

Short communication

## Visible-light-induced hydrogen production over Pt-Eosin Y catalysts with high surface area silica gel as matrix

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### Abstract

A new system for the production of hydrogen, constructed using silica gel as a matrix, Eosin Y as a photosensitizer, and Pt as a cocatalyst, has been reported. It was found that the rate of photosensitized hydrogen evolution in the presence of silica gel is enhanced about 10-fold relative to the homogeneous phase, i.e. in the absence of silica gel. The pH value of the solution and the concentration of Eosin Y have remarkable effects on the rate of hydrogen evolution. The optimal pH and concentration of Eosin Y are 7 and  $3.60 \times 10^{-4} \text{ mol dm}^{-3}$  ( $E/S = 1/3$ ) to  $7.24 \times 10^{-4} \text{ mol dm}^{-3}$  ( $E/S = 1/1$ ), respectively. Triethanolamine (TEOA) as an electron donor, the rate of hydrogen evolution and the apparent quantum efficiency in the silica gel system under visible-light irradiation ( $\lambda \geq 420 \text{ nm}$ ) can reach about  $43 \mu\text{mol h}^{-1}$  and 10.4%, respectively. In addition, the roles of silica gel, Pt and TEOA, respectively; and the probable mechanism of photosensitized hydrogen evolution have been discussed.  
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**Keywords:** Photosensitized; Silica gel; Eosin Y; Hydrogen evolution; Visible-light irradiation

### 1. Introduction

From the viewpoint of the solar energy conversion, photocatalytic production of hydrogen by splitting water has been considered a promising technology since photochemical hydrogen evolution under UV light irradiation was found in the early 1970s [1]. Many semiconductors, such as  $\text{TiO}_2$  [2],  $\text{SrTiO}_3$  [3], CdS [4] and so on, have been investigated for photocatalytic splitting water into hydrogen. In recent researches, some solid solution catalysts have also been reported to be active photocatalysts for  $\text{H}_2\text{O}$  decomposition [5–7]. Although remarkable improvements have been made in photocatalytic hydrogen production in the past decades, there are still some urgent problems to be resolved at the present time. For example, many stable semiconductors, such as  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{SrTiO}_3$ , etc. are active only in the ultraviolet region that only accounts for less than 5% of the solar spectrum. In contrast, some visible-light-driven

photocatalysts (e.g. CdS) are liable to lose their activities after long-term irradiation. From a practical point of view, the development of an active and stable catalyst driven by visible-light for the photodecomposition of water into hydrogen is urgently required. Therefore, many attempts, such as doping, sensitization, etc. have been made to extend the optical absorption edge or/and to improve the stability. In 1991, Grätzel et al. proved spectra sensitization, as a strategy for effective visible-light harvest, to be feasible [8]. They improved the photon-to-electric current conversion efficiency up to 7.1% using a ruthenium complex-sensitized porous  $\text{TiO}_2$  film with an extremely high surface area. It is generally accepted that the success of the dye-sensitized solar cells (DSC) mainly depends on the fact that a larger number of sensitizers can be adsorbed [8–10]. Experimentally, it is also proved that porous films are beneficial to the transfer of the interfacial charge, and further promote the efficiency of the utilization of charge [11].

Indeed, the spectral sensitization of wide band semiconductors in the solar energy conversion systems involving the photolysis of water to produce hydrogen has been studied actively. For example, Abe et al. used dye-sensitized Pt/ $\text{TiO}_2$  as

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a photocatalyst for hydrogen evolution from a water–acetonitrile mixed solution [12]. Although the dye-sensitized solar cell (DSC) is a good example of spectral sensitization of wide band semiconductors, the idea developed from DSC works less efficiently in the exploitation of photocatalysts used for hydrogen evolution. For instance, the photoenergy conversion efficiency and the stability of photocatalysts cannot be satisfied.

It has been reported that the separation of products formed in photoinduced electron-transfer processes is essential [13]. So, for the efficient solar energy conversion and storage, several other approaches, such as micelle [14,15], liposomes [16,17], microemulsion [18,19], and polyelectrolytes [20,21] in addition to semiconductors, have been adopted to assist the charge separation. Because silica gel has a very high and negative surface charge density that can promote charge separation, Willner et al. used silica gel as a means to control the photosensitized electron-transfer reaction [22]. In addition, silica gel has many other merits, such as high specific surface area and high transparency of visible-light. To the best of our knowledge, there is no report on photosensitized hydrogen production in organic dye and silica gel systems at present.

In the current study, we chose silica gel as a matrix to adsorb dye molecules and to promote the separation of products produced in photosensitized electron-transfer reactions, Eosin Y as a photosensitizer and Pt as a cocatalyst. In the presence of triethanolamine (TEOA) as an electron donor, the hydrogen evolution activity of the system under visible-light irradiation ( $\lambda \geq 420$  nm) has been studied. The effects of pH value and the Eosin Y concentration on the photocatalytic activity for hydrogen evolution have been investigated. In addition, the roles of silica gel, Pt and TEOA, respectively; and the probable mechanism for photosensitized hydrogen evolution have been discussed.

## 2. Experimental

Commercially available Eosin Y (2',4',5',7'-tetrabromo-fluorescein, disodium salt) and silica gel H (for thin-layer chromatography) were used without further purification. Other chemicals used in our experiments were of analytic reagent.

Loading of the dye sensitizer onto silica gel H was performed by an impregnation method with water as the solvent, that is, Eosin Y and silica gel H were simply mixed and stirred for 16 h in order that Eosin Y could be adsorbed onto silica gel H, and then dried at 333 K overnight. The weight ratio of Eosin Y and silica gel H (hereafter denoted as E/S) in the photocatalysts by an impregnation method is 1/2 unless otherwise stated. In order to enhance the photocatalytic activity for hydrogen evolution, Pt particles were loaded in situ by a photochemical method, which is similar to the method described in the reference [23], with an aqueous solution of  $\text{H}_2\text{PtCl}_6$ .

A 300 W tungsten halogen lamp, equipped with a 420 nm cut-off filter (Toshiba, S Y44.2), was used as the light source. The photocatalytic reaction was carried out in a Pyrex flask of ca. 108 ml with a flat window (with an efficient irradiation area of ca.  $10\text{ cm}^2$ ). The reaction mixtures inside the cell were maintained in suspension by means of a magnetic stirrer. In a typical photocat-

alytic experiment, 60 mg the composite of Eosin Y and silica gel H was suspended in 60 ml aqueous TEOA (15%, w/w) solution containing  $2.8\text{ ml } 7.67 \times 10^{-7}\text{ mol dm}^{-3}\text{ H}_2\text{PtCl}_6$  unless otherwise stated. Prior to irradiation, the suspension of the catalyst in the cell was dispersed for 1 min in an ultrasonic bath, and then Ar gas was bubbled through the reaction mixtures for 40 min to remove oxygen.

To investigate the effect of pH value on the rate of hydrogen evolution, the pH values of the solution determined on a Markson model 6200 pH meter were adjusted by the addition of hydrochloric acid or sodium hydroxide as required.

The photocatalytic activity was determined by measuring the amount of hydrogen evolved using a gas chromatograph (TCD, molecular sieve 13X column, Ar as gas carrier). The apparent quantum efficiency ( $\Phi_{\text{H}_2}$ ) is defined as follows:

$$\Phi_{\text{H}_2} = 2 \times \frac{(\text{mole of hydrogen evolved})}{(\text{mole of incident photon})} \quad (1)$$

In measuring the apparent quantum efficiency, the average photon flux of the incident light, which is  $230\text{ }\mu\text{mol (photon)}\text{ m}^{-2}\text{ s}^{-1}$ , was determined with a Ray virtual radiation actinometer (FU 100, Silicon ray detector, light spectrum: 400–700 nm, sensitivity:  $10\text{--}50\text{ }\mu\text{V }\mu\text{mol}^{-1}\text{ m}^{-2}\text{ s}^{-1}$ ), and then the apparent quantum efficiency was calculated according to Eq. (1).

UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were obtained using a U-3010 UV–vis spectrometer and were converted from reflectance to absorbance by the Kubelka–Munk method. UV–vis absorbance spectra of the samples were recorded on a HP8453 spectrophotometer. The BET surface area and pore size distributions were obtained by measuring  $\text{N}_2$  adsorption isotherms at 76.2 K using an ASAP 2010V surface analyzer, with a pretreatment temperature of 473 K.

## 3. Results and discussion

### 3.1. Characterization of catalyst

The specific surface area of silica gel H was found to be  $\sim 362\text{ m}^2\text{ g}^{-1}$ , and the average pore diameter was 9.9 nm using the BET method.

It is generally accepted that xanthene dyes exhibit substantial aggregation effects at high concentrations [24,25]. Eosin Y, one of xanthene dyes, tends to form dimers or larger aggregates in concentrated solution. The absorption spectrum of Eosin Y dimers displays a doublet with maximums at 485 nm and 540 nm, corresponding to the H-type dimer and J-type dimer, respectively [25]. Fig. 1 shows the UV–vis absorption spectrum of the  $6.00 \times 10^{-5}\text{ mol dm}^{-3}$  Eosin Y in aqueous silica gel H at pH 7. It can be seen that the spectrum shows a peak at around 510 nm with a shoulder at ca. 485 nm. These bands are attributed to that of the monomer and the dimer (H-type) of Eosin Y, respectively.

The UV–vis diffuse reflectance spectra of silica gel H, Eosin Y and the composite of Eosin Y and silica gel H are shown in Fig. 2. The absorption band edge of the composite of Eosin Y and silica gel H is apparently red shifted to about 600 nm compared

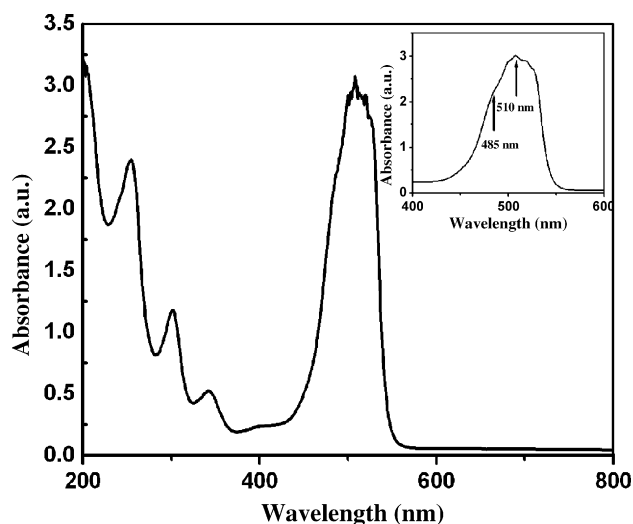


Fig. 1. UV-vis absorption spectrum of  $6.00 \times 10^{-5}$  mol  $\text{dm}^{-3}$  Eosin Y in aqueous silica gel H at pH 7. Inset is partial magnification of the absorption spectrum.

to that of silica gel H and blue shifted by ca. 50 nm compared to that of Eosin Y, which implies that it is possible that some interactions (e.g. hydrogen bond) between Eosin Y and silica gel H exist.

### 3.2. Effect of pH on the rate of hydrogen evolution

In general, pH values have notable effects on the photocatalytic activity for hydrogen evolution. Fig. 3 shows the effect of the pH value of the solution on the average rate of hydrogen evolution from an aqueous TEOA solution. When pH values vary from 2 to 13, the maximum average rate of hydrogen evolution and apparent quantum efficiency, about  $43 \mu\text{mol h}^{-1}$  and 10.4%, respectively, are achieved at pH 7, and either the strongly acidic or strongly basic solution is detrimental to hydrogen evolution.

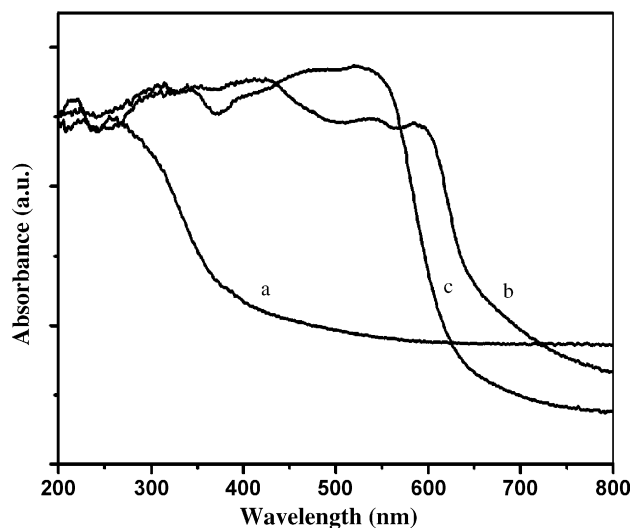


Fig. 2. UV-vis diffuse reflectance spectra of silica gel H, Eosin Y and the composite of Eosin Y and silica gel H. (a) Silica gel H, (b) Eosin Y, and (c) the composite of Eosin Y and silica gel H.

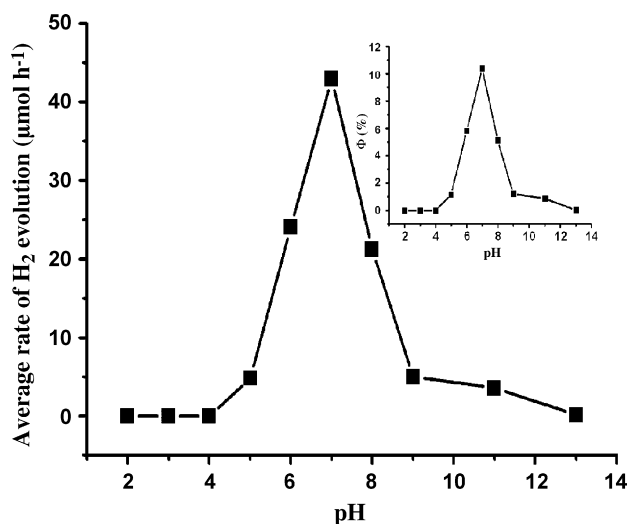


Fig. 3. Dependence of the average rate of hydrogen evolution upon pH. Reaction conditions: 60 mg the composite of Eosin Y and silica gel H (E/S = 1/2), irradiation time 10 h, Ar-saturated. Inset describes the apparent photon quantum efficiency as a function of pH.

In particular, when the pH value of the solution was adjusted to 2, 3 or 4, no hydrogen evolution was observed. The following are the reasons for rationalizing this phenomenon.

First, the pH value of the solution might have effects on the form of TEOA in aqueous solution and its adsorption on the surface of silica gel H. On the one hand, in strongly acidic solution, the protonated TEOA is hard to be adsorbed onto the surface of silica gel H because of electrostatic repulsion force resulting from the protonation of hydroxyl groups on the surface of silica gel H. On the other hand, the ability of donating electrons would be weakened because the electron donor TEOA undergoes total protonation [26]. 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.

Second, the pH value of the solution might have an effect on the interactions between Eosin Y and silica gel. It has been reported that silica gel particles are negatively charged at  $\text{pH} \geq 6$  [22]. In strongly basic solution, Eosin Y exists in the bivalent anionic form. As a result, dye species are difficult to interact with the surface of silica gel because of electrostatic repulsion force.

Third, 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  $\text{H}^+$ , the rate of hydrogen evolution should depend on the concentration of  $\text{H}^+$ . The higher the concentration of  $\text{H}^+$ , the faster the reduction of  $\text{H}^+$  would proceed. However, Kalyanasundaram et al. have reported that TEOA is oxidized by means of losing one of the unpaired electrons of the N atom [27], so the protonated forms of TEOA are difficult to oxidize. As a result, the photosensitized hydrogen evolution process should occur at an optimized pH.

In addition, it has been reported that dispersive force, hydrophobic force as well as electrostatic force provide a major contribution to the aggregation of Eosin Y [25]. When the system is in strongly basic solution, Eosin Y is difficult to aggregate

to form dimers when electrostatic repulsion force between bivalent anionic forms of the monomer Eosin Y is stronger than dispersive force and hydrophobic force. However, the dimers could play an extraordinary role in the photosensitized electron-transfer process, which will be discussed below. Consequently, in strongly basic solution, the rate of hydrogen evolution is very low.

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

Fig. 4 shows the effect of the Eosin Y concentration,  $0\text{--}9.60 \times 10^{-4} \text{ mol dm}^{-3}$  ( $E/S = 2/1$ ), on the average rate of hydrogen evolution from an aqueous TEOA solution at pH 7. As shown in Fig. 4, when the concentration of Eosin Y is in the range of  $3.60 \times 10^{-4} \text{ mol dm}^{-3}$  ( $E/S = 1/3$ ) to  $7.24 \times 10^{-4} \text{ mol dm}^{-3}$  ( $E/S = 1/1$ ), the rate of hydrogen evolution is relatively high, about  $43 \mu\text{mol h}^{-1}$ , when the apparent quantum efficiency is ca. 10%. If no Eosin Y is added, then no hydrogen evolution is observed. When the concentration of Eosin Y is lower than  $3.60 \times 10^{-4} \text{ mol dm}^{-3}$  ( $E/S = 1/3$ ), the rate of hydrogen evolution increases with increasing the concentration. On the contrary, when the concentration of Eosin Y is higher than  $7.24 \times 10^{-4} \text{ mol dm}^{-3}$  ( $E/S = 1/1$ ), the rate of hydrogen evolution decreases with increasing the concentration. The following are the reasons for explaining these behaviors.

The first, as shown in Fig. 2, silica gel H dose not absorb the visible light ( $\lambda \geq 420 \text{ nm}$ ), so no hydrogen evolution is observed in the absence of Eosin Y.

The second, in order to rationalize the phenomenon that the rate of hydrogen evolution decreases with increasing the concentration at a higher Eosin Y concentration (e.g.  $\geq 7.24 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $E/S = 1/1$ ), we consider first concentration quenching. When the concentration of Eosin is relatively high, the deactivation of excited dye species could be easier via

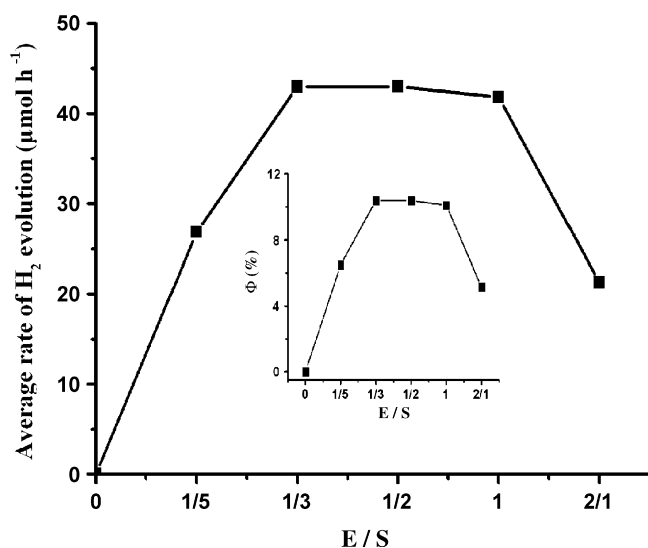


Fig. 4. Dependence of the average rate of hydrogen evolution upon E/S. Reaction conditions: 60 mg the composites of Eosin Y and silica gel H, pH 7, irradiation time 10 h, Ar-saturated. Inset describes the apparent photon quantum efficiency as a function of E/S.

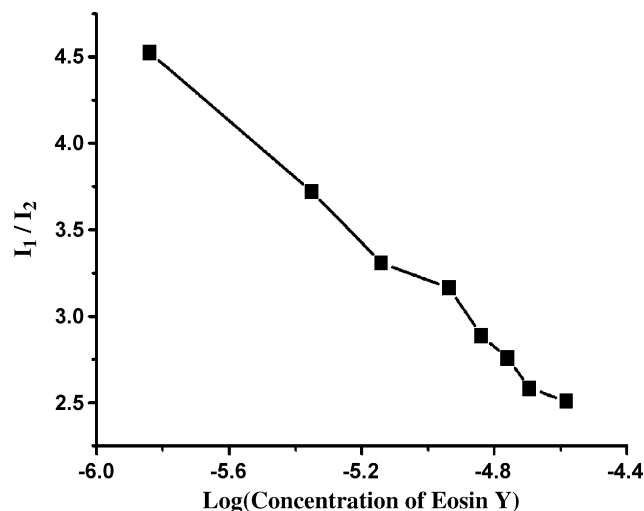


Fig. 5. Dependence of the ratio of peak intensity  $I_1/I_2$  upon the concentration of Eosin Y in TEOA aqueous solution at pH 7.

intersystem crossing as well as radiative and nonradiative transition [28]. The higher the concentration of Eosin Y, the closer the distance between adjacent dye species on the silica gel surface, the more efficient the concentration quenching, and the less efficiency utilized by the excited dye species. On the other hand, it may result from the decrease in the number of the photon absorbed by Eosin located on the surface of silica gel. When the concentration of Eosin Y is relatively higher, the number of Eosin Y adsorbed increases hardly with increasing the concentration of Eosin Y. As a result, the absorbance of Eosin Y free in solution increases. Consequently, the number of the photon absorbed by Eosin Y adsorbed on the surface of silica gel decreases. However, as it will be discussed below, the interactions between silica gel and Eosin Y have remarkable effects on the rate of hydrogen evolution.

The third, it could be caused by the increase in the Eosin Y dimers that the rate of hydrogen evolution increases with increasing the Eosin Y concentration ( $\leq 3.60 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $E/S = 1/3$ ). The intensities of peaks at 510 nm and 485 nm are denoted as  $I_1$  and  $I_2$ , respectively. The ratio of  $I_1/I_2$  represented the ratio of the concentration of monomer and dimer in the solution. Fig. 5 describes the effect of the concentration on the ratio of  $I_1/I_2$ . It can be seen that the  $I_1/I_2$  ratio drops with increasing the concentration of Eosin Y, that is, the concentration of the dimer increases when the concentration of Eosin Y is increased. The result is in accordance with what De et al. reported before [25]. The photosensitized electron transfer could be carried out via the dimers, so the rate of hydrogen evolution increases when the concentration of Eosin Y is increased.

## 4. Mechanism

### 4.1. Role of silica gel H

Fig. 6 compares the rate of hydrogen evolution in the presence and absence of silica gel H (40 mg) from an aqueous TEOA solution at pH 7 when the concentration of Eosin Y is

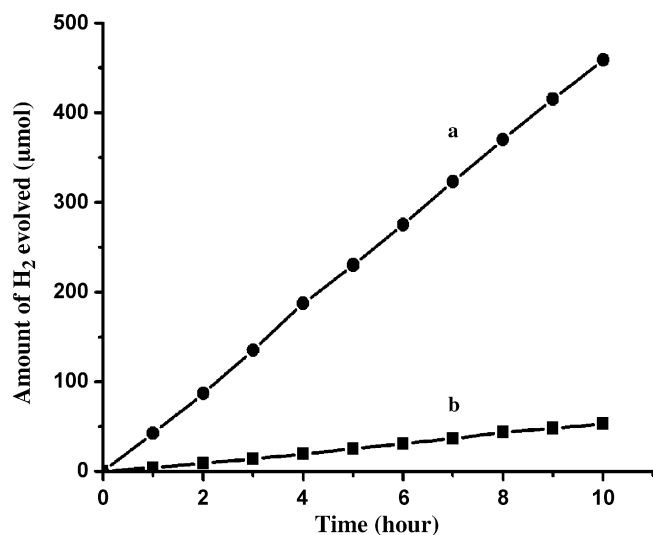


Fig. 6. Time courses of hydrogen evolution from an aqueous TEOA solution. Reaction conditions: 20 mg Eosin Y, pH 7, Ar-saturated. (a) In the presence of silica gel H (40 mg); (b) in the absence of silica gel H.

$3.60 \times 10^{-4} \text{ mol dm}^{-3}$ . It can be seen that the rate of hydrogen evolution in the absence of silica gel H is about  $4 \mu\text{mol h}^{-1}$ . In addition, the rate of hydrogen evolution in the presence of silica gel H is enhanced about 10-fold relative to the homogeneous phase, i.e. in the absence of silica gel H. On the basis of the results above, we conclude that silica gel H can accelerate the rate of hydrogen evolution, but it is not essential for the photosensitized hydrogen evolution process. We think that the enhanced rate of hydrogen evolution in the presence of silica gel H particles can be partly ascribed to the control of the electron-transfer reaction by means of electrostatic interaction. The idea is developed from the following considerations.

On the one hand, it has been reported that silanol groups on the particle surface are ionized at  $\text{pH} \geq 6$ . Consequently, in neutral or basic solution, the surface of the particle is negatively charged and a diffuse electrical double layer is produced in the vicinity of the solid interface. The particles could be used to exert electrostatic repulsive and attractive interactions with the components involved in photosensitized reactions [22]. On the other hand, it has been proposed by Pelet et al. that  $\text{EO}^{\bullet+}$  and  $\text{EO}^{\bullet-}$  could be produced via intermolecular electron transfer within Eosin Y dimer yielding  $(\text{EO}^{\bullet+}\text{EO}^{\bullet-})$  radical pairs on the surface of the nonreactive oxide (e.g.  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ) [29]. The charged interface provided by silica gel interacts with  $\text{EO}^{\bullet+}$  and  $\text{EO}^{\bullet-}$  produced. The positively charged dye species, i.e.  $\text{EO}^{\bullet+}$ , are adsorbed on the interface by means of electrostatic attractive interactions, while the negatively charged dye species, i.e.  $\text{EO}^{\bullet-}$ , are repelled by means of electrostatic repulsive interactions. Consequently, the separation of  $\text{EO}^{\bullet+}$  and  $\text{EO}^{\bullet-}$  would be promoted.

In addition, silica gel can supply enough large interfaces because of its high specific surface area, so that Pt particles as the active centers for hydrogen evolution can be highly dispersed. As a result, the rate of hydrogen evolution is enhanced remarkably.

It is noteworthy that EO (referred here and hereafter) represents Eosin Y species.

#### 4.2. Role of Pt

Whether in the presence or absence of silica gel in the system, Pt has a remarkable effect on the rate of photosensitized hydrogen evolution. When 60 mg the composite of Eosin Y and silica gel H was suspended in 60 ml aqueous TEOA solution at pH 7, the average rate of hydrogen evolution was only  $3.5 \times 10^{-2} \mu\text{mol h}^{-1}$  under visible-light irradiation. However, when Pt particles were loaded, the rate of hydrogen evolution was enhanced remarkably and about  $43 \mu\text{mol h}^{-1}$ . Similarly, the rate of hydrogen evolution in the absence of silica gel was only  $2.3 \times 10^{-2} \mu\text{mol h}^{-1}$  without Pt particles loaded, while the rate was about  $4 \mu\text{mol h}^{-1}$  in the presence of Pt particles. The reasons that the rate of hydrogen evolution is enhanced significantly in the presence of Pt particles are as follows.

On the one hand, since the overpotential of hydrogen on Pt is rather low, hydrogen evolution is easier in the presence of Pt particles. On the other hand, it has been reported that metal nanoparticles (e.g. Au and Ag) can accept electrons from sensitizers in metal particle-sensitizer nanoassemblies under photoexcitation [30,31]. Based on the fact, we inferred that Pt particles could play a similar role. Consequently, the rate of the regeneration of dye species would be enhanced, the back reaction of  $\text{EO}^{\bullet+}$  and  $\text{EO}^{\bullet-}$  would be retarded and the efficiency of the utilization of excited dye species would be improved. Finally, the rate of hydrogen evolution is enhanced remarkably.

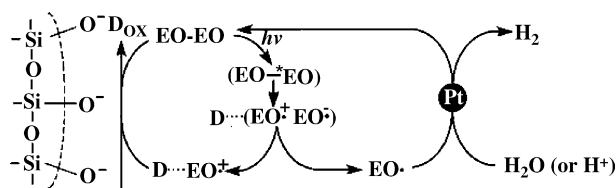
#### 4.3. Role of TEOA

TEOA could play a key role in the photosensitized hydrogen evolution process. The reason is that no hydrogen evolution was observed under visible-light irradiation for 40 h when 60 mg the composite of Eosin Y and silica gel H was suspended in 60 ml aqueous solution containing a certain amount of  $\text{H}_2\text{PtCl}_6$  at pH 7. The functions of TEOA in the photosensitized hydrogen evolution process could be demonstrated in the following two aspects:

On the one hand, TEOA, as an electron donor, could quench the excited dye species to the ground state by means of reacting with the oxidized dye species, i.e.  $\text{EO}^{\bullet+}$ . On the other hand, it could enhance the stability of  $(\text{EO}^{\bullet+}\text{EO}^{\bullet-})$  radical pairs through the Van der Waals interaction with these species. As a result, the production of  $(\text{EO}^{\bullet+}\text{EO}^{\bullet-})$  radical pairs would be easier and the lifetime of  $(\text{EO}^{\bullet+}\text{EO}^{\bullet-})$  radical pairs would be prolonged.

#### 4.4. Inference of photosensitized hydrogen evolution mechanism

By comparing the potential of the conduction band of  $\text{SiO}_2$  ( $\sim -4.2 \text{ V}$  (vs. NHE)) [32] and the  $\text{EO}^*(\text{S1})/\text{EO}^{\bullet+}$  couple ( $E^\circ = -1.2 \text{ V}$  (vs. NHE)) [28], the probability of electron injection from the excited dye species to the conduction band of  $\text{SiO}_2$  is ruled out. In the case of the reaction system in this study, the electron transfer could be carried out via  $(\text{EO}^{\bullet+}\text{EO}^{\bullet-})$  rad-

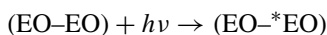


Scheme 1. Probable mechanism of photosensitized hydrogen evolution (note that EO, D and Dox represent the sensitizer, the electron donor, and the oxidized product of electron donor, respectively).

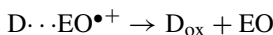
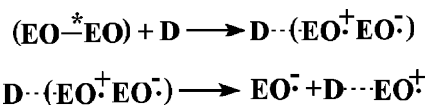
ical pairs produced through the intermolecular electron transfer within Eosin Y dimers. Based on the discussion above, a feasible mechanism for the photosensitized hydrogen evolution is proposed, as shown in Scheme 1.

The various steps involved in the mechanism are as follows:

(i) Absorption of light:



(ii) Electron transfer and regeneration of dye species:



(iii) Hydrogen evolution:



where the abbreviations are shown in the caption of Scheme 1.

## 5. Conclusion

A new and effective system for the production of hydrogen under visible-light irradiation ( $\lambda \geq 420$  nm), constructed using silica gel as a matrix, Eosin Y as a photosensitizer and Pt as a cocatalyst, has been reported. The optimal pH and Eosin Y concentration are 7 and  $3.60 \times 10^{-4}$  mol dm $^{-3}$  (E/S = 1/3) to  $7.24 \times 10^{-4}$  mol dm $^{-3}$  (E/S = 1/1), respectively. In the presence of triethanolamine (TEOA) as an electron donor, the rate of hydrogen evolution and the apparent quantum efficiency under visible-light irradiation ( $\lambda \geq 420$  nm) can reach about 43  $\mu\text{mol h}^{-1}$  and 10.4%, respectively. In addition, silica gel could enhance the rate of photosensitized hydrogen evolution by means of promoting the separation of  $\text{EO}^{\cdot+}$  and  $\text{EO}^{\cdot-}$  through electrostatic interaction. Pt could not only act as active centers for hydrogen evolution, but also improve the efficiency of the utilization of the excited dye species. TEOA could not

only regenerate the dye species, but also enhance the stability of ( $\text{EO}^{\cdot+} \text{EO}^{\cdot-}$ ) radical pairs through the Van der Waals interaction with these species and further enhance the rate of hydrogen evolution.

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