



Photosensitization of different ruthenium(II) complex dyes on TiO₂ for photocatalytic H₂ evolution under visible-light

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ABSTRACT

Hydrogen production over dye-sensitized Pt/P25 under visible-light irradiation was investigated by using methanol or TEOA as an electron donor. Ru₂(bpy)₄L₁-PF₆ shows the best photosensitization due to its largest conjugation system, widest range of visible-light and 'antenna effect' among the used three Ru(II)-bipyridyl dyes. Ru₂(bpy)₄L₁-PF₆ loosely linked with TiO₂ also exhibit more steady and higher increases in H₂ evolution upon prolonging the irradiation time than the tightly linked N719. The dynamic equilibrium between the linkage of ground dye and divorce of oxidized dye from TiO₂ can enhance the electron-injection and hinder the backward transfer, and then improve the H₂ evolution efficiency.

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1. Introduction

Photocatalytic water-splitting over semiconductors has received much attention due to its potential application in H₂ production [1,2]. As a widely applied photocatalyst, TiO₂ can only absorb UV light due to its wide energy gap. The development of photocatalyst that can effectively harvest the visible-light of sunlight is indispensable for H₂ production. An important way to improve the H₂ production over TiO₂ is coupling with narrow energy-band semiconductor and doping metal and/or nonmetal element. However, a reliable and reproducible photocatalyst of this type has seldom been established [2].

The dye photosensitization on TiO₂ has been reported in the dye-sensitized nanocrystalline solar cell (DSSCs) [3], in which dye was considered as antenna to collect energy and then transferred it to TiO₂. Similarly, dye-sensitized TiO₂ have also been applied for photocatalytic H₂ production from suspension containing sacrificial [4–7] or nonsacrificial reagents [8–10]. Up till now, xanthenes [6,7], merocyanines [11,12], and Ru(II) complex [5,8–10], have been used as sensitizer of TiO₂ for H₂ evolution. Most dyes can not oxidize water by themselves to O₂ and consequently are decomposed under irradiation without sacrificial reagent, because O₂ evolution from water is much more difficult than the kinetically simpler process of H₂ evolution [4–7,13]. This inability to produce O₂ over sensitizers has prevented the construction of dye-sensitized photocatalysts. Therefore, it is still meaningful to seek more effective sensitizer for the photocatalytic H₂ production.

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The firmly bound dye like N3 can be stabilized near TiO₂ surfaces, and leads to fast electron-injection of the excited dye into substrate because the probability of this process should depend on the overlap of the wave functions of the donor and acceptor [5,14], but injected electrons also possibly transfer backward the oxidized dye due to its tight linkage with TiO₂ [14]. Kajiwara et al. have also thought that it was probable that the thermal re-orientational motion of the loosely attached molecules enhanced the electron transfer [5]. Therefore, the linkage mode of dye with TiO₂ definitely influences the electron transfer. Herein, three kinds of dye possessing different terminal groups, which can attach to TiO₂ through tight or loose linkage, were selected to compare their photosensitizing behaviors.

2. Experimental

P25 (TiO₂, Degussa) and H₂PtCl₆·6H₂O were obtained from commercial sources. N719 [(*n*-Bu₄N)₂-*cis*-Ru(dcbpy)₂(SCN)₂], one of the best sensitizers for DSSCs with the same structure as N3 dye [8], was purchased from Solaronix and used as reference substance because it can tightly attach to TiO₂ through its carboxyl groups [8]. Ru(bpy)₂(him)₂-NO₃ and Ru₂(bpy)₄L₁-PF₆ were prepared according to previous literatures [15,16]. These complexes have no terminal group like N719 and can just loosely link with TiO₂. Fig. 1 gives structures of those Ru(II)-bipyridyl dyes.

H₂PtCl₆·6H₂O (0.01 g) and P25 (0.38 g) were added into 175 ml of 2.0 M Na₂CO₃ solution in a Pyrex glass cell, and then exposed to 500 W Hg-lamp for 5 h under stirring. After centrifugation, the sample was washed and dried at 120 °C to obtain 1.0 wt% Pt/P25. This Pt/P25 was immersed in 1 × 10⁻⁴ M dye aqueous solution for 72 h, then washed and dried at 80 °C to obtain dye-sensitized Pt/P25.

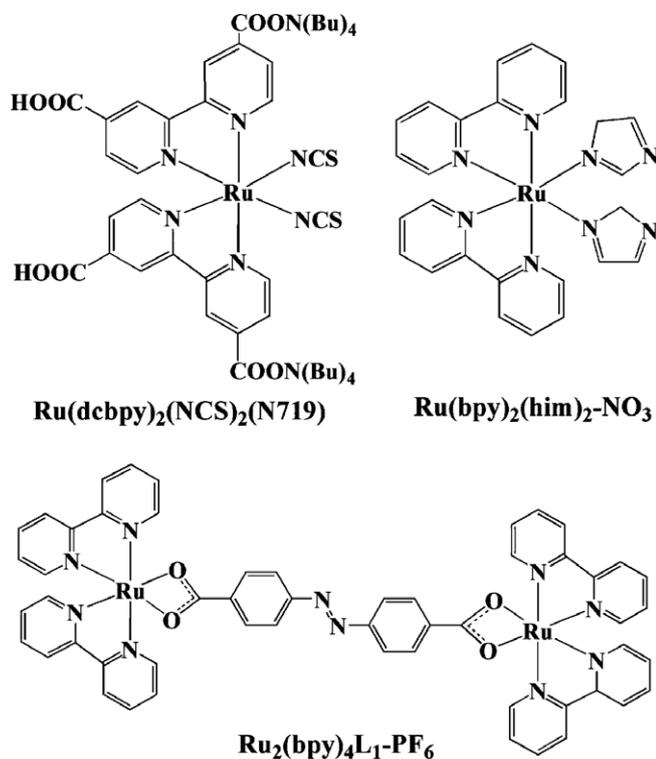


Fig. 1. Molecular structures of three Ru(II)-bipyridyl dyes.

H₂ production reactions were carried out in an outer irradiation-type photoreactor (Pyrex glass). A 500 W Xe-lamp was collimated and focalized into 5 cm² parallel faculae. A cut-off filter was employed to obtain the visible-light irradiation ($\lambda > 420$ nm). 100 ml aqueous suspension containing photocatalyst (40 mg) and sacrificial reagent solution (20 ml triethanolamine (TEOA) or methanol) was irradiated from top after thoroughly removing air. H₂ evolution rate was analyzed with gas chromatograph (TCD, 5 Å molecular sieve).

3. Results and discussion

3.1. UV-Vis absorption spectra of dyes

The λ_{max} in visible range for Ru₂(bpy)₄L₁-PF₆, Ru(bpy)₂(him)₂-NO₃ and N719 is 456, 436 and 502 nm (Fig. 2), respectively. Ru₂(bpy)₄L₁-PF₆ and Ru(bpy)₂(him)₂-NO₃ show broader absorption bands due to their larger molecular areas and delocalized conjugation system, although their λ_{max} are slightly shorter than N719 due to the presence of carboxyl groups. These properties of Ru(bpy)₂(him)₂-NO₃ and Ru₂(bpy)₄L₁-PF₆ are beneficial for the visible-light absorption and electron-injection of the excited dye [3,5]. Ru(II)-bipyridyl dyes have been used as sensitizers in DSSCs, and electron-injection from the excited dye to TiO₂ occurs efficiently [17,18]. For photocatalytic H₂ production, however, the solution must contain sacrificial reagent due to lack of I₃⁻/I⁻ redox mediator, otherwise Ru(II) dye might be decomposed during the light irradiation [19–21]. Therefore, methanol or TEOA was used as sacrificial reagent at the present system.

In the present work, H₂ evolution over Ru₂(bpy)₄L₁-PF₆ or Ru(bpy)₂(him)₂-NO₃ sensitized Pt/P25 indicates that the electron-injection did occur, although the two dyes have no any carboxyl group like N719 to tightly link with TiO₂. Still, Ru₂(bpy)₄L₁-PF₆ can loosely attach to TiO₂ through oxygen-bridge bonds derived from

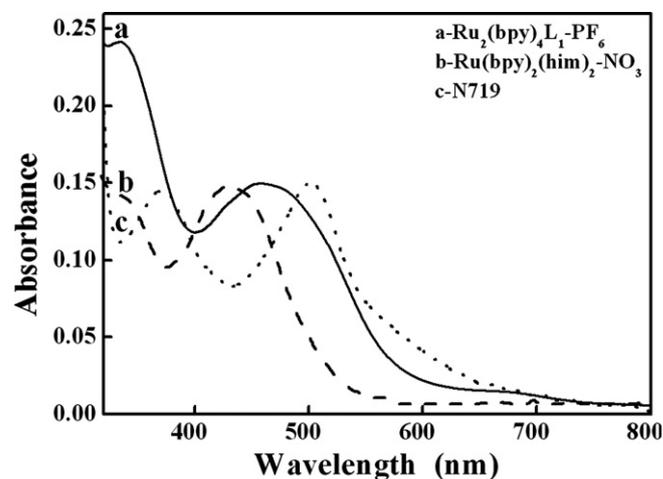


Fig. 2. UV-Vis spectra of the three Ru(II)-bipyridyl dyes.

the reaction of surface hydroxyl of TiO₂ and oxygen atoms from the azo-benzene carboxylic spacer (L). Similarly, Ru(bpy)₂(him)₂-NO₃ can also loosely attach to TiO₂ through hydrogen-bonds between un-coordinated N atom in imidazoles and surface hydroxyl. Therefore, it is reasonable to conclude that there exists different electron transfer mechanism between the tightly and loosely attached dyes in Pt/P25 suspension, which will be further discussed below.

3.2. Reaction of H₂ evolution over dye-sensitized Pt/P25

Primary results showed that there was no obvious H₂ production over Pt/P25 without dye or sacrificial reagent under visible-light irradiation, indicating that the band-gap excitation was not occurred. H₂ evolution was detected in water-methanol solution containing dye-sensitized Pt/P25, and partially produced by the conversion of methanol in this system [20]. Therefore, to check whether this reaction was photocatalytic or not, the reaction was repeated but using TEOA as sacrificial reagent, which could not contribute H₂ production during the photocatalytic reaction [7].

Table 1 shows the H₂ evolution rates over dye-sensitized Pt/P25 under visible-light for 1 h, and Fig. 3 presents the H₂ production amount as a function of time from different sacrificial reagents. As can be seen, all dyes show obvious photosensitization, indicating dyes can be efficiently excited and inject electrons into TiO₂, and then transport it to the loaded Pt to produce H₂ [8,12]. Furthermore, a much higher H₂ yield is obtained by using methanol in comparison with TEOA, which is similar to the previous report [20]. The following are the reasons for rationalizing this phenomenon.

First, methanol can be oxidized to CH₂O, HCOOH and transformed to CO₂ and H₂ in Pt/TiO₂ suspension [19–22], some methanol was consumed during the reaction and the formed CH₄ and H₂ were identified in the gas mixtures [19,20]. These findings indicate that H₂ is partially contributed from methanol, and the following reactions might take place in the water-methanol solution [12,19–22].

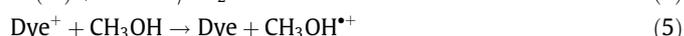


Table 1
Effect of different dyes on the H₂ production over Pt/P25 from different sacrificial reagent solutions

Dye sensitized Pt/P25	H ₂ evolution rate (TON ^a) from CH ₃ OH solution (μmol/g h)	H ₂ evolution rate (TON ^a) from TEOA solution (μmol/g h)	Dye adsorption amount on 40 mg catalyst (μmol)
Ru ₂ (bpy) ₄ L ₁ -PF ₆	874.3 (7055.1)	53.3 (554.3)	0.062
Ru(bpy) ₂ (him) ₂ -NO ₃	561.3 (2178.0)	48.8 (209.5)	0.027
N719	271.5 (2636.7)	43.7 (445.5)	0.024

^a Moles of H₂ produced per mole of ruthenium complex.

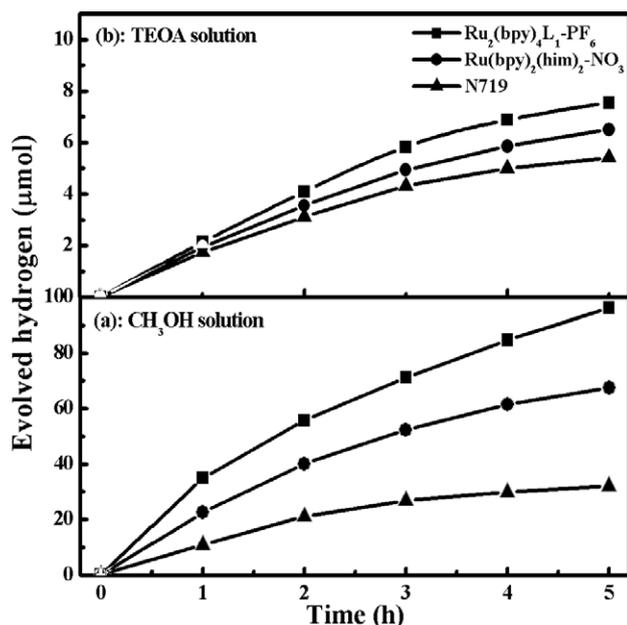
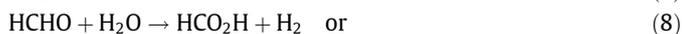


Fig. 3. Time courses of the photocatalytic H₂ production over the dye-sensitized Pt/P25.



Second, TEOA can be oxidized by means of losing one of the unpaired electrons of N atom [23], so the protonated TEOA are difficult to oxidize. The pH value might have effects on the adsorption of TEOA, and then on the reactions of H₂ evolution and TEOA oxidation. Namely, the photocatalytic H₂ evolution should occur at an optimal pH [23] but the present system is not possibly at the optimal value.

Third, the turn over numbers (TON) of photocatalytic H₂ evolution in TEOA solution are much lower than those in methanol solution (Table 1), also indicating that H₂ is at least partially produced by the conversion of methanol [20].

Theoretically, N719 should show a better photosensitization than the other dyes due to its much tight fixation, which is beneficial for the dye adsorption and electron-injection [5,14]. However, N719 exhibits the lowest photosensitization among the three dyes from both sacrificial reagent solutions (Table 1). For example, the TON of N719 sensitized Pt/P25 in both sacrificial reagent solutions are also much lower than those over Ru₂(bpy)₄L₁-PF₆ sensitized Pt/P25. H₂ evolution rates over Ru₂(bpy)₄L₁-PF₆ and Ru(bpy)₂(him)₂-NO₃ sensitized Pt/P25 in methanol solution are about 3.22 and 2.04 times as that over N719 sensitized Pt/P25, respectively.

These phenomena can be rationalized by considering the following reasons.

The injected electrons can also transfer backward the oxidized dye due to the tight linkage between N719 and TiO₂ [14]. Whereas this electron backward transfer can be retarded in Ru₂(bpy)₄L₁-PF₆ and Ru(bpy)₂(him)₂-NO₃ sensitized Pt/P25, because the coordination circumstances of Ru need change to meet with the increase of valence state after the electron-injection. And this change likely means the divorce of oxidized dyes from TiO₂ due to their loose linkage as well as the adsorbed ground state molecules usually locating the position of minimum energy on the surface [5]. Anyway, those loose linkages such as oxygen-bridges and hydrogen-bonds might promote the electron-injection, and the oxidized dye can divorce timely from TiO₂ to avoid the backward transfer, which results in higher H₂ production efficiency.

In addition to the widest visible-light harvesting (Fig. 2) due to its larger molecular area and conjugation system [4–7], the highest H₂ evolution efficiency over Ru₂(bpy)₄L₁-PF₆ sensitized Pt/P25 can be ascribed to the more efficient electron transfer. The excited electrons of this dye can be transferred through two ways, MLCT (metal-to-ligand) and MMCT (metal-to-metal), while Ru(bpy)₂(him)₂-NO₃ and N719 conduct a single electron transfer (MLCT). Amadelli et al. have reported two Ru(bpy)₂(CN)₂-units in a trinuclear dye [(Ru(bpy)₂(CN)₂)₂Ru(dcbpy)₂] acted like antenna to absorb light and transported it to the other Ru(dcbpy)₂-unit connected with TiO₂ through the tight chemical bonds [3]. According to this view, ‘antenna effect’ must exist in Ru₂(bpy)₄L₁-PF₆ sensitized Pt/P25, which can enhance the visible-light harvesting and electron transfer efficiency. Whereas the TON of Ru(bpy)₂(him)₂-NO₃ sensitized Pt/P25 in both sacrificial reagent solution are lower than those over Ru₂(bpy)₄L₁-PF₆ or N719 sensitized Pt/P25. It is possibly ascribed to the multilayer adsorption of Ru(bpy)₂(him)₂-NO₃ on the surface of catalyst due to the much higher adsorption amount (Table 1), which lead to the retardation of electron-injection and then to a lower TON value. The further researches are now under investigation.

3.3. Comparative investigation on the steady H₂ evolution over dye-sensitized Pt/P25

To observe the reproducibility of H₂ production, H₂ evolution rates were checked every 1 h, in which the next portion of methanol or TEOA (10 mL) was added into the same dye-sensitized Pt/P25 suspension. Ru₂(bpy)₄L₁-PF₆ and Ru(bpy)₂(him)₂-NO₃ sensitized Pt/P25 exhibit more steady and much higher increases in H₂ evolution than N719 sensitized one upon prolonging the irradiation time (Fig. 3), while H₂ evolution for N719 almost remain unchangeable after 3 h irradiation. Namely, N719 possesses several advantages such as stability and less influence of pH, but it shows the worst photosensitization in comparison with the loosely linked dyes.

Ru₂(bpy)₄L₁-PF₆ sensitized Pt/P25 have the pronounced advantages of high H₂ evolution efficiency and preferable durability. It may be attributed to the stable chemical structures, the lower risk of backward electron transfer and/or even the photodegradation

due to the oxidized dye molecules can be timely disengaged from TiO₂ as described above. The best photosensitization of Ru₂-(bpy)₄L₁-PF₆ is a demonstration of the operation of ‘antenna effect’ in TiO₂ sensitization process. Apparently, the photosensitizing behavior on Pt/P25 was related not only to the linkage mode between the dye and TiO₂, but also to the coordination circumstances and physicochemical properties of Ru(II)-bipyridyl dyes. The dynamic equilibrium between the linkage of ground state dye with TiO₂ and the divorce of oxidized dye from the surfaces seems to be beneficial for electron injecting and hindering the electron transfer backward, which can improve the electron transfer efficiency and then the H₂ evolution efficiency [4–7].

4. Conclusions

An efficient H₂ production over dye-sensitized Pt/P25 under visible-light irradiation was demonstrated in the presence of sacrificial reagent. Three Ru(II)-bipyridyl complex show different photosensitization due to their differences in coordination circumstances, physicochemical properties and interaction with TiO₂. The more steady increase in H₂ evolution for Ru₂(bpy)₄L₁-PF₆ indicates that the use of ‘antenna’ sensitizer may constitute a viable strategy to overcome problems of light-harvesting in the photosensitization process. The loosely attached Ru₂(bpy)₄L₁-PF₆ have the pronounced advantages of high H₂ evolution and preferable durability in comparison with N719. The dynamic equilibrium between the linkage of ground dye and divorce of oxidized dye seems to play a crucial role in the photochemical behavior in dye-sensitized Pt/P25, which can enhance the electron-injection and hinder the backward transfer, and then improve the H₂ evolution efficiency. These results suggested interesting possibilities for the preparation of more efficient dyes that can couple the functions of a sensitizer, which is bound to the surface of TiO₂ and inject the photoelectron, and an antenna, which can realize the intra-molecular energy

transfer from highly absorbing chromophoric groups by tuning the molecular components.

Acknowledgments

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