalytically active, directly leading to electron injection to electron transfer mediator [30]. Initially, this fraction increases with increasing Eosin Y concentration; hence, the hydrogen production amount increases significantly. If all electron