

Improved quantum yield for photocatalytic hydrogen generation under visible light irradiation over eosin sensitized TiO₂—Investigation of different noble metal loading

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Abstract

In the present study, visible light induced hydrogen generation (>420 nm) over the dye-sensitized M/TiO₂ (M = Pt, Ru and Rh) photocatalysts has been achieved in the presence of electron donors such as triethanolamine, acetonitrile and triethylamine. The significant enhancement of quantum yield was achieved via noble metal loading and subsequent dye sensitization of M/TiO₂. The highest quantum yield for hydrogen generation was 10.27% under irradiation with a wavelength longer than 420 nm. The strong adsorption of dye eosin has been found to enhance this high efficient hydrogen generation, which is supported by the comparison results of dye eosin adsorption per square nanometer on noble metal loading TiO₂, UV–vis adsorption spectra, activity tests and stability tests. In addition, improvement of adsorption of dye on the catalyst, for example, by multidentate co-ordination complexation, may result in higher photocatalytic efficiency of hydrogen generation under visible light illumination.

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1. Introduction

Harnessing the sun's clean and infinite energy is the main objective of all alternative energy strategies [1]. Hydrogen is considered to be an ideal source of future energy [2]. If we can convert even a tiny fraction of the solar energy reaching the earth into storable chemicals, such as hydrogen, we will solve many of our problems not only in energy, but also the global environmental and political [3]. Therefore, photocatalytic water splitting to produce hydrogen is an important process in the storage and conversion of solar energy [4]. Because of its high catalytic and photostability, TiO₂ powder has been widely used as a photocatalyst for light to energy conversion and chemical transformations. The difficulty with this semiconductor is its large bandgap energy of 3.2 eV that can only be excited by ultraviolet light with a wavelength of no longer than 387.5 nm, which accounts for only 4% of the incoming solar energy and thus renders the overall process impractical [4]. For this reason, considerable efforts have been invested in developing photocatalysts capa-

ble of using the less energetic but more abundant visible light, which accounts for about 43% of the incoming solar energy. Some progress has gradually been achieved in past decades, for example, research with photocatalysts such as In_{1-x}Ni_xTaO₄ ($x=0-0.2$) [5], ZnIn₂S₄ [6], TiO_{2-x}N_x [7], Ni₂O₃/TiO_{2-x}B_x [8], TiO₂/C [9], TiN_xO_yF_z [10], etc., suggest that the use of solar energy for photocatalytic water splitting might provide a viable source for "clean" hydrogen fuel. Although many of the mentioned above photocatalysts were found active in the visible light region, efficiency is still a serious problem [11,12]. Recently, sensitization of TiO₂ has been identified as a successful means of enhancing the quantum yield for hydrogen evolution induced by visible light (for example, the dye-sensitized solar cell, i.e., Grätzel Cell [13]). The dye-sensitized solar cell technology has been a major triumph during the past decade [3,14]. This specific breakthrough accomplished the efficient photosensitization of highly disordered wide-bandgap semiconductor electrodes with these ruthenium complexes. In addition, several groups have obtained white light conversion efficiencies of over 10% based on the dye-sensitized solar cells technologies [15]. Solar-driven AlGaAs/Si RuO₂/Pt_{black} photoelectrolysis cell yielded water splitting at 18.3% conversion efficiency and alternative

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dual bandgap systems are calculated to be capable of attaining over 30% solar photoelectrolysis conversion efficiency [16]. A highly efficient photo-induced electron transfer mechanism of this cell should be applicable to the system of dye-sensitized photocatalysts suspension for H₂ formation [17]. In the case of the sensitizer suspension system, the electrons were excited by visible light were injected into the conduction band (CB) of TiO₂. The CB subsequently acted as a mediator for transferring electrons from the sensitizer to substrate of electron acceptors on TiO₂ surface, whereas the valence band (VB) remained unaffected in a typical photosensitization. Presently, a number of studies have verified that certain noble metal dispersions are capable to mediate light induced hydrogen and oxygen evolution from water [18]. When loaded simultaneously with ultrafine Pt and RuO₂, these particles displayed extremely high activity as water decomposition [19].

To improve the hydrogen evolution, a loading metal was indispensable. Investigation on the reaction mechanism of the loading metal is a very interesting subject, because the metal loading influence the dye adsorption, electron transfer and the H₂ evolution greatly. In the present study, the influence of various noble metal loading on visible light (>420 nm) induced hydrogen production was investigated in the presence of electron donors such as triethanolamine, acetonitrile and triethylamine over dye-sensitized M/TiO₂ (M = Pt, Ru and Rh) photocatalysts. This study will lead to a better understanding of their roles and the nature of efficiency improvement. In addition, comparatively high quantum efficiencies (for example, ~10.27%) and very good stability have been obtained using eosin dye-sensitized M/TiO₂ photocatalysts.

2. Experimental

In this work, an eosin Y dye supplied by the Shanghai Chemical Co. (China) was used as a photosensitizer for the catalysts. Degussa P25 TiO₂ powder (Germany) was used as the source of TiO₂. Pt, Ru and Rh-loaded TiO₂ catalysts (Pt/TiO₂, Ru/TiO₂ and Rh/TiO₂) were prepared as follows: TiO₂ powder was stirred in an aqueous ethanol solution containing a certain amount of H₂PtCl₆, RuCl₃ and RhCl₃ and irradiated by a Hg lamp for 12 h. Photoreduction of H₂PtCl₆, RuCl₃ and RhCl₃ took place under this condition and highly dispersed Pt, Ru and Rh were deposited on the TiO₂ surface. After filtrating and washing with distilled water, the powders were heated at 200 °C for 2 h in a vacuum to remove ethanol from the catalyst. The dye was adsorbed onto M/TiO₂ by stirring the M/TiO₂ (1 g) in a mixture of eosin and diethanolamine/water mixed solution (DEA–H₂O) (0.1 mmol of eosin dissolved in 70 ml a 15% (v/v) diethanolamine/water mixed solution) at room temperature for 12 h in the dark. After filtration and washing with by acetone, the sample was dried and kept in the dark (denoted as Eo-M/TiO₂). The Eo-M/TiO₂ powder showed a broad absorption from 400 to 650 nm, as measured by a UV–vis spectrometer (Shimadzu-160A spectrophotometer). Photocatalytic experiments were conducted in a one-compartment Pyrex cell ca. 118 cm³ having a flat window ca. 10.2 cm² for illumination. A 200 W halogen lamp was used as the light source. The

light source was equipped with a cutoff filter (Toshiba Y44.2, $\lambda > 420$ nm) to remove radiation below 420 nm and to ensure illumination of visible light only. The reaction Pyrex cell was 28 cm away from the halogen lamp. All the other chemicals were of an analytic reagent grade and used without further purification and all the solutions were prepared in triple distilled water whose conductivity is less than 1×10^{-4} s/m, pH 6.6.

In a typical photocatalytic experiment, 20 mg of catalyst was suspended in 70 ml a DEA–H₂O mixture by means of a magnetic stirrer. Prior to irradiation, the suspension of the catalyst was dispersed in an ultrasonic bath for 3 min and argon was bubbled through the reaction mixture for 40 min to completely remove oxygen.

The photocatalytic activity was determined by measuring the amount of hydrogen produced using gas chromatography (TCD, molecular sieve 5 A column, Ar as gas carrier). The pH values of the reaction solution were determined with a Markson 6200 pH meter, which was adjusted by adding of nitric acid or sodium hydroxide.

The incident light intensity was measured with a Ray Virtual Radiation Actinometer (FU100, silicon ray detector, light spectrum: 400–700 nm, sensitivity: 10–50 $\mu\text{V}/\mu\text{mol m}^2 \text{ s}$) and thus the quantum efficiency of H₂ evolution was calculated. The quantum efficiency was re-confirmed by the method of the Liquid-Phase Actinometers (potassium ferrioxalate actinometer) as described in reference [20].

3. Results and discussion

3.1. Absorption measurements

The amount of the adsorbed dye molecules in TiO₂, Pt/TiO₂, Ru/TiO₂ and Rh/TiO₂ was evaluated by monitoring the decrease of the concentration of dye (ΔC) in the aqueous solutions containing powdered TiO₂, Pt/TiO₂, Ru/TiO₂ and Rh/TiO₂ stirred in the dark at room temperature for 12 h. The concentration of dye (eosin) was measured spectrophotometrically. Table 1 illustrates that eosin can be more heavily adsorbed by the metal loading TiO₂ than on pure TiO₂. The amount of adsorbed eosin was increased with the increase of the loaded metal. This result difference implies that the combination between eosin and metal was much stronger than that between eosin and TiO₂. The same adsorption behaviors were observed not only in the eosin/water solution but also in a 15% (v/v) eosin–diethanolamine/water mixed solution. We speculated that eosin was adhered strongly to the loaded metal by complex action and such complexation resulted in the enhanced adsorption of eosin, as well as the hydrogen evolution in the process of photocatalytic reaction. For Degussa P25 TiO₂ powder, the BET area is $55 \pm 15 \text{ m}^2 \text{ g}^{-1}$. Since the diameter of an eosin molecule is 10.84 Å, each eosin molecule occupies 92.24 \AA^2 as shown in Fig. 1. Therefore, the maximum amount of monolayer adsorption of eosin on TiO₂ powder should be $99.05 \mu\text{mol g}^{-1}$ (namely 108 molecules/10,000 Å²). In this experiment, 11.4 μmol eosin was adsorbed in 1 g TiO₂ powder, while 72.5, 89.4 and 91.6 μmol of eosin were adsorbed in 1 g Pt/TiO₂ (1.0 wt.%), Ru/TiO₂ (1.0 wt.%) and Rh/TiO₂ (1.0 wt.%),

Table 1
Adsorption of eosin Y on Degussa P25 TiO₂ and metal loading P25 TiO₂ in various solutions

Solution	Degussa P25 TiO ₂	Pt/TiO ₂			Ru/TiO ₂			Rh/TiO ₂		
		0.5%	1.0%	2.0%	0.5%	1.0%	2.0%	0.5%	1.0%	2.0%
a. Amount of adsorbed eosin (μmol/g catalyst)										
25 ml 5 × 10 ⁻⁵ M eosin	11.5	67.8	72.5	90.6	74.3	89.4	95.8	78.7	91.6	97.5
25 ml 5 × 10 ⁻⁵ M eosin + 15% (v/v) DEA–H ₂ O	11.3	66.4	73.8	87.2	76.9	86.2	93.0	75.8	90.3	96.7
b. The number of adsorbed eosin molecular (molecular numbers/10,000 Å ² catalyst surface)										
25 ml 5 × 10 ⁻⁵ M eosin	11.5	73.9	79.0	98.7	81.0	97.4	104.4	85.8	99.8	106.3
25 ml 5 × 10 ⁻⁵ M eosin + 15% (v/v) DEA–H ₂ O	11.3	72.4	80.44	95.0	83.8	94.0	101.4	82.6	98.4	105.4

respectively. Because the deposited Pt, Ru and Rh particles on TiO₂ occupy only a very small portion of surface based on TEM analysis, it is believed that the multidentate complexation or multilayer adsorption on metal has occurred.

3.2. Photocatalytic activities over various eosin-sensitized catalysts for hydrogen evolution

Fig. 2 shows the time course of H₂ evolution from a Eo-M/TiO₂(1.0 wt.%) suspension under irradiation of visible light ($\lambda > 420$ nm). For example, the rate of H₂ evolution from DEA–H₂O solution (15%, v/v) was 0.368 ml/h over Eo-Rh/TiO₂(1.0 wt.%) photocatalyst.

Fig. 3 gives the comparison of H₂ evolution over various noble metal loading TiO₂ catalysts from DEA–H₂O solution (15%, v/v) under irradiation of visible light ($\lambda > 420$ nm). For

example, the rate of H₂ evolution was 0.55 ml/h over 10.0 wt.% Eo-Rh/TiO₂, while the rate was 0.368 ml/h over 1.0 wt.% Eo-Rh/TiO₂ photocatalyst under same condition. Generally, the 0.5–1.0 wt.% of noble metal loading is high active for photocatalysis [21], but in our case, the H₂ evolution was enhanced with the increase of the loading metal. It is speculated that there is more complicated behavior of loading metal in dye-sensitized TiO₂, which is different from the no-sensitizer suspension system. The visible light excites the sensitizer molecules adsorbed by TiO₂ and by the loading metal as well, the electrons were subsequently injected into conduction band (CB) of TiO₂ directly or through the loading metals indirectly. Here, the CB and loading metals act as a mediator for transferring electrons from the sensitizer to substrate of electron acceptors on the TiO₂ surface, the valence band (VB) remains unaffected in a typical photosensitization.

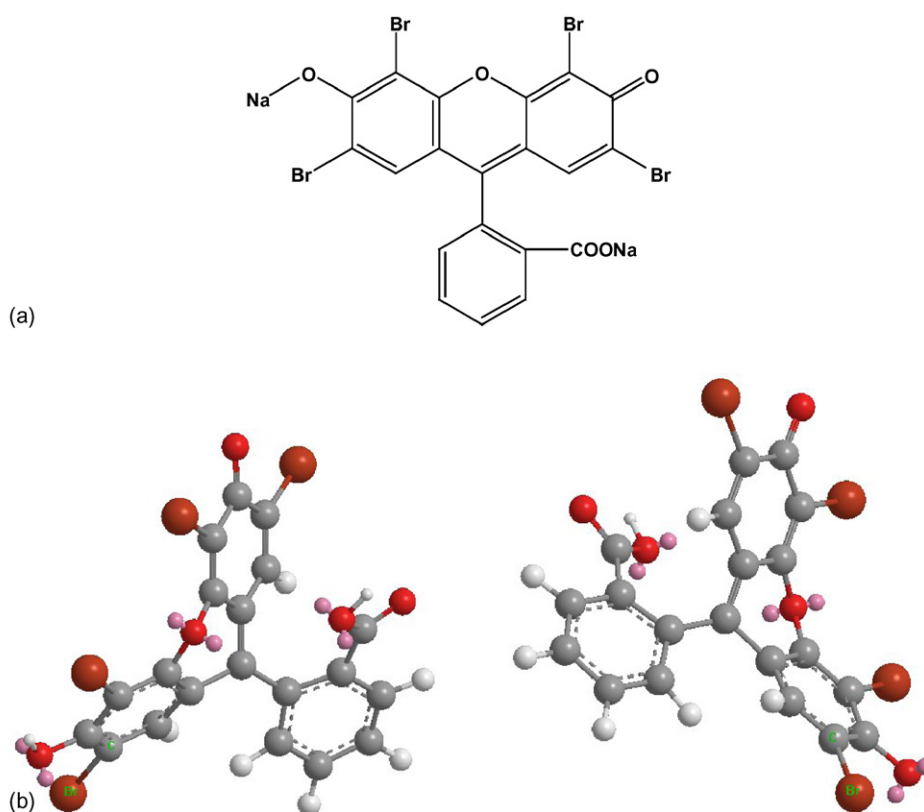


Fig. 1. Molecular structure of eosin Y.

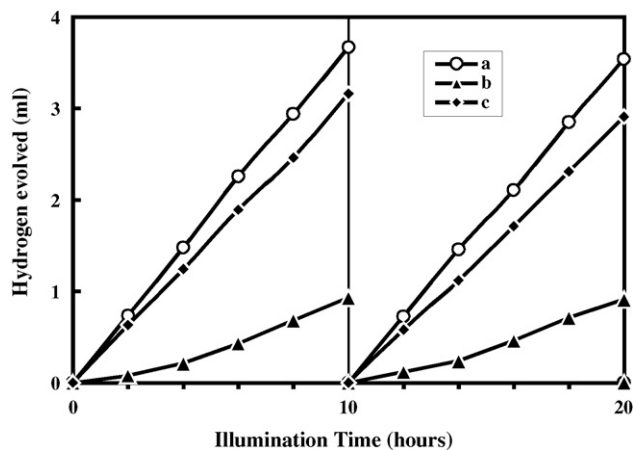


Fig. 2. Hydrogen evolution from 15% (v/v) DEA–H₂O solution under visible light ($\lambda > 420$ nm) irradiation over (a) 1.0 wt.% Eo-Rh/TiO₂; (b) 1.0 wt.% Eo-Pt/TiO₂ and (c) 1.0 wt.% Eo-Ru/TiO₂ photocatalysts.

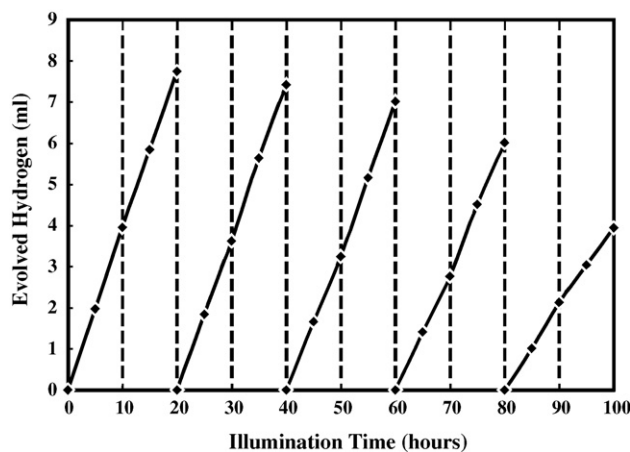


Fig. 4. Stability test of 5.0 wt.% Eo-Rh/TiO₂ photocatalysts in 70 ml 15% (v/v) DEA–H₂O solution under visible light ($\lambda > 420$ nm) irradiation.

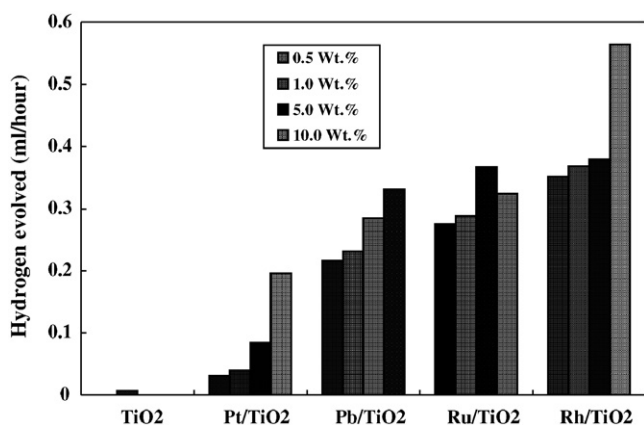
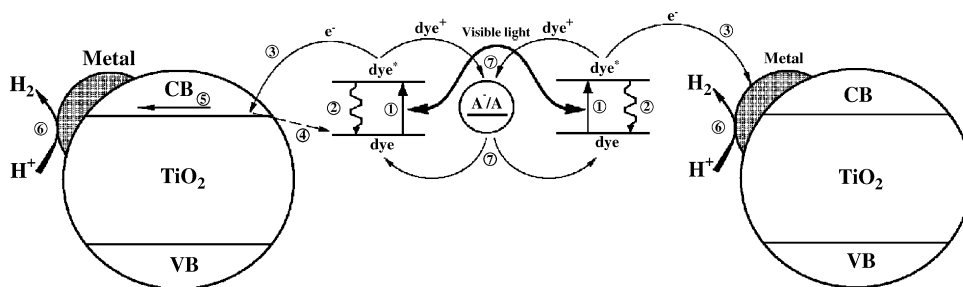


Fig. 3. Comparison of H₂ evolution over various noble metal loading TiO₂ from 15% (v/v) DEA–H₂O solution under visible light ($\lambda > 420$ nm) irradiation.

Noble metal loading enhances both the adsorption of eosin (adsorption effect) [22] and the charge separation of e_{CB}^- and h_{VB}^+ pairs (charge separation effect) [23]. These effects increase the rate of reduction of H₂O to H₂. The high-resolution transmission electron micrograph images of 1.0 wt.% Pt/TiO₂ demonstrated that Pt particles of diameter 1–3 nm are dispersed on the surface of TiO₂. The amount of adsorption of eosin Y increased with loading of Pt (11.4 $\mu\text{mol/g}$ for TiO₂, 67.8 $\mu\text{mol/g}$

for 1.0 wt.% Pt/TiO₂ and 90.6 $\mu\text{mol/g}$ for 2.0 wt.% Pt/TiO₂ at an equilibrium concentration of 4.0×10^{-5} M eosin solution). These results indicated that eosin Y adsorbed preferentially on metal atom, such as Pt, other than on the surface of TiO₂. It was reported that the adsorption of azobenzene on Pt involved interaction of δ -bonding [π orbital (azobenzene) \rightarrow d orbital (Pt)] and π -backbonding [d orbitals (Pt) \rightarrow π^* orbital (azobenzene)] [24,25]. Here, we believed that the same situation occurred in this study. The number of adsorbed eosin increased with increase of noble metal loading significantly. Obviously, more metal loading enhances the adsorption of eosin, then subsequently enhances the electron transfer and hydrogen evolution in photocatalytic reaction. The efficiency order of photocatalytic hydrogen evolution is consistent with the order of the adsorption affinity of the eosin on M/TiO₂ determined spectrophotometrically. The principle of photosensitization of TiO₂ is illustrated in Scheme 1 which indicates the primary electronic pathways.

In a long-term photocatalytic reaction carried out for 100 h, the total amount of evolved hydrogen reached 32.7 ml from the DEA–H₂O aqueous solution mixture (15%, v/v) over Eo-Rh/TiO₂ (5.0 wt.%) photocatalyst (shown in Fig. 4). No H₂ evolution was observed over pure M/TiO₂ photocatalysts in the absence of dye under irradiation by visible light ($\lambda > 420$ nm). This indicated that no direct photo-excitation of TiO₂ semiconductor had taken place. The H₂ evolution rates in the presence of



Scheme 1. Possible excitation processes using dye molecule sensitizer for hydrogen evolution over Eo-M/TiO₂ photocatalyst (dye stands for electronically excited sensitizer (dye⁺) oxidized sensitizer (A) sacrificial electron donors for regenerating the sensitizer. The number represents the primary electronic pathways in photosensitization: (1) excitation of dye; (2) fluorescent decay of dye⁺; (3) electron injection into CB or loading metal; (4) back electron transfer; (5) electron migration within the lattice onto the surface of TiO₂ semiconductor; (6) electron transfer to A for hydrogen production; (7) sensitizer regeneration by A).

Table 2

Comparison of H₂ evolution rate in the presence of various electron donors over various photocatalysts under visible light ($\lambda > 420$ nm) irradiation.

Reaction conditions			Amount of hydrogen evolution (ml/10 h)
Catalyst (20 mg)	Sensitizer	Aqueous solutions	
1.0 wt.%Rh/TiO ₂	Eosin	DEA–H ₂ O solution	3.67
1.0 wt.%Rh/TiO ₂	Eosin	TEA–H ₂ O solution	3.43
1.0 wt.%Rh/TiO ₂	Eosin	TE–H ₂ O solution	3.49
1.0 wt.%Rh/TiO ₂	Rhodamine B	DEA–H ₂ O solution	0.14
1.0 wt.%Ru/TiO ₂	eosin	DEA–H ₂ O solution	2.89
1.0 wt.%Ru/TiO ₂	eosin	TEA–H ₂ O solution	2.76
1.0 wt.%Ru/TiO ₂	eosin	TE–H ₂ O solution	2.64
1.0 wt.%Ru/TiO ₂	Rhodamine B	DEA–H ₂ O solution	0.09
1.0 wt.%Pt/TiO ₂	eosin	DEA–H ₂ O solution	0.9
1.0 wt.%Pt/TiO ₂	eosin	TEA–H ₂ O solution	1.27
1.0 wt.%Pt/TiO ₂	eosin	TE–H ₂ O solution	1.01
1.0 wt.%Pt/TiO ₂	Rhodamine B	DEA–H ₂ O solution	0.04

Note: DEA–H₂O solution (diethanolamine–water (DEA:H₂O = 15:85, v/v)) TEA–H₂O solution (triethanolamine–water (TEA:H₂O = 15:85, v/v)) TE–H₂O solution (triethylamine–water (TE:H₂O = 15:85, v/v)).

Table 3

The quantum efficiency of H₂ evolution under various irradiation conditions over 1.0 wt.% Eo-Rh/TiO₂

Irradiation condition (irradiation with 200 W halogen lamp)	Hydrogen evolution ($\mu\text{mol/h}$)	The incident light intensity ($\mu\text{mol/m}^2 \text{ s}$)	Quantum efficiency of H ₂ evolution measured by A Ray Radiation Actinometer
Directly irradiation	16.43	165.8	7.12
Directly irradiation	23.71	165.8	10.27 (over 10.0 wt.% Eo-Rh/TiO ₂)
With $\delta = 3$ mm glass	15.34	153.8	7.13
With cutoff filter ($\lambda > 420$ nm)	14.63	148.0	7.10
With cutoff filter ($\lambda > 460$ nm)	14.19	142.3	7.16

various electron donors over various photocatalysts were given in Table 2. It can be seen that RhB-sensitized M/TiO₂ photocatalysts (RhB-M/TiO₂) were also active for hydrogen generation. But the rate of hydrogen generation over Eo-M/TiO₂ was about 60 times higher than the rate over RhB-M/TiO₂ under the same experimental conditions.

3.3. Quantum efficiency of H₂ evolution

Fig. 5 gives the UV–vis diffuse reflectance absorption spectra of pure TiO₂, a Rhodamine B and an eosin dye-sensitized TiO₂ photocatalysts, respectively. Obviously, compared to pure TiO₂,

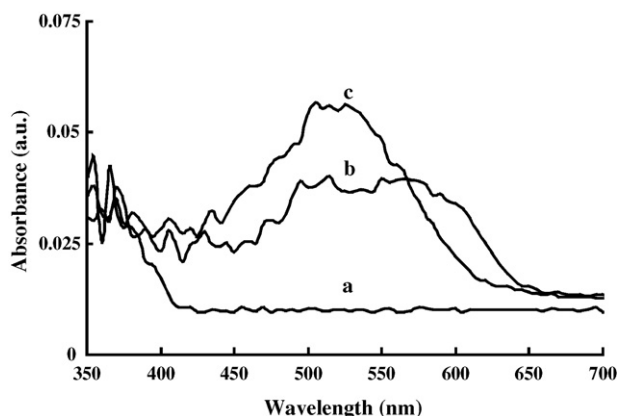


Fig. 5. UV–vis diffuse reflectance spectra of (a) TiO₂, (b) RhB-TiO₂ and (c) Eo-TiO₂.

the absorption region of dye-sensitized TiO₂ powder extended significantly into the visible region, especially for an eosin dye-sensitized TiO₂ photocatalyst. These absorption features strongly suggest that the dye-sensitized TiO₂ photocatalysts can be activated by visible light.

We examined the quantum yields for the H₂ evolution over 1.0 wt.% Eo-Rh/TiO₂ photocatalyst according to the formula (1) shown in Table 3.

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

Here, we employed the method of the Liquid-Phase Actinometers (potassium ferrioxalate actinometer), as described in the reference [20] to the remeasured quantum efficiency of H₂ evolution, under the same conditions and the results were in agreement with the data obtained by Ray Radiation Actinometer. The quantum yields were determined to be 10.27% for 10.0 wt.% Eo-Rh/TiO₂ photocatalysts under visible light irradiation ($\lambda > 420$ nm) in DEA–H₂O solution.

4. Conclusion

We have demonstrated that the dye-sensitized M/TiO₂ (M = Pt, Ru and Rh) can be used as photocatalysts for hydrogen production from a DEA–H₂O mixture with high quantum efficiencies and has good stability under visible light irradiation ($\lambda > 420$ nm) in the presence of electron donors, such as triethanolamine, acetonitrile and triethylamine, etc. The H₂ evo-

lution was enhanced with the increase of the metal loading, which may have resulted from the strong adsorption of eosin on the loading metal by multidentate complexation. In addition, comparatively high quantum efficiencies (for example, ~10.27%) have been obtained using an eosin dye-sensitized 10.0 wt.% Eo-Rh/TiO₂ photocatalyst.

Acknowledgements

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