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A noble-metal-free photocatalytic hydrogen production system based on cobalt(III) complex and eosin Y-sensitized TiO_2

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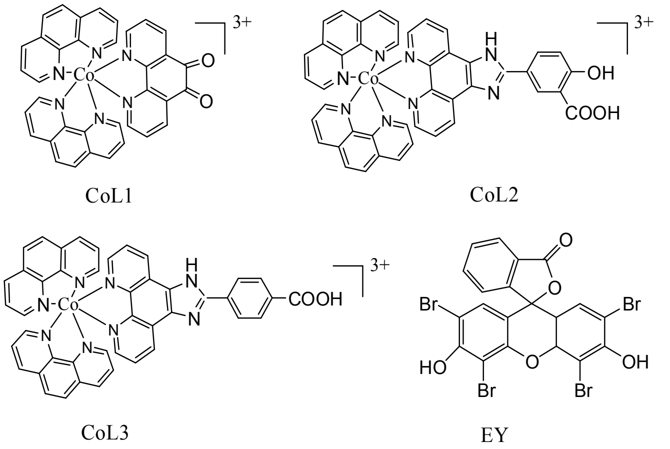
Abstract: Although dye-sensitized TiO_2 for photocatalytic H_2 production have been investigated for more than 20 years, the researches on using low-cost transition metal complexes as catalysts for proton reduction on TiO_2 are still relatively rare. In this paper, three cobalt complexes (CoL1~CoL3) were prepared and fistly used as hydrogen evolution catalyst, and a noble-metal-free H_2-evolving system was fabricated by using an organic dye eosin Y (EY) as photosensitizer and triethylamine (TEA) as sacrificial agent. Under visible light irradiation, a turnover number of 90 (based on CoL2) was obtained for 2wt%CoL2/TiO_2 within 6h in aqueous solution under the optimal conditions of 4 μmol EY, 5% TEA (v/v) and pH 11. In addition, much higher hydrogen production efficiency and stability were achieved for the heterogeneous system, in comparison with the homogeneous one.

Keywords: photocatalytic hydrogen production, dye-sensitized TiO_2, eosin Y, cobalt complex, H_2-evolving cocatalyst

1 Introduction

Since Fujishima and Honda discovered that water could be decomposed into H_2 and O_2 on a TiO_2 photoelectrode[1], more and more attention has been paid to photocatalytic hydrogen production from water splitting using semiconductor materials, and TiO_2 has been considered as one of the most promising photocatalyst due to its low cost, nontoxicity, and photostability[2]. However, pure TiO_2 requires UV irradiation, shows fast electron-hole recombination rate and a high overpotential for hydrogen generation[3,4]. It is well-known that the absorption wavelength range can be extended to visible-light region by dye sensitization[5,6], and the recombination rate can be restrained by loading Pt or enzymes known as hydrogenases. The loaded catalyst not only acts as electron sink to suppress the recombination of the photoexcited electrons and holes, but also serves as active sites to lower the H_2 evolution overpotential[7,8].

Up to now, the most effective catalyst for proton reduction is Pt, whereas it apparently raises the cost of hydrogen production and limits its practical application. Therefore, numerous efforts have been made to replace Pt with low-cost alternatives, in which transition metal complexes have also been investigated[8]. For example, Reisner et al. reported the attachment of a complex Db[NiFeSe]-H to Ru(II) complex-sensitized TiO_2. A turnover frequency of approximately 50 (mol H_2) s^{-1} (mol total hydrogenase)$^{-1}$ was obtained[9]. However, to the best of our knowledge, researches on the photocatalytic hydrogen production based on transition metal complexes almost all focused on its use as H_2-evolving molecular catalysts in homogeneous systems[10-19], though the heterogeneous systems usually possess better stability and practicality than the homogeneous ones. For instance, organic solvents are usually indispensable for the homogeneous systems, while for the heterogeneous ones, most reactions can proceed in an aqueous solution. In addition, the catalyst recovery is often difficult for the homogeneous systems. In comparison, studies on the application of cobalt complexes in the heterogeneous systems are relatively rare[20-25]. For example, Ji et al. reported the photoelectrochemical hydrogen production of $CodmgBF_2$ (dmg = dimethylglyoxime anion), which was linked to a Ru(II) sensitizer anchored onto NiO film. The resultant photoelectrode exhibited superior stability in aqueous solutions[24]. In particular, for the exploiting of cobalt complexes in heterogeneous TiO_2 systems, the only example was a cobaloxime complex $[Co^{III}(dmgH)_2(pyridyl\text{-}4\text{-}hydrophosphonate)Cl]$ (abbreviated as CoP), which was anchored on TiO_2 and acted as the H_2 evolution catalyst[26-29]. With phosphonate-functionalized $Ru(bpy)_3^{2+}$ (RuP) as photosensitizer (PS), 53 TON (based on CoP) of H_2 was generated within 5h under visible light irradiation[26]. However, the PS was still precious $Ru(bpy)_3^{2+}$ derivative in the above systems.



CoL1 CoL2

CoL3 EY

Fig. 1 Structures of cobalt complexes CoL1, CoL2, CoL3 and EY.

In order to investigate the utilization of new kinds of cobalt complexes as H_2 evolution catalysts of heterogeneous TiO_2 system and construct noble-metal-free hydrogen evolution systems, herein, three cobalt(III) complexes (abbreviated as CoL1~CoL3, as depicted in Fig. 1) were prepared and loaded onto TiO_2 surface through different bridging groups. Their hydrogen production performances were studied by using an organic dye eosin Y (abbreviated as EY, Fig. 1) as the PS and triethylamine (TEA) as the sacrificial agent under visible light irradiation. In addition, the influences of experimental parameters, such as the loading amount of CoL2 on TiO_2, the concentration of EY and TEA, and the pH value of the reaction system on hydrogen production activity were investigated in detail. Furthermore, the hydrogen evolution performance of CoL1~CoL3 was compared and the deactivation reason was explored preliminarily.

2 Experimental

2.1 Materials

1,10-phenanthroline-5,6-dione (L1)[30], $[Co(phen)_2Cl_2]Cl$[31] and 5-aldehydosalicylic acid[32] were prepared and recrystallized according to literature procedures. TiO_2 used in this work was Degussa P25 obtained from a commercial source. SiO_2 was the silica gel used for thin-layer chromatography. All other chemicals were of analytical grade purity, obtained form Sinopharm Chemical Reagent Co. and used as received without further purification.

2.2 Photocatalyst preparation

2.2.1 Synthesis of $[Co(phen)_2L1](PF_6)_3$ (abbreviated as CoL1)

CoL1 was synthesized according to the method reported by Song et al.[33]. $[Co(phen)_2Cl_2]Cl$ (0.50 g, 0.95 mmol) and 1,10-phenanthroline-5,6-dione (0.24 g, 1.14 mmol) was refluxed for 4h in 60 ml 1:1 (v/v) ethanol/water. After that, the reaction mixture was cooled to room temperature and a precipitation was obtained by adding saturated aqueous NH_4PF_6 solution. The precipitation was collected, washed with water and ether, and then recrystallized from acetonitrile-ether. After filtrated and dried in vacuo for 24 h, the complex was achieved (yield: 65% based on Co). Anal. Calcd (%) for $C_{36}H_{22}CoF_{18}N_6O_2P_3$: C, 40.52;

H, 2.06; N, 7.88. Found: C, 40.83; H, 2.18; N, 7.62.

2.2.2 Synthesis of [Co(phen)$_2$L2](PF$_6$)$_3$ (abbreviated as CoL2)

For the synthesis of [Co(phen)$_2$L2](PF$_6$)$_3$ (abbreviated as CoL2), a mixture of CoL1 (0.4775 g, 0.5 mmol), 5-aldehydosalicylic acid (0.1163 g, 0.7 mmol) and ammonium acetate (0.8004 g, 10 mmol) in 5 ml glacial acetic acid was refluxed for 3h under nitrogen. After cooled, diluted with 40 ml H_2O and neutralized with ammonia to pH 5, the obtained precipitation was filtered off and washed repeatedly with water and diethyl ether to get a brown solid (yield: 63% based on Co). Anal. Calcd (%) for $C_{44}H_{28}CoF_{18}N_8O_3P_3$: C, 43.93; H, 2.33; N, 9.32. Found: C, 44.03; H, 2.38; N, 9.02. IR (KBr, cm^{-1}): 3406 (O-H), 1625 (C=O), 1581 (C=N), 643 (Co-N (L2)), 558 (Co-N (phen)); ^{1}H NMR (300 MHz, DMSO-d$_6$, δ ppm): 9.15 (6H, d); 8.56 (6H, s); 7.96 (7H, m); 7.66 (6H, d).

2.2.3 Synthesis of [Co(phen)$_2$L3](PF$_6$)$_3$ (abbreviated as CoL3)

It was prepared by the same procedure with CoL2, expect that 5-aldehydosalicylic acid was replaced by 4-carboxybenzaldehyde (0.1051 g, 0.7 mmol) (yield: 65% based on Co). Anal. Calcd (%) for $C_{44}H_{28}CoF_{18}N_8O_2P_3$: C, 44.52; H, 2.36; N, 9.44. Found: C, 44.80; H, 2.40; N, 9.22. IR (KBr, cm^{-1}): 3395 (O-H), 1592 (C=O), 1544 (C=N), 643 (Co-N (L3)), 557 (Co-N (phen)); ^{1}H NMR (300 MHz , DMSO-d$_6$, δ ppm): 9.18 (6H, d); 8.56 (6H, s); 7.97 (7H, m); 7.72 (2H, m); 7.67 (4H, d).

2.2.4 Preparation of photocatalyst CoL/TiO$_2$

2 ml DMF solution of a certain amount of CoL was added dropwise to a stirred dispersion of 1.0 g TiO_2 in 150 mL water. Then the mixture was stirred at room temperature for 24 h in dark. After centrifuged, the obtained solid was washed thoroughly with water and

ethanol before dried at 60 ºC for 12h.

The amount of CoL loaded onto TiO_2 was determined by the UV-vis absorption spectra through measuring the absorbance difference of the clear supernatants before and after adding TiO_2. The results showed that almost both CoL2 and CoL3 were loaded onto TiO_2 when less than 6wt% CoL was used because no absorption spectra of CoL2 and CoL3 were detected for the supernatants after the loading reaction. While the loading amount of CoL1 was only 50% due to the weak interaction between it and TiO_2, in comparison to that of CoL2 or CoL3.

2.2.5 Preparation of photocatalyst CoL2/SiO_2

2 ml DMF solution of 20 mg CoL2 was added dropwise to a stirred dispersion of 1.0 g SiO_2 in 150 mL water. Then the mixture was stirred at room temperature for 24 h in dark. After centrifuged, the obtained solid was washed thoroughly with water and ethanol before dried at 60 ºC for 12h. The amount of CoL2 loaded onto SiO_2 was also determined by the UV-vis spectra and the result showed that only about 20% of CoL2 was adsorbed onto SiO_2.

2.3 Characterization

The ^1H NMR spectra were carried out on a Bruker 300 MHz NMR spectrometer by using DMSO-d_6 as the solvent and TMS as an internal standard. The IR spectra were recorded in the region of 4000-400 cm^{-1} on a Nicolet IR-470 infrared spectrometer with pressed KBr pellets. The diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer using $BaSO_4$ as reference, and transformed to the absorption spectra according to Kubelka-Munk relationship. The UV-vis absorption spectra were recorded using a Hitachi U2000 spectrophotometer. The cyclic voltammetries of the three CoL complexes were determined on a CHI-630B electrochemical workstation by using a glassy carbon as the working electrode, a Pt flag as the counter electrode, and a saturated calomel as the reference electrode (SCE) with a scan rate of 100 mV/s. All three electrodes were immersed in a 1:1 CH_3CN-H_2O (v/v) solution containing 0.05 mol/L n-Bu_4NPF_6 as the electrolyte.

2.4 Photocatalytic hydrogen production test

The photocatalytic hydrogen production experiments were performed in a 230 ml quartz reactor with a flat window. 50 mg CoL/TiO_2 and a certain amount of EY were added to a 100 ml aqueous TEA solution. The pH was adjusted to a certain value by hydrochloric acid. The mixture was ultrasonically dispersed for 5 min, and then bubbled with nitrogen for 15 min before irradiated by a 300W Xe lamp equipped with 420 nm cut-off filter. During the reaction, a continuous magnetic stir was applied and the temperature was kept to 30 ºC through a circulating water system. The H_2 evolved was detected by Gas Chromatograph (GC, Agilent 4890D) equipped with a thermal conductivity detector (TCD) and a porapak Q stainless column. Nitrogen served as the carrier gas at a flow rate of 20 ml/min.

3 Results and discussion

3.1 Co(III) complexes preparation

In order to avoid the coordination of carboxylate group on ligands L2 and L3 with Co^{3+}, complex CoL2 or CoL3 was prepared by reacting CoL1 with 5-aldehydosalicylic acid or 4-carboxybenzaldehyde, respectively. The IR and ^{1}H NMR results confirmed the successful achievement of CoL2 and CoL3.

3.2 UV-vis diffuse reflectance spectra of CoL2/TiO_2

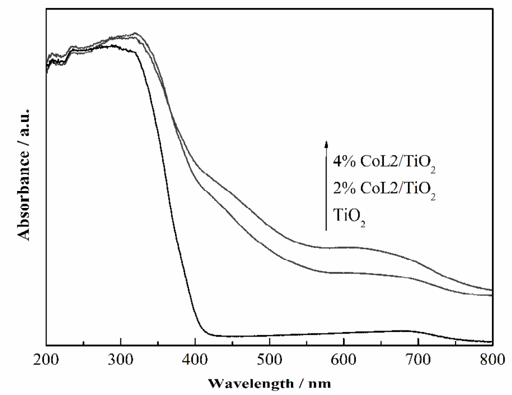


Fig. 2 UV-vis diffuse reflectance spectra of TiO_2 and CoL2/TiO_2

The UV-vis diffuse reflectance spectra (Fig. 2) of TiO_2, 2wt%CoL2/TiO_2 and 4wt%CoL2/TiO_2 show that in comparison to pure TiO_2, CoL2/TiO_2 exhibits a broad absorption band in the region of 400~800 nm, and it increases gradually with the increasing of CoL2 from 2wt% to 4wt%, indicating the successful attachment of CoL2 to TiO_2 surface.

3.3 Effect of different parameters on hydrogen production performance

The photocatalytic hydrogen production activities of CoL/TiO_2 catalysts were tested in a closed system. As a representative, firstly, various experimental factors, such as the amounts of CoL2, EY and TEA, and the pH value of the reaction system were studied to investigate their influences on hydrogen evolution activities.

3.3.1 Effect of CoL2 loading amount

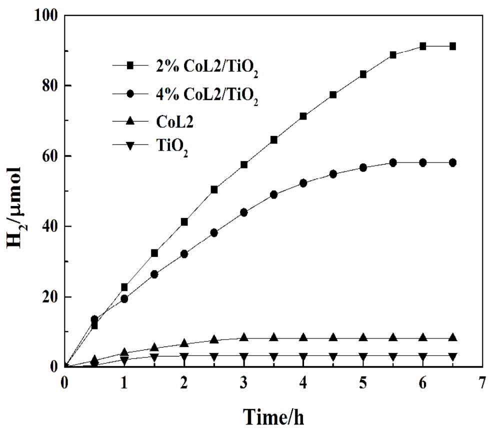


Fig. 3 Time courses of the photocatalytic hydrogen production of CoL2, TiO_2 and CoL2/TiO_2 (EY 4 μmol, catalyst 50 mg, TEA 5mL and pH = 11; for the homogeneous system, the amount of CoL2 is 1 mg).

The hydrogen production activities of TiO_2, CoL2 and CoL2/TiO_2 are given in Fig. 3. It indicates that when EY was used as sensitizer, almost no or only trace of H_2 was detected for either TiO_2 or CoL2, whereas attaching CoL2 on TiO_2 surface leads to a significant improvement on the hydrogen generation activity. For 2wt%CoL2/TiO_2, the TON (vs. CoL2) reached to 90 within 6h, indicating that the TiO_2 and CoL2 are both indispensable for hydrogen generation. However, for 4wt%CoL2/TiO_2, the H_2-evolving activity decreased and the TON was only 58.

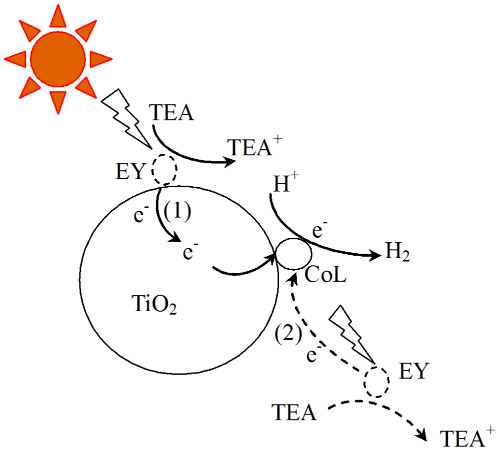


Fig. 4 Schematic representation of the possible electron transfers from EY to CoL in the heterogeneous EY-sensitized CoL/TiO_2 system (EY and CoL molecules are simplified as circles).

It is probably due to the following causes: (i) excessive loading of CoL2 decreases (or shields) the active sites of TiO_2 surface, leading to a decrease in the adsorption amount of EY on TiO_2 [28]; (ii) more loading of CoL2 will result in more reverse reaction of hydrogen evolution; (iii) excessive loading of CoL2 will lead to more direct electron transfers between EY and CoL2, as the electron transfer route (2) shown in Fig. 4, which results in a lower hydrogen production efficiency. Correspondingly, the much higher H_2-evolving performance of CoL2/TiO$_2$ can be attributed to the efficient electron transfer from the excited EY* to the CB of TiO$_2$, and then to the H$_2$ evolution catalyst CoL, as the route (1) depicted in Fig. 4 [27, 28, 34,35].

3.3.2 Effect of the pH value

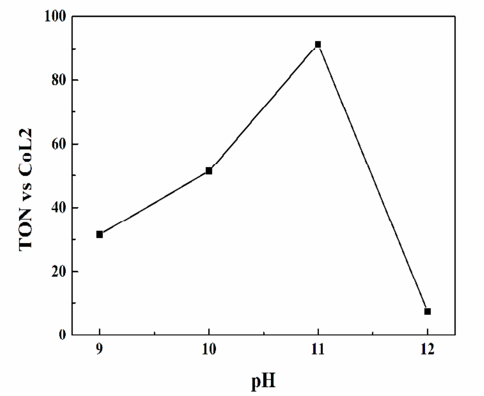


Fig. 5 The amounts of hydrogen evolved under different pH values for 2wt%CoL2/TiO$_2$ (EY 4 μmol, catalyst 50 mg, TEA 5 mL).

On the other hand, the pH value of the reaction systems also affects its hydrogen production activity. As shown in Fig. 5, for 2wt%CoL2/TiO$_2$, with the increase of pH from 9 to 11, the H$_2$ evolution activity was improved and achieved a maximum at pH 11. However, the TON drastically decreased to about 7 at pH 12. The low activity at lower pH value is probably due to the fact that the rate of Co^{I} species formation is apparently slowed, and it is difficult for TEA to be oxidized at the lower pH to provide electrons, whereas the activity decrease at higher pH value is possibly owing to the fact that the driving force for H$_2$ production is greatly reduced, and the protonation of the Co catalyst, an essential step postulated in forming H$_2$, may become very unfavorable[17,18,36].

3.3.3 Effect of the EY and TEA concentrations

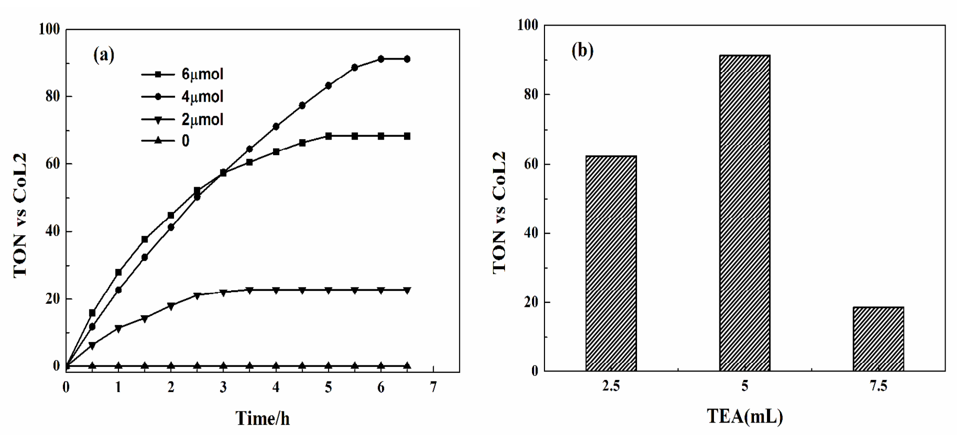


Fig. 6 (a) Time courses of hydrogen generation with various EY concentrations for 2wt%CoL2/TiO_2 (catalyst 50 mg, TEA 5 mL and pH = 11). (b) The amounts of H_2 evolved with different amounts of TEA (EY 4 μmol, catalyst 50 mg, pH = 11).

As illustrated in Fig. 6a, increasing the EY amount from 2 to 4 μmol results in an obvious improvement on hydrogen evolution efficiency due to the enhancement of light harvesting ability, whereas when the EY amount was further increased to 6 μmol, the H_2-evolving efficiency decreased because that some dye molecules absorbing input light can not participate in the electron transfer to the CB of TiO_2, which leads to loss of part of the incident light. On the other hand, the higher concentration of EY, the closer distance between adjacent dye molecules, results in more serious concentration quenching[34,37]. It results in less efficient utilization of dye molecules and a lower hydrogen evolution rate. However, from Fig. 6a, it can also be seen that when 6 μmol EY was used, the initial hydrogen evolution rate (from 0~2.5 h) was higher than that of 4 μmol EY, which indicates that except for the heterogeneous reaction, the homogeneous one also occurs namely the direct electron transfer from EY to CoL happens. So the activity decrease after 3 h can be attributed to the deactivation of homogeneous system, as discussed later. Similarly, when the TEA amount was increased from 2.5 to 5.0 mL, the H_2 produced increased, while it dramatically decreased at

7.5 mL and only 20 TON was produced within 6h, as illustrated in Fig. 6b. Control experiments showed that no hydrogen was detected in the absence of either the sensitizer EY or TEA.

3.3.4 Effect of CoL species and TiO_2 on hydrogen production

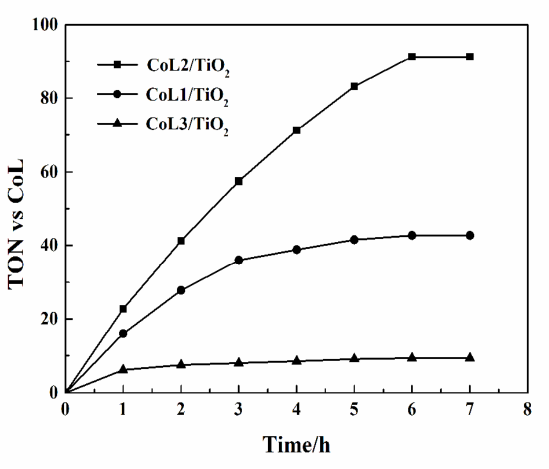


Fig. 7 Time courses of hydrogen production over different 2wt%CoL/TiO_2 (EY 4 μmol, catalyst 50 mg, TEA 5 mL and pH = 11).

As the H_2-evolving catalyst, the species of CoL will determine its H_2 evolution performance. So the hydrogen production activities of CoL1~CoL3 were investigated under the same conditions of 50 mg 2wt%CoL/TiO_2, 4 μmol EY, 5% (v/v) TEA and pH 11. As shown in Fig. 7, the results indicated that CoL2 was the most effective and the TON (vs. CoL2) was up to 90 after 6h, which was higher than that of the RuP-sensitized CoP-TiO_2 system (53 vs. CoP) [26]. While when CoL1 or CoL3 was utilized, the amount of H_2 produced decreased significantly and the TON was only 43 or 9, respectively. This can be explained by the redox potential of CoL and the interaction between it and TiO_2 [26]. The cyclic voltammetry results show that the redox potential of Co(II)/Co(I) occurs at −0.45 V, −0.61V, and −0.64V (vs. NHE) for CoL1, CoL2 and CoL3, respectively, and there is no significant difference in the redox potential of CoL2 and CoL3 possibly due to their similar structures. Then the electron transfer form CB of TiO_2 (−0.70 V vs. NHE) to CoL catalysts is thermodynamically favorable [27] and in principle CoL1 with more positive potential should be more active than the other two CoL catalysts. However, the results indicated that the hydrogen-evolving activity of CoL1 was lower than that of CoL2. It is probably because that except for the redox potential, the interaction between CoL and TiO_2 also plays an important role in its H_2-evolving activity, namely the anchoring group on ligand L also affects its activity. Therefore, CoL2 with carboxylate and hydroxyl groups will result in stronger interaction with TiO_2 and exhibits higher hydrogen evolution activity than CoL1 possessing diketone ligand.

As we all know, TiO_2 serves not only as a catalyst carrier, but also a critical electronic component for the photocatalytic process. It harvests electrons from the excited EY molecules, facilitates the formation of a long-lived charge-separated state and transfers electrons to CoL [26]. In order to confirm this point, an electronically inert support SiO_2 was used to replace TiO_2 and the result showed that only 3.7 μmol H_2 was produced within 3h under the same conditions.

3.4 The deactivation reason and the stability of CoL2

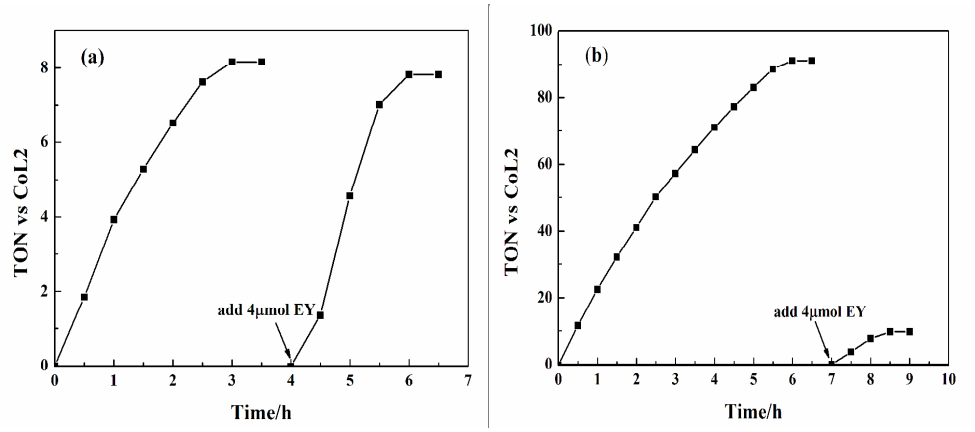


Fig. 8 Two runs of hydrogen production for (a) the homogeneous system containing CoL2 (1 mg) and (b)

the heterogeneous system containing 2wt%CoL2/TiO_2 (50 mg) with 5mL TEA, 4 μmol EY and pH = 11.

From the above results, it can be seen that after about 6h, the hydrogen evolution of 2wt%CoL2/TiO_2 ceased. To better understand the deactivation reason and the stability of CoL2, a homogeneous system was also investigated, in which CoL2 was used as molecular catalyst, EY as photosensitizer and TEA as the sacrificial electron donor. As shown in Fig. 8, its H_2-evolving activity is obviously lower than that of heterogeneous system and the hydrogen evolution ceases only after 3h. However, readdition of EY (4 μmol) to the system leads to a recovered and only a little lower activity. In comparison, for the heterogeneous system, after the cessation of hydrogen evolution, readdition of EY only results in a slight recovery (Fig. 8b). And it is worth to note that the recovered hydrogen production activity for the heterogeneous system is almost the same as that of the homogeneous one. All this suggests that CoL2 is relatively stable, and the deterioration of hydrogen production activity can be ascribed to the desorption of CoL2 from TiO_2 surface and photolysis of the EY sensitizer[18,38].

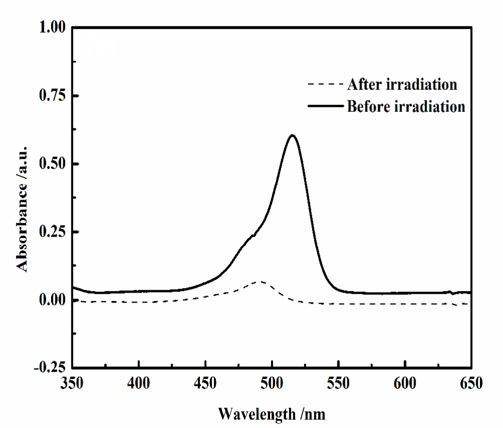


Fig. 9 UV-vis absorption spectra of the clear solutions containing EY only and after photocatalytic hydrogen evolution reaction for EY-sensitized 2wt%CoL2/TiO_2 system.

This deduction was further verified by the change of absorption spectra of EY before and after photocatalytic reaction. From Fig. 9, it can be seen that the absorption spectrum of the resulting clear solution is different from that of the original EY solution. The strong characteristic absorption peak at 520 nm for EY shifts to about 490 nm and it is very weak after irradiated by visible light for 6h, which indicates that the sensitizer EY may be almost completely degraded during the reaction.

4. Conclusions

In summary, as an inexpensive alternative to Pt, three cobalt complexes have been synthesized and acted as H_2 evolution catalysts, which were loaded onto TiO_2 by different bridging groups. By using an organic dye EY as photosensitizer and TEA as sacrificial electron donor, noble-metal free heterogeneous hydrogen production systems based on cobalt complexes have been firstly constructed and 90 turnovers of H_2 (based on CoL2) was produced within 6h under visible light irradiation. This system is facile to assemble and can work in aqueous solution (free of organic solvents). The results also indicate that compared with the homogeneous system, the heterogeneous one displays much higher hydrogen-evolving activity and better stability. It will pave a way for the fabrication of noble-metal-free heterogeneous photocatalytic hydrogen production systems based on transition metal complexes, though the sensitizer and the composite catalyst CoL/TiO_2 were unstable in the present system. More researches on improving the activity and stability of cobalt complexes and exploiting more stable sensitizer are undergoing in our lab.

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Figure Captions

Fig. 1 Structures of cobalt complexes CoL1, CoL2, CoL3 and EY.

Fig. 2 UV-vis diffuse reflectance spectra of TiO_2 and CoL2/TiO_2.

Fig. 3 Time courses of the photocatalytic hydrogen production of CoL2, TiO_2 and CoL2/TiO_2 (EY 4 μmol, catalyst 50 mg, TEA 5mL and pH = 11; for the homogeneous system, the amount of CoL2 is 1 mg).

Fig. 4 Schematic representation of the possible electron transfer routes from EY to CoL in the heterogeneous EY-sensitized CoL/TiO_2 system (EY and CoL molecules are simplified as circles).

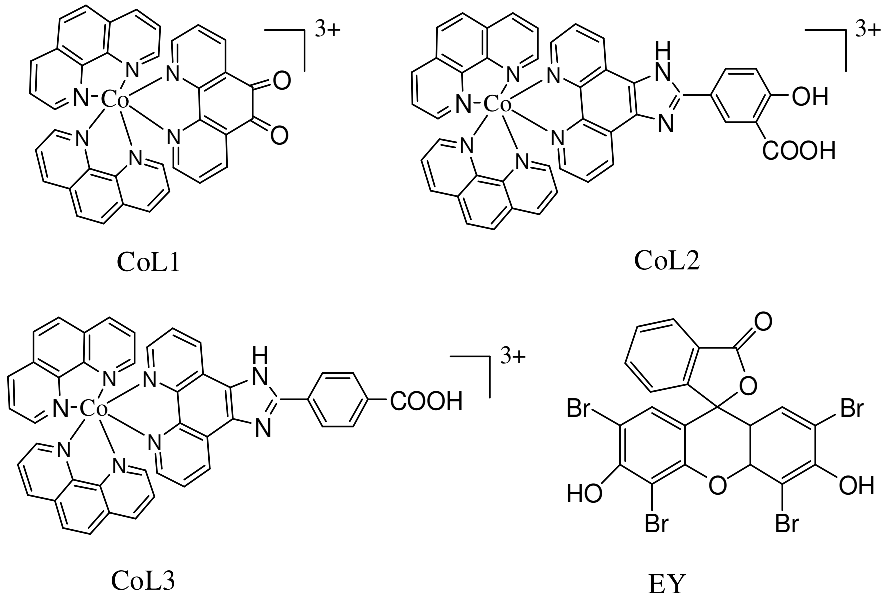
Fig. 5 The amounts of hydrogen evolved under different pH values for 2wt%CoL2/TiO_2 **(**EY 4 μmol, catalyst 50 mg, TEA 5 mL).

Fig. 6 (a) Time courses of hydrogen generation with various EY concentrations for 2wt%CoL2/TiO_2 (catalyst 50 mg, TEA 5 mL and pH = 11). (b) The amounts of H_2 evolved with different amounts of TEA (EY 4 μmol, catalyst 50 mg, pH = 11).

Fig. 7 Time courses of hydrogen production over different 2wt%CoL/TiO_2 (EY 4 μmol, catalyst 50 mg, TEA 5 mL and pH = 11).

Fig. 8 Two runs of hydrogen production for (a) the homogeneous system containing CoL2 (1mg) and (b) the heterogeneous system containing 2wt%CoL2/TiO_2 (50 mg) with 5mL TEA, 4 μmol EY and pH = 11.

Fig. 9 UV-vis absorption spectra of the clear solutions containing EY only and after photocatalytic hydrogen evolution reaction for EY-sensitized 2wt%CoL2/TiO_2 system.



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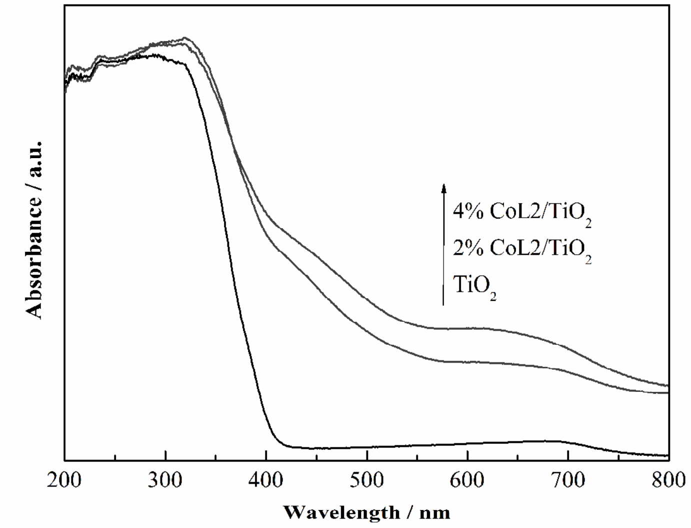

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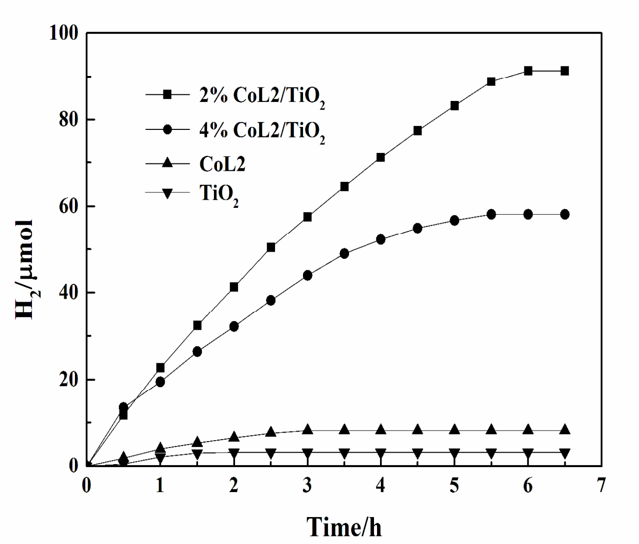

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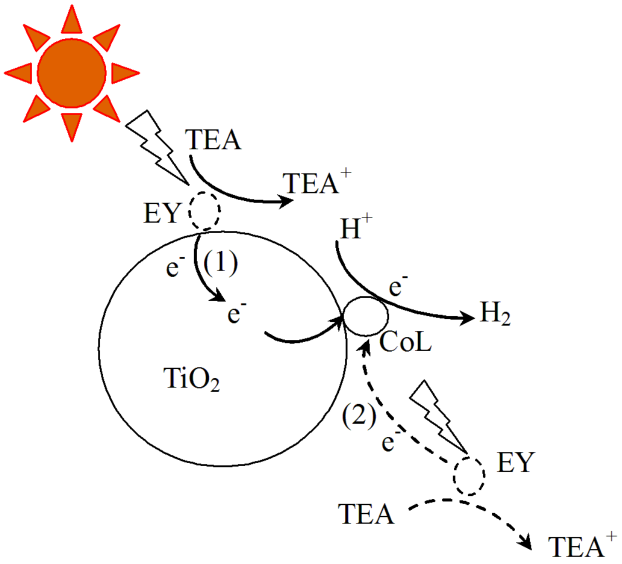

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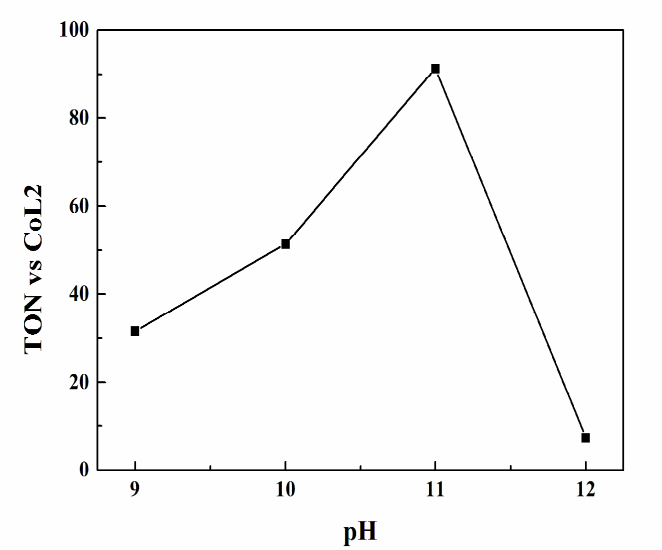

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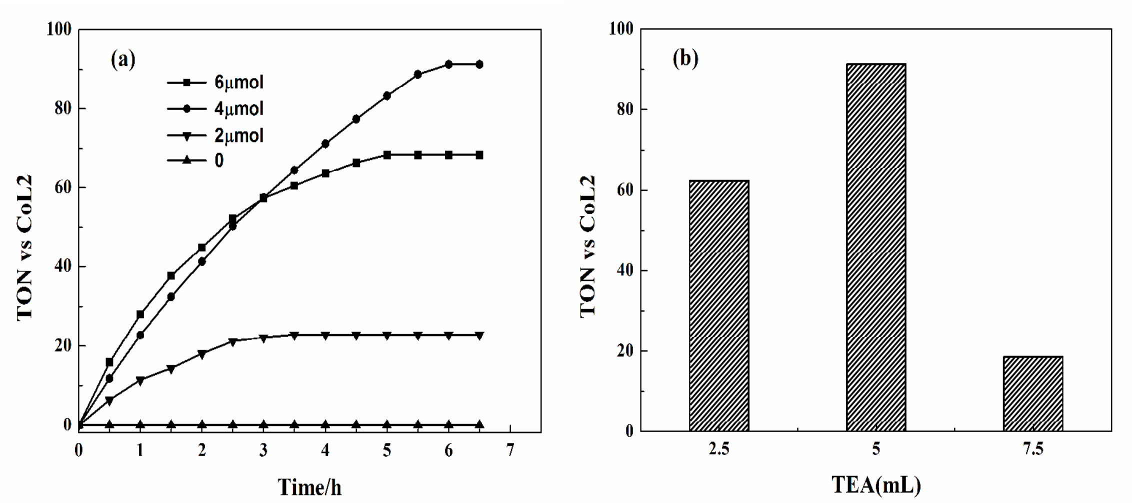

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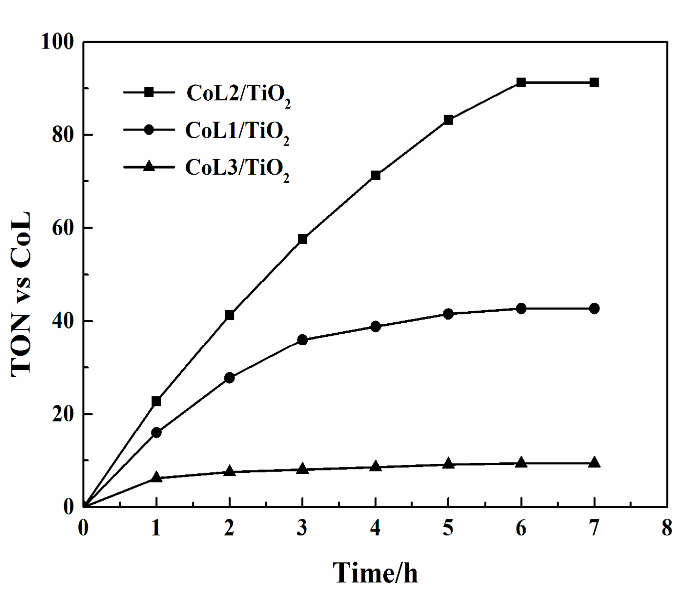

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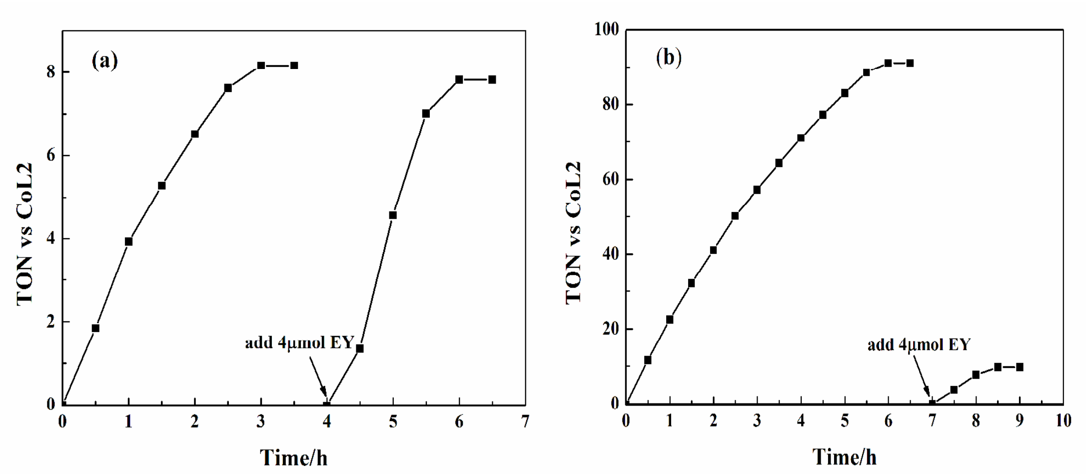

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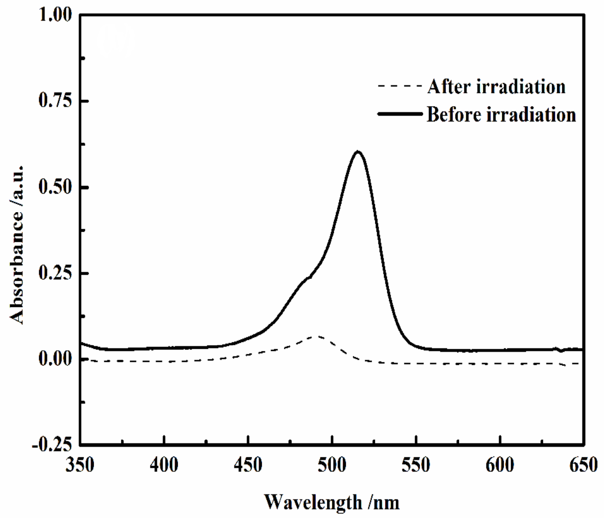

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