Photocatalytic H₂ generation based on noble-metal-free Co(II) photocatalyst under visible-light-driven

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Abstract: A noble-metal-free catalyst, namely Co(II) complex [Co(dbp)₂]Cl₂ (dbp= 4,4'-dimethyl-2,2'-bipyridyl), had been prepared for photocatalytic H₂ generation. The H₂ generation was achieved by the constructed homogeneous photocatalytic system comprising of [Co(dbp)₂]Cl₂ as catalyst, Eosin Y as photosensitizer and triethanolamine as sacrifice agent under visible-light-driven ($\lambda > 420$ nm). The maximum H₂ yield of 169.2 μ mol appeared at target catalyst of 4.0×10^{-4} M, EY²⁻ of 4.0×10^{-4} M and 10% TEOA (v/v) at pH 9 in CH₃CN/H₂O of 1:1(v/v), indicating that this complex could also be used as a potential photocatalytic material for H₂ evolution under the irradiation of visible light. In addition, the H₂ generation mechanism was also briefly discussed.

Keywords: Cobalt(II) photocatalyst, Photocatalytic system based solely upon noble-metal-free system, Photocatalysis, H₂ generation, Mechanism.

1. Introduction

To meet the serious challenge of the growing global energy depletion and environmental pollution problems, people try to develop a novel, renewable and clean energy [1-3]. H₂ energy is considered to be a clean and efficient energy source, and has been deemed as a potential energy carrier in the 21st century. It is believed that hydrogen-based economy may contribute to meeting the growth in world energy demand. Among different H₂ generation methods, the photocatalytic H₂ generation utilizing solar energy has attracted considerable attention because of its potential applications in recycling utilization of renewable resource, reducing the

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consumption of fossil fuel and subsequent emissions of greenhouse gases. However, the majority of photocatalytic systems still employ noble metals as catalyst or photosensitizer (PS, such as Ru, Pd, Pt etc.) [4-6]. Not long ago, Eisenberg et al. found that a Co (III) complex, namely $[\text{Co}(\text{dmgH})_2(\text{py})\text{Cl}]$, could be used as a photocatalyst in a homogeneous system for H_2 generation by visible-light-driven, and affording a maximum H_2 generation of 181 TON (vs. Cat.) when the Rose Bengal (RB^{2-}) and triethanolamine (TEOA) was used as PS and sacrificial agent, respectively[7]. More recently, Sun and his co-workers also reported a photocatalytic system comprising $[\text{Co}(\text{bpy})_3]\text{Cl}_2$, RB^{2-} and triethylamine (TEA), and the corresponding H_2 evolution of 207.6 TON (vs. Cat.) was observed in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ under optimal conditions[8].

Until recent times, Natali and co-workers prepared a new Co(II) porphyrin catalyst $\text{Co}(\text{II})\text{NMeTPyP}^{4+}$ {where, NMeTPyP^{4+} = meso-tetrakis (1-methyl-pyridinium-4-yl) -porphyrin}, and constructed a high-efficiency photocatalytic system combined with $\text{Ru}(\text{bpy})_3^{2+}$ sensitizer and ascorbic acid sacrificial donor for H_2 production by visible light-driven, a high hydrogen evolution of 725 TON was recorded [9]. Thummel et al. also introduced a Co(II) quinoline complex $[\text{Co}(\text{ppq})\text{Cl}_2]$ {where, ppq = 8-(1'',10''-phenanthrol-2''-yl)-2-(pyrid-2'-yl) quinoline} which could be soluble in water at pH 7, displaying a relative high H_2 activity in pH 4 together with $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as PS and ascorbic acid as sacrificial electron donor under the irradiation of visible light [10]. Lately, Rao and co-authors further reported a photocatalytic system based solely upon noble-metal-free in combination with $[\text{Co}(\text{dmbp})_3]\text{Cl}_2$ catalyst (where, dmbp = 4,4'-dimethyl- 2,2'- bipyridyl), EY^{2-} sensitizer and triethylamine (TEA) sacrificial agent in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1,v/v), affording a H_2 evolution of 249.2 TON (vs. Cat.) over 2h irradiation [11]. As mentioned above, the noble-metal-based PS, such as $\text{Ru}(\text{bpy})_3^{2-}$, was still used in most of photocatalytic systems so far. The information about photocatalytic H_2 generation based solely on noble-metal-free molecular catalyst was still lacking in the past researches. Thus more efforts should be made for the above purpose.

Taking into account these reasons, in the present work, we constructed a noble-metal-free photocatalytic system based on Co (II) complex $[\text{Co}(\text{dbp})_2]\text{Cl}_2$ as photocatalyst, the effects of several key parameters on H_2 generation, such as sacrificial agent, pH value and reaction solvent, were carefully investigated. In addition, the mechanism of H_2 generation in the system was also briefly discussed.

Scheme 1.

2. Experimental Section

2.1 Reagents and instruments

The complex $[\text{Co}(\text{dbp})_2]\text{Cl}_2$ (dbp=4,4'-dimethyl-2,2'-bipyridyl) was prepared according to the literature procedures[12]. Yield: 71 % (based on Co). Anal. calcd for $\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{CoN}_4$ (%): C: 57.85, H: 4.85, N: 11.24; found (%): C:58.02, H: 4.77, N: 11.27. IR(KBr, cm^{-1}): 3047 m, 2920 w, 1615 s, 1557 m, 1487 m, 1447 s, 1408 m, 1383 w, 919 w, 833 s. ^1H NMR (400 MHz, CD_3OD): δ 8.82 (s, 4H, py), δ 7.64 (d, 4H, py), δ 7.31(d, 4H, py), δ 2.70 (s, 12H, methyl). MS(ESI-MS): m/z: 497.1(M^+).

All chemicals from commercial sources were of reagent grade and used without further purification unless otherwise specified. Elemental analyses (C, H, N) were performed on a Carlo-Erba 1160 elemental analyzer. IR spectra were obtained in the region of 4000–400 cm^{-1} on a Shimadzu IR 435 spectrophotometer with pressed KBr pellets. UV-vis absorption spectra were recorded by using a Hitachi U2000 scanning spectrophotometer (200-1100 nm). ^1H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz).

2.2 Experimental procedure

The batch experiments were performed with 40 mL Quartz Glass bottle as batch reactor filled with a volume of 20 mL in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ containing the target complex as catalyst, photosensitizer (PS) and sacrificial agent. The mixture was magnetically stirred under N_2 atmosphere for 15 min to keep the anaerobic environment of reactor. The medium pH value was adjusted using dilute HCl and measured on a PHS-25 pH meter. The reaction solution was irradiated from the top of the bottle by a 300 W Xe lamp with 420 nm cut off filter at 25 °C.

The evolution of H_2 was measured by on-line Gas Chromatograph (GC, Agilent 4890D) equipped with a thermal conductivity detector (TCD) and a porapak Q stainless column. The temperatures of the injection port, the oven and the detector were 100 °C, 80 °C and 150 °C, respectively. Nitrogen served as the carrier gas at a flow rate of 20 mL/min. The total gas volume was measured by releasing the pressure in the bottles using displacement of saturated brine equipment. All the experiments were carried out independently in triplicates.

3 Results and discussion

3.1 Effect of sacrificial reagent on H₂ generation

The variety and dosage of sacrificial reagent significantly affects the activity of H₂ generation in photocatalytic system. Herein, the effect of three different sacrificial reagents (such as TEOA, TEA and Vitamin C) on H₂ generation was investigated at the fixed target catalyst of 4.0×10⁻⁴ M, EY²⁻ of 4.0×10⁻⁴ M and sacrificial reagent dosage of 10% in CH₃CN/H₂O (1:1, v/v) over 2 h irradiation ($\lambda > 420$ nm), and the result was presented in Fig.1. As shown in Fig.1, the maximal H₂ generation was 76.2 μ mol (vs. PS) for TEOA of 10%, next was 50.5 μ mol (vs. PS) for TEA of 10%, and the last one was 3.9 μ mol (vs. PS) for Vitamin C of 10%. According to the experiment results, TEOA was employed as the sacrificial reagent in the following experiments.

Fig. 1

The effect of TEOA dosage on H₂ generation was presented in Fig. 2 at the fixed EY²⁻ of 4.0×10⁻⁴ M, [Co(dbp)₂]Cl₂ of 4.0×10⁻⁴ M in CH₃CN/H₂O (1:1, v/v) over 2 h irradiation ($\lambda > 420$ nm). As shown in Fig. 2, the maximal H₂ generation 169.2 μ mol (vs. Cat. in all cases) occurred at TEOA dosage of 10% (v/v). When the TEOA dosage deviated the above value, the variable trend was reversed and the corresponding H₂ generation was obviously decreased. *e. g.*, the H₂ generation decreased to 128.0 μ mol and 115.6 μ mol when TEOA dosage was 5% and 15%(v/v), respectively. The developing trend was in agreement with that of our previous reports [2, 3]. The result indicated that TEOA dosage should be controlled at a reasonable level to generate much more H₂. Since the TEOA was usually involved in the reductive quenching of the excited state PS in the photolytic process [7].

Fig. 2

3.2 Effect of medium pH value on H₂ generation

The medium pH value is an important factor to affect H₂ generation in the photocatalytic system. The effect of pH value on H₂ generation was presented in Fig.3 at the fixed catalyst of 4.0×10⁻⁴ M, EY²⁻ of 4.0×10⁻⁴ M and 10% TEOA in CH₃CN/H₂O (1:1, v/v) over 2 h irradiation($\lambda > 420$ nm). As shown in Fig.3, the maximum H₂ generation of 169.2 μ mol appeared at pH 9, and a more acidic or more basic pH value would lead to a noticeable decline of H₂ generation. For instance, a lower H₂ generation of 72.3 μ mol and 59.1 μ mol was observed

when medium pH value was decreased to 7.0 and increased to 10.0, respectively. This phenomenon could be explained that TEOA might be protonated at a lower pH value (≤ 8.0) which would lead to lose electron donor role. Instead, a higher pH level (≥ 10.0) would be unfavorable for the protonation of the reduced cobalt catalyst to form the cobalt hydride species which was an essential intermediate for proton reduction to H_2 at the metal center of the molecular catalyst [13-14]. The results showed that the pH value had an extraordinary influence on H_2 generation in the photolytic system. Therefore, the reasonable adjustment of pH value would be in favor of H_2 generation in the photolytic system, but the activity of catalyst would be inhibited when pH deviated from the optimum pH value.

Fig. 3

3.3 Effect of ratio of CH_3CN to H_2O on H_2 generation

The effects of ratio of CH_3CN to H_2O (v/v) on H_2 generation were also investigated in the present system containing $[Co(dbp)_2]Cl_2$ of $4.0 \times 10^{-4} M$, EY^{2-} of $4.0 \times 10^{-4} M$ and 10% TEOA at pH 9 under the irradiation of visible light ($\lambda > 420 \text{ nm}$), and the result was listed in Fig.4. As shown in Fig.4, the maximal H_2 generation of 169.2 μmol (vs.Cat.) appeared in 1:1 ratio of CH_3CN to H_2O (v/v), the following one was 123.5 μmol with 1:2 ratio of CH_3CN to H_2O (v/v), the last one was 78.6 μmol with 2:1 ratio of CH_3CN to H_2O (v/v). The result showed that the H_2 generation would sharply decline when the ratio of CH_3CN to H_2O (v/v) deviated from 1:1. Despite the increase in the ratio of CH_3CN to H_2O could improve the solubility of the photocatalyst, but the dielectric constant of solution would be declined in that cases, and the electron transfer between excited states of EY^{2-} and $[Co(dbp)_2]Cl_2$ would be inhibited in the photocatalysis reaction. Contrarily, decreasing the ratio of CH_3CN to H_2O would be unfavorable for the solubility of the photocatalyst. The phenomenon could be easily understood because the properties of solvent, such as polarity, dielectric constant and diffusion coefficient, significantly affected the photocatalytic reaction[2,15].

Fig. 4

3.4 Stability of system

We also observed that the present system was deactivated after 3 h irradiation. In order to clarify the cause of the deactivation of system, the following experiments were arranged and the result was presented in Fig.5. As shown in Fig.5, there was no extra H₂ to be discovered when extra [Co(dbp)₂]Cl₂ or TEOA was added to the inactive system after the irradiation of 3 h, implying that the inactivation of system had no bearing on the dosage of catalyst and TEOA because the concentration of TEOA was great excess in the photolytic system.

Fig. 5

Fig. 6

Interestingly, an additional H₂ of 83 μmol was recorded after 3 h irradiation when extra EY²⁻ was added to the inactive system, indicating the inactivation of system was mainly due to the photo-degradation of EY²⁻. Furthermore, a higher added H₂ of 130.1 μmol was observed after 3 h irradiation when extra [Co(dbp)₂]Cl₂ and EY²⁻ were simultaneously added to the inactivated system, indicating the synergetic effect of both catalyst and PS on H₂ generation, and also implying the photodegradation of the target complex was another factor affecting the inactivation of photocatalytic system in the photolysis process. The observations were also consistent with the earlier reports by our research group and some similar studies in the literatures [2,3,7,16]. This deduction was further demonstrated by the changes in the absorption spectra of EY²⁻ before and after irradiation with visible light (Fig. 6). It can be seen in Fig. 6, the strong absorption of EY²⁻ was shifted from 520 nm before irradiation to about 500 nm after irradiating of 15 min to 3h, respectively. Besides, the strength of the absorption peak weakened dramatically with the increase in the irradiation time from 15 min to 3 h. After 3 h irradiation, the absorption peak at 500 nm was almost disappeared, further confirming that the EY²⁻ had almost completely degraded.

4. Conclusion

We constructed a homogeneous photocatalytic system based solely upon noble-metal-free comprising [Co(dbp)₂]Cl₂ complex as catalyst, EY²⁻ as PS and TEOA as sacrificial reagent for H₂ generation under the visible-light-driven, affording a H₂ generation of 169.2 μmol (vs. Cat.) under the optimized conditions. The results showed the target complex could be used as a potential photocatalytic material for H₂ evolution under the irradiation of visible light. The

inactivation of the present photocatalytic system was mainly due to the photo-degradation of EY^{2-} . Additionally, it was also linked with the photodegradation of the target complex.

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Captions

Scheme 1. Structure schematic diagrams of photocatalyst $[\text{Co}(\text{dbp})_2]\text{Cl}_2$, photosensitizer EY^{2-} (alcohol soluble) and EY^{2-} (water soluble) .

Fig.1 Effect of variety of sacrificial reagent on H_2 generation at the fixed catalyst ($4.0 \times 10^{-4} \text{M}$), EY^{2-} ($4.0 \times 10^{-4} \text{M}$) at pH 10 in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v) over 3 h irradiation ($\lambda > 420 \text{ nm}$).

Fig.2 Effect of TEOA dosage on H_2 generation at the fixed catalyst ($4.0 \times 10^{-4} \text{M}$) and EY^{2-} ($4.0 \times 10^{-4} \text{M}$) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v) with 3 h irradiation ($\lambda > 420 \text{ nm}$)

Fig.3 Effect of pH level on H_2 generation under the conditions with catalyst ($4.0 \times 10^{-4} \text{M}$), EY^{2-} ($4.0 \times 10^{-4} \text{M}$) and TEOA (10%) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v/v).

Fig.4 Effect of ratio of CH_3CN and H_2O (v/v) on H_2 generation at the fixed catalyst ($4.0 \times 10^{-4} \text{M}$), EY^{2-} ($4.0 \times 10^{-4} \text{M}$) and TEA (10%) at pH 9.0.

Fig.5. Effect of catalyst and EY^{2-} on H_2 generation at the fixed EY^{2-} ($4.0 \times 10^{-4} \text{M}$), catalyst ($4.0 \times 10^{-4} \text{M}$) and TEOA (10%) at pH 9 in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1, v:v); **1.** extra $[\text{Co}(\text{dbp})_2]\text{Cl}_2$ (8 μmol) or TEOA (10%) was added to the inactivation of system after 3 h irradiation; **2.** extra EY^{2-} (8 μmol) was added to the inactivation of system after 3 h irradiation; **3.** extra catalyst (8 μmol) and EY^{2-} (8 μmol) were simultaneously added to the inactivation of system after 3 h irradiation.

Fig.6. Change of absorption spectra with irradiation time at the fixed EY^{2-} ($4.0 \times 10^{-4} \text{M}$), catalyst ($4.0 \times 10^{-4} \text{M}$) and 10% TEOA at pH 9.0.

Scheme 1

Fig.1

Fig.2

Fig.3

Fig.4

Fig. 5

Fig.6