Unraveling a Single-Step Simultaneous Two-Electron Transfer Process from Semiconductor to Molecular Catalyst in a CoPy/CdS Hybrid System for Photocatalytic H$_2$ Evolution under Strong Alkaline Conditions

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Ⓢ *Supporting Information*

ABSTRACT: Electron transfer processes from semiconductor to molecular catalysts was studied in a model hybrid photocatalytic hydrogen evolution system composed of [Co$^{(III)}$(dmgH)$_2$PyCl] (CoPy) and CdS under different pH conditions. Thermodynamic and kinetic studies revealed that photocatalytic H$_2$ evolution under high pH conditions (pH 13.5) can only account for the thermodynamically more favorable single-step simultaneous two-electron transfer from photoirradiated CdS to Co(III)Py to produce unavoidable intermediate Co(I)Py, rather than a two-step successive one-electron transfer process. This finding not only provides new insight into the charge transfer processes between semiconductors and molecular catalysts but also opens up a new avenue for the assembly and optimization of semiconductor–molecular catalyst hybrid systems processed through multielectron transfer processes.

A hybrid photocatalytic system composed of a semiconductor and a molecular catalyst has been intensively investigated for solar fuel production because such a system may take advantage of both semiconductors (broad light absorption with high stability) and molecular catalysts (high activity and flexibility).[1−4] For the construction of hybrid photocatalytic systems, the matching of energy levels between the semiconductor and molecular catalyst is a crucial factor to consider.[5,6] The underlying charge transfer mechanism from the semiconductor to the molecular catalyst also plays a crucial role.

Currently, a two-step successive one-electron transfer process is the dominating mechanism for the reduction of a majority of proton reduction molecular catalysts, such as nickel(II) complexes,[5,7] cobalt(III) complexes,[8,9] and [FeFe]-hydrogenase mimics,[3,10] in which the second reduction process of the molecular catalysts to produce the active proton reduction intermediates is usually proceeded at relatively negative reduction potentials. This largely limits the availability of

semiconductors and molecular catalysts for the construction of efficient hybrid photocatalytic systems. Since semiconductors have the capacity to deliver multielectrons,[11,12] the library of the hybrid photocatalytic systems would be much more extended if an energetically more favorable single-step simultaneous multielectron transfer process is applicable. However, as far as we know, the possibility of single-step simultaneous multielectron transfer reduction of molecular catalysts by photoirradiated semiconductors is yet unknown.

In this work, the electron transfer processes from photoirradiated CdS to [Co$^{(III)}$(dmgH)$_2$PyCl] (CoPy) in CoPy/CdS hybrid systems under different pH conditions have been investigated. Energy level analysis indicates that two-step successive one-electron transfer reduction of CoPy under high pH conditions (pH >10.0) is thermodynamically unfavorable. However, photocatalytic H$_2$ evolution activity of the CoPy/CdS hybrid system was indeed observed at pH 13.5. In addition to thermodynamic driving force, charge transfer dynamics revealed by time-resolved photoluminescence (PL), electron paramagnetic resonance (EPR) spectra, and UV–vis absorption strongly support that a single-step simultaneous two-electron transfer from CdS to Co(III)Py in the CoPy/CdS hybrid system at pH 13.5 is the plausible mechanism accounting for the photocatalytic H$_2$ evolution activity at pH 13.5.

The scheme of the CoPy/CdS hybrid photocatalytic system for H$_2$ evolution is illustrated in Figure 1a, where CdS is the light harvester, CoPy is the proton reduction catalyst, and methanol is the electron donor. Figure 1b depicts the photocatalytic H$_2$ evolution performance of CoPy/CdS hybrid systems under different pH conditions. The activities of CoPy/CdS hybrid systems were very low at pH 4.0−8.0; negligible activities were obtained at pH 10.0 and 12.2, while remarkably enhanced activity was achieved at pH 13.5. It should be noted that CoPy and CdS are relatively stable under strong alkaline conditions at pH 13.5, and the interaction between CoPy and CdS through a kind of
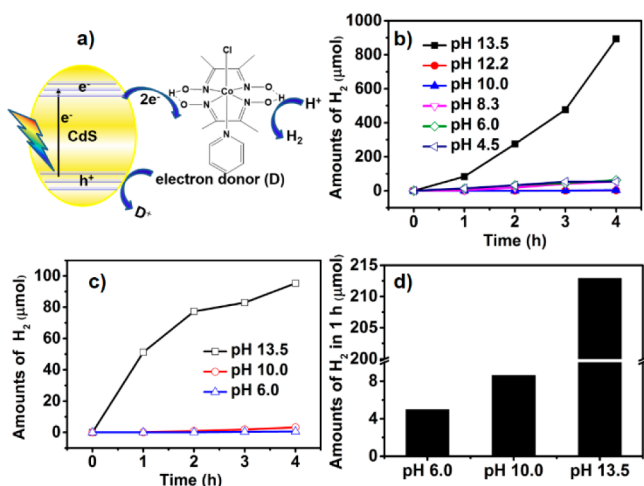
Figure 1. (a) Scheme of photocatalytic H_2 evolution reaction in CoPy/CdS hybrid systems; photocatalytic H_2 evolution performance of (b) CoPy/CdS hybrid systems, (c) CdS alone, and (d) Pt/CdS. Reaction conditions: 100 mg of CdS or Pt/CdS; 100 mL of aqueous methanol solution (20 vol %); 300 W Xe lamp ($\lambda \geq 420$ nm); and 0.25 mM CoPy in CoPy/CdS hybrid systems.

Figure 2. (a) Energy diagram showing the pH dependence of E_{fb} of CdS (black square), Co(II)Py/Co(I)Py redox potential (red circle), and H^+/H_2 reduction potential (blue triangle) for a two-step successive one-electron transfer process in CoPy/CdS hybrid systems. (b) Scheme of two-electron transfer processes from photoirradiated CdS to CoPy at pH 13.5. The inset is the element potential diagram.

weak Cd−O−[CoPy] chemical bond linkage can be inferred by Raman spectroscopy (Figure S1d).

To understand the remarkably different photocatalytic performance of the hybrid system under high pH conditions, methanol oxidation on CdS was first examined. Figure 1c,d shows that the photocatalytic H_2 evolution activities of CdS alone and 0.1 wt % Pt-loaded CdS (Pt/CdS) increase as the pH value of the reaction mixture increases. The results illustrate that the oxidation of methanol by photoirradiated CdS is accelerated as the pH value increases, and much accelerated methanol oxidation can be obtained under strong alkaline conditions. For the CoPy/CdS hybrid system at pH 13.5, the color of CdS nanoparticles changes from yellow to brown-green due to the accumulation of electrons which results in the in situ formation of reduced CdS (R-CdS, Figure S2 and Table S1).

Though the oxidation of methanol could be accelerated with the increase of the pH, it cannot be used to explain the opposite trends of the negligible activities of the CoPy/CdS hybrid system at high pH conditions. The photocatalytic behavior of the CoPy/CdS hybrid system at pH >10.0 might be associated with the proton reduction process rather than the methanol oxidation process. It should be pointed out that the negligible activity of the CoPy/CdS hybrid system at pH 10.0 and 12.2 could not be due to the changes of CoPy itself, for the CoPy/C_3N_4 hybrid system showed H_2 evolution activity at pH 10.4.[13] This hints that the two-electron transfer process from photoirradiated CdS to CoPy to form Co(I)Py might be a thermodynamically unfavorable process at pH 10.0, which leads to a negligible photocatalytic H_2 evolution activity of the hybrid system.

In the proton reduction process catalyzed by CoPy, Co(I)Py is an unavoidable intermediate for CoPy to reduce protons to molecular H_2.[14−17] Therefore, it is necessary to study the driving force for the reduction of Co(II)Py to Co(I)Py by photoirradiated CdS under different pH conditions. According to the energy diagram in Figure 2a (flat bands (E_{fb}) of CdS and Co(II)Py/Co(I)Py redox potentials were obtained according to the Mott−Schottky plots and cyclic voltammograms as depicted in Figures S3−S5 and Tables S2−S4), the driving force at pH 4.0 for the reduction of Co(II)Py to Co(I)Py by photoirradiated
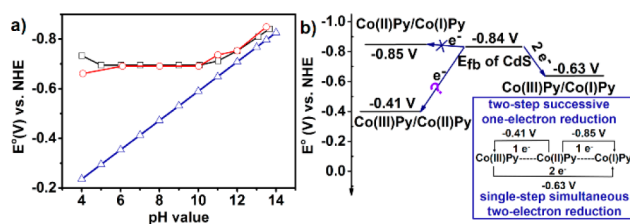
CdS is the largest, and it becomes much smaller or even negative at higher pH conditions. Therefore, thermodynamically unfavorable electron transfer from photoirradiated CdS to Co(II)Py is the main reason for the negligible activity at pH 10 and 12.2. However, enhanced photocatalytic activity at pH 13.5 was indeed observed, which indicates that a thermodynamically allowed but different electron transfer process occurs at pH 13.5. Two mechanisms may be considered. One is the reduction of Co(II)Py to Co(I)Py by photoirradiated CdS that is allowed by a negative shift of the flat band due to in situ formation of R-CdS, and the other is the reduction of CoPy goes through a thermodynamically more favorable single-step simultaneous two-electron reduction process rather than a two-step successive one-electron reduction process.

The exact flat band of R-CdS could not be obtained due to the instability of the reduced species. However, it has been reported that the flat bands remain almost constant in many reduced semiconductors, such as R-TiO_2,[18,19] R-ZnO,[20] and R-WO_3.[21] Our computational results also indicate that there's no change of the conduction band minimum for the reduced R-CdS, except formation of a gap state in the vicinity of the valence band maximum caused by the S vacancies (Figure S6). Thus, enabling the reduction of Co(II)Py to Co(I)Py by a negative shift of the CdS flat band can be ruled out.

The reduction potential for a single-step simultaneous two-electron transfer reduction of Co(III)Py at pH 13.5 is $E_{Co(III)Py/Co(I)Py}$ = −0.63 V, which is the average value of $E_{1/2[Co(III)Py/Co(II)Py]}$ = −0.41 V and $E_{1/2[Co(II)Py/Co(I)Py]}$ = −0.85 V, as depicted in the element potential diagram shown in Figure 2b according to Hess's law. It is obvious that the reduction of Co(III)Py by a single-step simultaneous two-electron transfer process is energetically more favorable than a two-step successive one-electron transfer process. Considering that E_{fb}(CdS) = −0.84 V at pH 13.5, a single-step simultaneous two-electron transfer process from CdS to Co(III)Py to give Co(I)Py is thermodynamically allowed (ΔG = −0.21 eV), while the second electron transfer from CdS to Co(II)Py to produce Co(I)Py in a two-step successive one-electron transfer process is thermodynamically unfavorable (ΔG = 0.01 eV), as illustrated in Figure 2b.

To further investigate the charge transfer dynamics in CoPy/CdS hybrid systems, time-resolved PL spectroscopy (Figure S7) was employed at selected pH conditions of pH 6.0, 10.0, and 13.5. Table 1 lists the PL decays of CdS band-edge emission of diluted CoPy/CdS hybrid systems excited at 406.8 nm. In the presence of methanol as a hole scavenger, both electron transfer from CdS to CoPy and hole transfer from CdS to methanol contribute to the accelerated PL decay in CoPy/CdS hybrid systems.[22] While in the absence of methanol, the accelerated PL

Table 1. PL Lifetimes of CdS Band-Edge Emission in CoPy/CdS Hybrid Systems Revealed by Time-Resolved PL Spectroscopy in the Absence[a] or Presence[b] of Methanol under Various Experimental Conditions

entry	conditions	τ (ns)[d]	D_n (100%)
1	pH 6.0,[a] 0 μL CoPy[c]	217.12	
2	pH 6.0,[a] 20 μL CoPy	197.76	8.9%
3	pH 6.0,[b] 0 μL CoPy	199.93	7.9%
4	pH 6.0,[b] 20 μL CoPy	72.89	66.4%
5	pH 10.0,[a] 0 μL CoPy	237.27	
6	pH 10.0,[a] 20 μL CoPy	131.17	44.7%
7	pH 10.0,[b] 0 μL CoPy	146.61	38.2%
8	pH 10.0,[b] 20 μL CoPy	46.46	80.4%
9	pH 13.5,[a] 0 μL CoPy	198.47	
10	pH 13.5,[a] 20 μL CoPy	110.56	44.3%
11	pH 13.5,[b] 0 μL CoPy	26.86	86.5%
12	pH 13.5,[b] 20 μL CoPy	40.73	79.5%

[a]Aqueous solution without methanol. [b]Methanol aqueous solution (CH$_3$OH/H$_2$O = 1:2.4). [c]Saturated CoPy DMF solution (∼20 mM) at room temperature. [d]Average lifetimes derived from the three exponent fitting of the time-resolved PL traces.

decay in CoPy/CdS hybrid systems can be ascribed to the electron transfer from CdS to CoPy.[23] Similarly, in the absence of CoPy but presence of methanol, the accelerated PL decay can be ascribed to the hole transfer from CdS to methanol. To compare the differences of charge transfer dynamics in the absence/presence of CoPy and methanol, the degrees of CdS PL decay in the presence of CoPy and/or methanol under different pH conditions is defined as D, which can be expressed with the following formula: $D_n = (1 - \tau_n/\tau_{on}) \times 100\%$, where τ_o and τ represent the PL lifetimes in the absence and presence of relevant quenchers, respectively, and n represents the entry of Table 1. Therefore, a larger value of D implies a faster PL decay. It can be seen that the degrees of CdS PL decay in CoPy/CdS hybrid systems in the presence of CoPy/methanol are in the following order: D_2 (8.9%, pH 6.0) < D_6 (44.7%, pH 10.0) ~ D_{10} (44.3%, pH 13.5) and D_3 (7.9%, pH 6.0) < D_7 (38.2%, pH 10.0) < D_{11} (86.5%, pH 13.5), indicating that electron/hole transfer from photoirradiated CdS to CoPy/methanol is accelerated under alkaline conditions. In the presence of methanol, the PL decay degrees are both increased when adding CoPy at pH 6.0 and 10.0 in the following order: D_4 (66.4%, 20 μL CoPy) > D_3 (7.92%, 0 μL CoPy) for pH 6.0, and D_8 (80.4%, 20 μL CoPy) > D_7 (38.2%, 0 μL CoPy) for pH 10.0. However, the PL decay degree at pH 13.5 in the presence of CoPy (D_{12} = 79.5%) becomes slightly smaller than that in the absence of CoPy (D_{11} = 86.5%). Therefore, one-electron reduction of CoPy to Co(II)Py at pH 10.0 can be inferred, though the second electron reduction of CoPy (Co(II)Py to Co(I)Py) by photoirradiated CdS is thermodynamically unfavorable. No electron transfer from photoirradiated CdS to CoPy at the initial photoirradiation stage of the CoPy/CdS hybrid system under pH 13.5 conditions is consistent with the formation of R-CdS during the photocatalytic reactions.

Single-step simultaneous two-electron transfer process was evidenced by the detection of reduced CoPy species using semi-in situ EPR and UV−vis absorption spectroscopy. Semi-in situ X-band EPR spectra (100 K) of CoPy/CdS hybrid systems under different pH conditions were measured by quenching the samples immediately in liquid nitrogen after 5−90 min photoirradiation. The reference EPR spectrum of Co(II)Py ($g_\perp$

= 2.26; $g_\parallel$ = 2.14) generated by reducing Co(III)Py using NaBH$_4$ in alkaline condition is similar to that reported in the literature (Figure 3a).[24] Under the same pH conditions (pH 6.0, 10.0, and
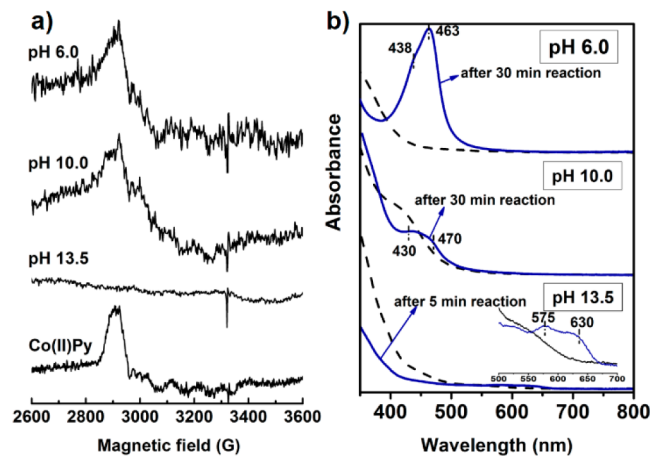

Figure 3. (a) X-band EPR (100 K) spectra of Co(II)Py (NaBH$_4$ reduced CoPy) and CoPy/CdS hybrid systems after photoirradiation ($\lambda \geq$ 420 nm) for 90 min under particular pH conditions. (b) UV−vis absorption spectra of the supernatant solutions of CoPy/CdS hybrid systems before and after photocatalytic reactions for a certain time performed under different pH conditions. For those measured after photocatalytic reactions, the solutions were obtained in the cuvette using a 0.2 μm syringe filter and then sealed with PARAFILM under operation in a glovebox.

13.5), CoPy/CdS hybrid systems showed similar EPR spectra in all cases during 5−90 min photoirradiation time (Figure S8). The typical EPR spectra of CoPy/CdS hybrid systems measured immediately after 90 min photoirradiation at pH 6.0, 10.0, and 13.5 are shown in Figure 3a. Observation of the Co(II) EPR signals indicates that one-electron transfer reduction of Co(III)-Py to form Co(II)Py is an affirmative process at pH 6.0 and 10.0. However, no Co(II)Py EPR signal could be detected at pH 13.5, which implies that one-electron reduction of Co(III)Py under such condition is skipped.

Figure 3b shows the UV−vis absorption spectra of the supernatant reaction solutions of CoPy/CdS hybrid systems before and after photocatalytic reactions under different pH conditions. The solutions of the reaction mixtures at pH 6.0 and 10.0 after 30 min photoirradiation show absorption peaks of d−d transition of Co(II) due to reduction of Co(III)Py to Co(II)Py.[25,26] Interestingly, no Co(II)Py formation is observed for the reaction mixtures at pH 13.5 after 5 min photoirradiation; instead, expansion of the spectrum in the range of 500−700 nm clearly shows a broad absorption peak of Co(I)Py with maxima at 575−630 nm.[25]

Based on the above experimental results, the electron transfer mechanism in CoPy/CdS hybrid systems under different pH conditions can be summarized as follows. Under acidic conditions, a two-step successive one-electron transfer process from CdS to CoPy governs the sequential reduction processes of Co(III) Py → Co(II)Py → Co(I)Py. With the pH value increased to 10.0 and 12.0, though one-electron reduction of Co(III)Py to Co(II)Py by photoirradiated CdS is allowed, further reduction of Co(II)Py to Co(I)Py becomes energetically unfavorable, which may lead to negligible photocatalytic activities. With the pH value further increased to 13.5, the energetically more favorable single-step simultaneous two-

electron transfer from CdS to CoPy takes place, allowing reduction of Co(III)Py to Co(I)Py to reduce protons to H_2. Such photocatalytic H_2 evolution reaction may be further enhanced by accelerated methanol oxidation at pH 13.5.

In conclusion, a single-step simultaneous two-electron transfer from semiconductors to molecular catalysts in CoPy/CdS hybrid systems under strong alkaline conditions (pH 13.5) has been revealed in this work. Our study demonstrates that such a single-step simultaneous two-electron transfer process is energetically more favorable than a two-step successive one-electron transfer process, which is the key process for enabling the photocatalytic H_2 evolution in CoPy/CdS hybrid systems under strong alkaline conditions. This finding may open up a new avenue for the assembly and optimization of hybrid systems for solar fuel production which possess a multielectron transfer process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04080.

> Figures S1−S9, Tables S1−S4, further statements of syntheses, characterizations (PDF)

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Notes
The authors declare no competing financial interest.

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