Synthesis, characterization of a new photosensitive compound

[Ru(bpy)₂ (TPAD)](PF₆)₂ and its application for photocatalytic hydrogen production

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Abstract

A new photosensitive compound based on triphenylamine donor and ruthenium(II), namely [Ru(bpy)₂(TPAD)](PF₆)₂ (**PS1**, bpy=2,2'-bipyridine, TPAD=N-(4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenyl)-N-phenylbenzenamine), had been synthesized and characterized by elemental analysis, ¹H NMR, MS spectra, UV, PL and CV measurements. The target photocatalyst, **PS1**/0.5wt%Pt/TiO₂, was prepared by sensitizing **PS1** to 0.5wt%Pt/TiO₂ and characterized by SEM and XRD. The **highest** hydrogen evolution reached to 9500 μmol·(g catalyst)⁻¹ (475 μmol, 31.7 TON and TOF 5.8 vs. **PS1**) under the optimal conditions with 0.05 g·L⁻¹ of **PS1**, and 5% of TEOA at pH 11 with the irradiation of 5.5h. The mechanism of hydrogen evolution was also briefly discussed in the present work.

Keywords: Triphenylamine derivative; Ruthenium(II) photosensitive complex; TiO₂ photosensitive catalyst; Photo-catalytic hydrogen production

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1 Introduction

Photocatalytic H₂ evolution utilizing solar energy has attracted considerable attentions in recent years, which provides a new alternative to solve environmental and energy issue [1-4]. Among the reported semi-conductors, TiO₂ has been widely used as a promising photocatalytic material because of its excellent photocatalytic performance, long-term stability and non-toxicity[3]. However, its wide band gap (3.2eV), which can only utilize ultraviolet light, limits its application in photocatalytic H₂ evolution through visible light that occupies a large portion of solar spectrum (approximately 42%) near the earth's surface. To extend the light-absorbing range of nano-TiO₂ to improve its catalytic activity, the dye sensitization is usually seen as an effective strategy which has been successfully applied in dye-sensitized solar cells (DSSCs) [5- 9].

Ruthenium (II) polypyridine complexes have been widely used as photosensitizer (PS) based on their wide and strong metal-to-ligand charge transfer (MLCT) absorption, high chemical stability of the excited states, appropriate oxidation potential [5-7] and the unique structural properties which can be tuned through ligand modification [8-10]. It has also been found that triphenylamine(TPA) and its derivatives are also an excellent electronic donor which have been applied in the area of dye-sensitized solar cell (DSSC)[11-15]. However, few information was reported in solar photolysis water to release hydrogen so far. For example, Hirano and Suzuki reported a maximum H₂ evolution rate of 23.1μL·h⁻¹ in the photocatalytic system consisted of Pt/TiO₂ of 0.3wt % as catalyst, Ru(bpy)₃²⁺ (1mM) as PS and EDTA (ethylenediaminetetraacetic acid disodium salt) (0.1M) as sacrificial reagent over irradiation for 1 hour with 500w Xe lamp[16]. Park and Choi reported a TiO₂ composite photocatalyst containing Ru(bpy)₃²⁺, in which Ru(bpy)₃²⁺ cation was bound to perfluorosulfonate polymer (Nafion) layer on surface of TiO₂ particles, the maximum hydrogen generation rate of 80 μmol/h was recorded under the optimal conditions with TiO₂(P25) of 0.5 g/L, Nafion of 45mg/g-TiO₂, Ru(bpy)₃²⁺ of 20μM and EDTA of 2mM, pH=6, corresponding to an photonic efficiency of 2.6% [17]. Very recently, Choi and co-workers constructed a photocatalytic

system containing TPA derivative-supported TiO_2 as catalyst and triethanolamine (TEOA) as sacrificial reagent (SR), in which a hydrogen evolution of $41\mu\text{mol}$ was recorded at pH 10 [18].

Scheme 1

As stated above, in these ruthenium complexes as photosensitizer reported in the literatures, some organic compounds containing anchoring groups (such as $-\text{COOH}$, $-\text{PO}_3\text{H}_2$) were mostly used as ligands to improve the adhesion force of the target photosensitizer on TiO_2 [18,19] (Scheme 1), in which the anchoring groups as mentioned above were introduced into the organic molecules that were conducive to the electron-injection from the excited dye to catalyst in the photolytic reaction; on the other hand, the injected electrons might also be returned to the ground state of dye due to its tight linkage with TiO_2 [19,20,21].

Inspired by the above work, considering the TPA moiety contains three benzene rings which has a strong electron-donating ability, and it can suppress intermolecular aggregation because of its non-planar and the disturbance of the π - π stacking, in the present work, we attempted to design and synthesize a new organic ligand based on TPA derivative, namely TPAD (TPAD= N-4-(1H-imidazo[4,5-f] [1,10] phenanthroline-2-yl)phenyl)-N-phenyl-benzenamine), to replace those traditional organic ligands containing the anchoring groups (such as $-\text{COOH}$, $-\text{PO}_3\text{H}_2$) for preparing ruthenium photosensitive complexes. Significantly, it does not contain the anchoring groups in the synthesized TPAD molecule. And then, in order to adjust the electronic environment around Ru(II) ion center and the energy level of Ru(II) complex, a new photosensitive complex of ruthenium(II), namely $[\text{Ru}(\text{bpy})_2(\text{TPAD})](\text{PF}_6)_2$ (PS1, bpy = 2,2'-bipyridine) was synthesized and used to prepare the target composite catalyst PS1/0.5wt%Pt/ TiO_2 by sensitizing PS1 onto Pt/ TiO_2 (namely physical adsorption). Physical adsorption is a type of loose linkage, which can avoid the electrons in excited state return to the oxidized photosensitizer. All of those would be favorable to greatly improve the efficiency of sensitization of TiO_2 . Furthermore, the hydrogen evolution activity of the target catalyst PS1/0.5wt%Pt/ TiO_2 was further evaluated through the constructed photocatalytic hydrogen system under the irradiation of visible light.

2 Experimental

2.1 Chemicals and instruments

4-(diphenylamino) benzaldehyde was synthesized by Vilsmeier-Haack formylation reaction to treat TPA with POCl₃ in DMF [22]. 1,10-phenanthroline-5,6-dione, [Ru(bpy)₂Cl₂].2H₂O and TPAD were synthesized according to literatures methods [22-24]. The [Ru(bpy)₂(TPAD)](PF₆)₂ was prepared by a modified literature procedure [25]. Degussa P25 (nano-TiO₂) purchased through traditional commercial channel; all other chemicals were analytical grades and used without further purification.

Elemental analyses for C, H and N were performed on a Carlo-Erba 1160 elemental analyzer. ¹H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz). Electrospray ionization mass spectroscopy (ESI-MS) was performed with a Bruker Esquire-3000 instrument using methanol as eluant. The diffuse reflectance spectra (DRS) were recorded on a Varian Cary 5000 UV-Vis spectrophotometer using BaSO₄ as reference, and transformed to the absorption spectra according to Kubelka-Munk relationship. The X-ray diffraction (XRD) patterns were measured on an X' Pert PRO X-ray powder diffractometer with Cu-K α radiation ($\lambda = 1.5418\text{\AA}$).

2.2 Synthesis of photosensitive complex [Ru(bpy)₂(TPAD)](PF₆)₂ (PS1)

The photosensitive complex PS1 was synthesized by multi-step reaction, and the synthetic route was shown in Scheme 2.

Scheme 2

2.2.1 Synthesis of triphenylamine derivative TPAD

The TPAD was synthesized by refluxing a mixture of 1,10-phenanthroline-5,6-dione (0.21g, 1mmol), 4-(diphenylamino) benzaldehyde (0.273g, 1mmol) and ammonium acetate (1.54g, 20mmol) in glacial acetic acid (15mL) for 4h under N₂ atmosphere. After cooling to room temperature, the solution was poured into cold water and adjusted to pH 7 with dilute aqua ammonia to give a yellow solid. The crude product was collected, washed with water and purified by recrystallization from

ethanol to get a yellow powder (yield: 80%). Anal. Calcd. for $C_{31}H_{21}N_5$ (%): C 80.32, H 4.57, N 15.11; Found (%): C 80.97, H 4.61, N 14.42. 1H NMR (400 MHz, $CDCl_3$): δ 8.72-8.87 (4H), 8.02-8.18 (2H), 7.30-7.43 (2H), 7.17-7.26 (4H), 6.91-7.10 (8H). ESI-MS m/z : 464.4.

2.2.2 Synthesis of $[Ru(bpy)_2(TPAD)](PF_6)_2$ (PS1)

PS1 was synthesized according to a modified literature procedure [25]. A mixture of *cis*- $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (0.52 g, 1mmol), TPAD (0.45 g, 0.98mmol), ethanol (16mL) and H_2O (4mL) was refluxed at 80 °C for 16h under nitrogen atmosphere, resulting in a red-brown solution. Then it was cooled to room temperature and vacuum evaporation to remove the solvent using a rotary evaporator. The resulting solid was dissolved in minimum amount of methanol. After filtered, a four-fold excessive of NH_4PF_6 solution was added drop wise into the above filtrate and an orange precipitate was obtained (yield: 60%). Anal. Calcd. for $C_{51}H_{37}RuN_9P_2F_{12}$ (%): C 52.49, H 3.20, N 10.80; Found (%): C 53.17, H 3.93, N 11.41. 1H NMR (400 MHz, $DMSO-d_6$): δ 9.12-9.21 (2H), 9.05 (1H), 7.75 (1H), 7.54-7.79 (7H), 7.38-7.49 (4H), 7.21-7.34 (10H), 7.06-7.13 (8H), 6.92-7.06 (4H). ESI-MS m/z : 1022.2 ($[M-PF_6]^+$), 876.3 ($[M-2PF_6]^+$).

2.3 Preparation of the target photocatalyst PS1/0.5wt%Pt/TiO₂

According to the literature [26], the amount of Pt-loaded was 0.5%, the H_2 production activity was the highest, therefore, 0.5% Pt-loaded TiO_2 was prepared by photo-deposition method as described by literature [26]. Then, the above sample (0.5wt%Pt/ TiO_2 , 0.40g) was treated by ultrasound with 0.5% CH_3CN solution. Thereafter certain amount of **PS1** was added into the processed sample. The reaction mixture was stirred overnight away from sunlight to establish the absorption-desorption equilibrium. After centrifuged, the crude solid was washed repeatedly with water and dried at 90°C for 12h to give a target photocatalyst **PS1/0.5wt%Pt/TiO₂**.

2.4 Experimental procedure of photocatalytic H_2 evolution

The hydrogen evolution activity of the photosensitive catalyst **PS1**/0.5wt% Pt/TiO₂ was evaluated on a quartz glass reactor (230mL) with a quartz window. A 300W Xenon lamp equipped with a cut-off filter ($\lambda > 420$ nm) was used as the light source. The photocatalytic reaction was carried out with 100mL aqueous suspension containing 50mg catalyst and proper amount of sacrificial reagent under continuous magnetic stirring. The pH was adjusted by dilute hydrochloric acid or sodium hydroxide. Before irradiation, the reaction mixture was pre-purged with N₂ for 20min to remove O₂. During the reaction, the temperature was kept constant by circulating water. The hydrogen evolved was detected by a HP4890D gas chromatograph equipped with a thermal conductivity detector (TCD) and a 6 feet stainless column packed with porapak Q6 (80/100 mesh).

3 Results and discussion

3.1 UV-Vis spectra

Fig.1

Fig.1a displayed the UV-visible spectra of **PS1** in CH₃CN solution ($\times 10^{-5}$ M). As can be seen from **Fig.1a**, there were four absorption peaks at about 219, 283, 363 and 469nm observed in the UV-visible spectra of **PS1**. The strong absorptions at about 219nm and 283nm were assigned to be the $\pi \rightarrow \pi^*$ electronic transition for **TPAD** (219nm) and bpy (283nm), the two broad absorption bands at around 363nm and 469nm could be attributed to $d \rightarrow \pi^*$ electron transition from metal to ligand **TPAD** (219nm) and bpy (MLCT) [27,28], indicating that UV-Vis spectra of **PS1** was extended to the visible-light responding region. **Fig.1b** displayed the solid state diffuse reflectance UV-Vis spectra of TiO₂, 0.5wt%Pt/TiO₂ and **PS1**/0.5wt%Pt/TiO₂, respectively. The strong absorption band at about 300 nm was originated from TiO₂. For **PS1**/0.5wt%Pt/TiO₂, the broad absorption band at about 450 nm could be attributed to the MLCT transition of **PS1** [14].

3.1 XRD patterns

The XRD pattern of TiO₂, 0.5wt%Pt/TiO₂ and **PS1**/0.5wt%Pt/TiO₂ were shown in **Fig. 2**.

Fig. 2

As shown in Fig.2, the diffraction peaks located at 25.2°, 37.9°, 48.1°, 53.9°, 62.7°, 68.8° and 75.3°, corresponding to the crystalline planes of (101), (103), (200), (105), (213), (116) and (107) of anatase TiO₂. The results indicated that the crystal phase of TiO₂ did not change in the processes of Pt deposition and **PS1** loading. However, the diffraction peak of Pt (39.8°) was not observed probably due to its high dispersion and its unusually low content in the target photosensitive catalyst.

3.2 SEM-EDS images

To investigate the morphology information of TiO₂, 0.5wt%Pt-TiO₂ and target photosensitive catalyst **PS1**/0.5wt%Pt/TiO₂, the SEM and EDS images of the three samples were performed and shown in Fig.3.

Fig.3

As shown in Fig.3a, the spherical particles with a non uniform particle sizes could be observed in the SEM images for P25 (commercially available TiO₂ powders), and the diameters of sample particles changed from 20nm to 50nm which indicated more packed clusters and less segregated particles. The EDS mapping showed that the existence of Ti and O element in the P25 (Fig.3d). Compared with P25, the sample of 0.5wt% Pt-loaded TiO₂ powders exhibited a lower agglomeration degree in its SEM image (Fig.3b), the size distributions were more uniformly with around 20-30nm in diameters, and Pt element was observed in the EDS mapping for 0.5wt % Pt-loaded TiO₂ sample (Fig.3e). The SEM image of the target catalyst (**PS1**/0.5wt%Pt/TiO₂, see Fig.3c) displayed loose and unconsolidated nano-particles with diameters ranging from 15nm to 25nm, and there were no packing clusters of initial P25 sample as observed in the target photosensitive catalyst **PS1**/0.5wt%Pt/TiO₂, and its corresponding EDS mapping showed that all elements were well dispersed. In addition, Ru element was also found in the target sample (Fig.3f), confirming **PS1** had been sensitized onto the 0.5wt % Pt/TiO₂. However, in the EDS images of the three samples, both Pt and Ru displayed very weak signal strength separately in comparison with that of Ti and O, which was due to the content of Pt deposition and **PS1** on TiO₂ in the target photocatalyst was too

low to be detected for the signals. Actually, a similar phenomenon had also been reported in some literatures [29].

3.3 Parameter optimization for photo-catalytic hydrogen evolution

As is known to us all, H₂ evolution activity is significantly impacted by some key factors, such as the dosage of PS, the types and concentration of sacrificial reagent, the pH level of the medium [14,29]. Therefore, several key parameters of influencing H₂ evolution were further optimized in the present work by the constructed photocatalytic system consisted of target photosensitive catalyst of 0.05 g·L⁻¹, sacrificial reagent of 5% (v: v) with the irradiation time of 5.5 h, and the result was displayed in Fig. 4.

Fig.4

3.3.1 Effect of PS1 concentration

Fig.4a presented the developing trend of hydrogen evolution with **PS1** concentration ranging from 0 to 2.5×10⁻⁴ mol·L⁻¹. As shown in Fig.4a, the hydrogen evolution increased from 151μmol to 475μmol (31.7 TON and TOF 5.8 vs. **PS1**) with the increase of **PS1** concentration in the range from 0.5×10⁻⁴ to 1.5×10⁻⁴ mol·L⁻¹, however, the variation trend was reversed with the further increase of **PS1** concentration from 1.5×10⁻⁴ to 2.5×10⁻⁴ mol·L⁻¹. In the several concentrations of **PS1**, the highest hydrogen evolution (when the concentration of PS1 was 1.5×10⁻⁴ mol·L⁻¹) is higher than the lowest hydrogen evolution (when the concentration of PS1 was 0.5×10⁻⁴ mol·L⁻¹) about 2 times, the result indicated that **PS1** sensitization was of critical importance to hydrogen evolution of target catalyst. However, an excessive **PS1** was sensitized onto 0.5wt%Pt/TiO₂ that would lead to a dramatic fall of hydrogen evolution because the excessive PS molecule could become an electron-hole recombination center to result in the decline of hydrogen evolution for the target sample [28].

In comparison, the hydrogen evolution of the target catalyst (9500μmol·g⁻¹catalyst⁻¹) in the present work was higher than that of [Ru(bpy)₂(dcbpy)](PF₆)₂ (1533 μmol·g⁻¹) [30] and triphenylamine derivative (2050 μmol·g⁻¹) in early reports [21], the result implied triphenylamine

derivative was introduced to photosensitive complex that could significantly improve the hydrogen evolution of the target catalyst.

3.3.2 Effect of sacrificial reagent

Fig.4b depicted the changing trend of hydrogen evolution with different types of sacrificial reagents. It can be seen that the types of sacrificial reagent had a significant effect on hydrogen evolution. The maximum hydrogen yield of 475 μ mol (31.7 TON and TOF 5.8 vs. **PS1**) was observed for TEOA in 5.5h, following by 378 μ mol (25.2 TON and TOF 4.6 vs. **PS1**) for ascorbic acid and 252 μ mol for EDTA in 4.5h. In comparison, when triethylamine(TEA) was used as sacrificial reagent, the hydrogen evolution was only 58 μ mol in 2h irradiation. This phenomenon might be attributed to the different electron-donating ability of the four sacrificial reagents.

According to the above result, TEOA was used as SR in the present work, the effect of TEOA concentration (varying from 3% (v:v) to 11% (v:v)) on hydrogen production was further discussed and the result was illustrated in Fig.4c. As shown in Fig.4c, the hydrogen evolution of 372 μ mol (25.1 TON and TOF 4.5 vs. **PS1**) occurred at 3% (v:v) of TEOA, and the maximum hydrogen evolution of 475 μ mol occurred at 5% (v:v) of TEOA. Thereafter, the hydrogen evolution decreased to 404 μ mol (26.9 TON and TOF 4.9 vs. **PS1**) with 7% (v:v) of TEOA, which was probably due to the increasing of adsorbed TEOA on TiO₂ surface. Though the **PS1** molecule could be regenerated by accepting electron from TEOA, a competitive adsorption between TEOA and **PS1** reduced the adsorption efficiency of **PS1** on TiO₂ surface which caused a decrease of hydrogen evolution.

3.3.3 Effect of pH

The pH value of medium is another important factor effecting hydrogen evolution. Fig.4d depicted the trend of hydrogen evolution with pH value ranging from 5 to 13 in irradiation of 5.5h. As illustrated in Fig.4d, the maximum hydrogen evolution of 475 μ mol (31.7 TON and TOF 5.8 vs. **PS1**) appeared at pH 11. However, a higher or lower pH level would lead to a remarkable decrease in hydrogen evolution (such as 125 μ mol at pH 9 and 152 μ mol at pH 13). The phenomenon could be

expected because it might cause protonation of TEOA at a lower pH level, which would lead to the partial loss of its electron donor ability. Likewise, it was not favorable for H₂ production at a higher pH level because the concentration of H⁺ was too low [30,31].

3.4 The electrochemical behavior of PS1 and probable mechanism of H₂ evolution

To explain the possible electron transfer mechanism from the excited **PS1** molecule to the conductive band (CB) of TiO₂, both the fluorescence property and electrochemical behavior of **PS1** had been investigated by fluorescence spectra and cyclic voltammograms (CV), the results were displayed in Fig.5a and Fig.5b, respectively. Correspondingly, both the electrochemical potentials and energy levels of **PS1** were listed in Tab.1.

Fig.5

As shown in Fig.5a, the excitation of **PS1** at 480nm resulted in a maximal fluorescence emission at 605nm in CH₃CN solution (10⁻⁵M). The excited state energy (E_g) of **PS1** could be calculated according to $E_g = hc/\lambda_o = 1240/\lambda_o$ ($\lambda_o = 550\text{nm}$, $E_g = 2.25\text{eV}$).

Tab.1

As shown in Fig.5b, **PS1** exhibited two irreversible oxidation peaks and reduction peaks, the first and the second oxidation peak was observed at 0.72V and 1.52V separately, which could be attributed to Ru(II)/Ru(III) couple and Ru(III)/Ru(IV) couple. At the same time, the first and the second reduction peak for the Ru(II) complex was observed at -1.43V and -1.71V, respectively. Both the first and the second reduction potentials of **PS1** are more positive than that of [Ru(bpy)₃](PF₆)₂ (-1.85 V), indicating a greater electronic impact of chelation on **TPAD** than 2,2'-bpy. We could see from Tab.1 that **PS1** displays more positive reduction potential in comparison with [Ru(bpy)₃](PF₆)₂, which supports the belief that ligand **TPAD** decreased the LUMO energy and enhanced the electron affinity of **PS1** molecule. This phenomenon was consistent with some earlier observations [32,33].

The oxidation potential of **PS1** was somewhat less positive than that of [Ru(bpy)₃]²⁺, indicating the increase of the HOMO level. For **PS1**, the electron-donating group (**TPAD**) may be responsible

for this. Using the CV data, the electrochemical energy gaps of **PS1** had been calculated, and the results were listed in Tab.1. As shown in Tab.1, the E_g of **PS1** was 2.25eV, which was smaller than that of $[\text{Ru}(\text{bpy})_3]^{2+}$ [32], the result was consistent with the phenomenon that the emission spectrum of **PS1** ($\lambda_{\text{em}}=605\text{nm}$) undergone significant redshift compared to $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\lambda_{\text{em}}=600\text{nm}$ [33]). The E_{HOMO} of **PS1** (-5.52eV) was much higher than the E_{VB} of TiO_2 (-7.6eV). Similarly, the E_{LOMO} of **PS1** (-3.27eV) was significantly higher than E_{CB} (conduction band energy) of TiO_2 (-4.40eV), indicating that the **PS1** molecule could be excited under visible light irradiation to become the excited **PS1*** which can inject electrons to the conduction band (CB) of TiO_2 to initiate the following photocatalytic reactions.

According to energy gap data, combined with the result reported in the literature [34], a possible mechanism for photocatalytic H_2 evolution was speculated as follows (Fig.6). As shown in Fig.6, the ground state **PS1** molecule was excited to form the excited **PS1*** under the irradiation of visible light, then the **PS1*** injected electron to conduction band (CB) of TiO_2 to initiate the photocatalytic reaction and **PS1*** changed itself into a reduced state **PS1⁺** at the same time. Meanwhile, the excited **PS1⁺** could accept electron transferred from TEOA to regenerate the ground state **PS1** molecule and completed a reaction cycle (as shown in Fig. 6). Because the Fermi level of Pt was lower than that of TiO_2 , hence the electron could migrate from the conduction band of TiO_2 to Pt, the hydrogen was generated by the reduction of proton [35].

Fig.6

4 Conclusions

A new photosensitive compound, namely $[\text{Ru}(\text{bpy})_2(\text{TPAD})](\text{PF}_6)_2(\text{PS1})$, had been synthesized and characterized. Thereafter, the target photosensitive catalyst **PS1**/0.5wt%Pt/ TiO_2 was prepared by sensitizing **PS1** to Pt/ TiO_2 . A maximum hydrogen evolution of $9500\mu\text{mol}\cdot(\text{g catalyst})^{-1}$ (475 μmol , 31.7 TON and TOF 5.8 vs. **PS1**) was observed under the optimal condition with 0.05 g·L⁻¹ of **PS1**, and 5% of TEOA at pH 11 with the irradiation of 5.5h. The results showed

that **PS1** could be used as a potential photosensitive material for conversion of solar energy to clean hydrogen. In addition, the mechanism of hydrogen evolution was also discussed in the present work.

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Table

Tab.1 Electrochemical potentials ^a and energy levels of compound **PS1**

Tab.1

Complex	$E_{1/2}^{red1}$	$E_{1/2}^{red2}$	$E_{1/2}^{ox1}$	$E_{1/2}^{ox2}$	E _g (eV)	E _{HOMO} (eV)	E _{LUMO} (eV)
[Ru(bpy) ₃](PF ₆) ₂ ^b	-1.85	-2.03	0.70		2.29	-5.44	
PS1	-1.43	-1.71	0.72	1.52	2.25	-5.52	-3.27

a. Oxidation potential measured by CV, $E_g = hc/\lambda_{00}$ ($h = 6.626 \times 10^{-34}$ J·S, $c = 3.0 \times 10^8$ m/s, $\lambda_{00} = 550$ nm (See Fig.5a), $E_{HOMO} = -|eE_{ox} + 4.74|$, $E_g = E_{LUMO} - E_{HOMO}$; b. Reference [32]

Figure captions

Scheme 1 The structures of four Ru(II)-bipyridyl complexes

Scheme 2 Graphical synthetic route of **PS1**

Fig.1 (a) UV-Vis spectra of complex **PS1** ($\times 10^{-5}$ M) in CH_3CN solution; (b) The solid state diffuse reflectance UV-Vis spectra of TiO_2

Fig. 2 XRD patterns of TiO_2 , 0.5wt%Pt/ TiO_2 , and **PS1**/0.5wt%Pt/ TiO_2

Fig.3 The SEM and the EDS images of pure TiO_2 (P25)(a),(d)), 0.5wt%Pt- TiO_2 ((b),(e)), **PS1**-0.5wt%Pt- TiO_2 ((c),(f))

Fig.4 Effects of key parameters on hydrogen evolution at the fixed catalyst of $0.05 \text{ g}\cdot\text{L}^{-1}$, sacrificial reagent (SR) of 5% (v:v) with irradiation time of 5.5h: (a) **PS1** concentration; (b) SR types ; (c) Concentration of TEOA; (d) pH level of medium

Fig.5 (a) Excitation and emission spectra of **PS1**; (b) The CV gram of **PS1** with sample concentration of $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ in $0.05 \text{ mol}\cdot\text{L}^{-1}$ n-Bu₄NPF₆/DMF solution at a scan rate of 100mV/s; working electrode: glassy carbon, auxiliary electrode: Pt wire, reference electrode: Saturated calomel electrode (SCE)

Fig.6 Possible hydrogen evolution mechanism for the present photocatalytic system

Scheme 1

Scheme 2

Fig.1

Fig. 2

Fig.3

Fig.4

Fig.5

Fig.6