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A novel Co-O cluster based coordination polymer for efficient hydrogen production photocatalysis



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<i>Keywords:</i> Coordination polymer Non-precious photocatalyst Hydrogen production	The development of efficient and economical catalysts for photocatalytic water splitting and hydrogen pro- duction is one of the promising methods to alleviate the current energy crisis. In this work, we synthesized a novel Co-O cluster based coordination polymer, $[Co_2(HL)_2(DMF)_2H_2O]$ -solvents (Co-CP) by a facile sol- vothermal method from amino-functionalized ligand and non-precious cobalt salt. The Co-CP possesses a bandgap of 2.65 eV, whose conduction and valence band are -0.8 and 1.85 eV, respectively. Efficiently, the visible-light driven photocatalytic hydrogen evolution rate of Co-CP reaches 1778 µmol g ⁻¹ h ⁻¹ , due to the rapid charge transfer and efficient suppression of electron-hole recombination as determined by photocurrent response and photoluminescence measurement. Possible photocatalytic mechanisms are proposed, for which the Co-O clusters are predicted to be the active sites.

1. Introduction

With the fast growing of global energy crisis, hydrogen stands out as one of the green renewable energy sources most likely to replace traditional fossil energy [1]. Since Fujishima firstly achieved photocatalytic hydrogen evolution from water by using TiO₂ in 1972 [2], photocatalytic water splitting has been proved to be an efficient and feasible way to transform the endless solar energy into clean chemical energy. However, semiconductor catalysts such as TiO₂, CdS, BiVO₄, g-C₃N₄, and so on [3–5], often suffer from insufficient activity due to their large bandgaps, which can only absorb ultraviolet light, accounting for only 4% of the whole solar spectrum.

Coordination polymers (CPs), a kind of crystalline material self-assembled from metal ions and organic linkers, have been widely studied in gas adsorption and separation, sensing, drug delivery, etc [6–10]. Benefiting from the adjustable porous structure, functionally modified ligands, and uniformly dispersed active sites, CPs can serve as potential photocatalysts for hydrogen production [11]. In attempt to obtain photocatalytically active CPs, there are multiple strategies as proposed in the literatures. One of the strategies is to design CPs containing precious metal catalytic centers, such as Pt-, Ru-, Rh-, and so on, by insitu or post-synthetic method [12,13]. Another strategy is to use nonprecious metal-based CPs, which is definitely more economical. Among which, cobalt-based complexes are proved to be the most versatile nonprecious metal catalysts for water splitting, while its practical industrial application suffers from such problems as instability in the acid-base environment and non-recyclability, which should be solved [19,20]. On the other hand, there is another strategy to improve the photocatalytic activity of CPs by applying organic ligand with visible light absorbing abilities, such as dye-sensitized ligands [14], porphyrins [15], and amino-functionalized ligands, etc [16–18].

Inspired by the researches mentioned above, we designed and synthesized a Co(II)-CP that can absorb visible light by using earth-rich metal cobalt and amino-modified ligand (2'-amino-[1,1':4',1''-terphenyl]-3,3",5,5"- tetracarboxylic acid (H₄L)). The photocatalytic hydrogen production of Co-CP under visible light irradiation and involved mechanisms were explored in detail.

2. Experimental sections

2.1. Chemicals and materials

2,5-dibromoaniline was purchased from Sigma-Aldrich. 3, 5-bis (methoxycarbonyl) benzeneboronic acid pinacolester was purchased from UCHEM Inc. Cesium fluoride, tetrakis (triphenylphosphine) palladium and $Co(NO_3)_2$ ·6H₂O were purchased from Alfa aesar. Ru (bpy)₃Cl₂ was purchased from HWRK Chem. Triethanolamine (TEOA) was purchased from Sigma-Aldrich. All chemicals and solvents

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purchased from the commercial sources were of AR grade and used without further purification.

2.2. Characterization and methods

Electron Paramagnetic Resonance (EPR) experiments were carried out by using Bruker Electron ParaMagnetic Resonance (A300). The powder sample was sealed into the capillary and tested at X-band microwave frequency in Continuous Wave (CW) mode at 100 K. Elemental analysis (EA) measurement was performed on a Vario EL CHNS elemental analyzer. The UV-vis diffuse reflectance spectra were recorded on a SHIMADZU UV-3600. Photoluminescence spectra were tested by an EDINBURGH FLS980 fluorescence spectrophotometer. FT-IR spectra were performed on a Nicolet/Nexus-670 spectrometer in the range of 4000-500 cm⁻¹. The thermogravimetric analysis (TGA) curve was recorded on a STA 449 F3 Jupiter instrument under nitrogen flow at a heating rate of 5 °C per minute. Powder X-ray diffraction (PXRD) were measured on a Rigaku SmartLab X-ray diffractometer with Cu-Ka radiation ($\lambda = 1.54056$ Å) at room temperature. Single-crystal X-ray crystallography (SCXRD) data were collected on a Rigaku Oxford SuperNova X-RAY diffractometer system equipped with a Cu sealed tube ($\lambda = 1.54184$ Å) at 150 K. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific Nexsa with a monochromatic Al Ka X-ray source.

2.3. Synthesis of [Co₂(HL)₂·(DMF)₂·H₂O] solvents (Co-CP)

The 2'-amino-[1,1':4',1"-terphenyl]-3,3",5,5"ligand tetracarboxylic acid (H₄L) was synthesized according to the previous literature [21], and characterized by ¹H NMR (400 MHz, DMSO-d₆) δ 13.38 (s, 4 H), 8.47 - 8.42 (m, 2 H), 8.40 (d, J = 1.5 Hz, 2 H), 8.23 (d, J = 1.5 Hz, 2 H), 7.23 (d, J = 1.6 Hz, 1 H), 7.20 (d, J = 7.9 Hz, 1 H), 7.05 (dd, J = 7.9, 1.6 Hz, 1 H), 5.20 (s, 2 H). The Co-CP was synthesized by a mild solvothermal method. Briefly, H₄L (0.0105 g, 0.025 mmol) and Co (NO₃)₂·6H₂O (0.0291 g,0.1 mmol) were dissolved in a DMF-methanol- H_2O (v/v/v 5/2/1) mixture solution (8 mL) and ultrasound for 30 min, which was then sealed in a 20-mL Teflon reactor and heated in an oven at 85 °C for 24 h. After being centrifuged and washed with DMF and water for several times, the obtained purple crystals were finally dried at 80 °C for 2 4 h in a vacuum oven. Among these crystals, the appropriate one was selected for SC-XRD measurement (Yield: 62.3%, based H4L). for on EA calcd. C₃₄H₅₁Co₂N₅O₁₉ ([Co₂(HL)₂·(DMF)₂·H₂O]·DMF·6H₂O): C 42.90%, H 5.36%, N 7.36%; found: C 42.78%, H 5.39%, N 7.07%. (CCDC number: 1945367).

2.4. Photocatalytic hydrogen evolution

Typically, the photocatalytic experiments were carried out in a 55 mL Pyrex reactor, in which 4 mg of Co-CP as photocatalyst, 4 mg of Ru(bpy)₃Cl₂ as photosensitizer (PS) and 1 mL of TEOA as sacrificial agent were dispersed in 5 mL of 4:1 (v/v) mixed solution of DMF-H₂O. Before irradiation, the suspension was purged by nitrogen for at least 20 min. Then the resultant mixtures were irradiated by a white LED lamp ($\lambda = 420$ –780 nm, 100 mW cm⁻²) and stirred, cooling with the flowing air. After the reaction, 200 µL headspace samples were analyzed for H₂ concentration by a gas chromatograph (GC9790, Fuli Analytical Instrument Co., Ltd) equipped with TCD detector.

2.5. Electrochemical measurement

The photoelectrochemical measurement was performed on a CHI 660e electrochemical work station (Chenhua Instrument, Shanghai, China) in a standard three-electrode system with a platinum plate as the counter electrode, a standard Ag/AgCl (saturated KCl) as a reference electrode and a photocatalyst-coated ITO as the working electrode. A $0.2 \text{ M} \text{ Na}_2\text{SO}_4$ aqueous solution was used as electrolyte. To be specific,



Fig. 1. The crystal structure of **Co-CP**: a) coordination mode of Co-O clusters; b) linking mode of the ligand; c) 3D packing mode along *a* axis. Color code: red, O; gray C; blue N; purple Co; H atoms are omitted for clarity.

2 mg of the Co-CP were dispersed into a mixed solution with 20 μ L Nafion and 2 mL of ethanol to form a suspension, which was then applied by drop coating onto a 0.5 cm*0.5 cm indium-tin oxide (ITO) glass electrode. As for photocurrent tests, a 300 W Xenon lamp with a UV-cut off filter ($\lambda > 420$ nm) was used as light source. Mott-Schottky tests were performed with the potentials ranging from -0.8 to 0.8 V at different frequencies (500, 1000, and 1500 Hz, respectively), measuring by Impedance-Potential technique. The amplitude was fixed at 10 mV. Cyclic voltammetry (CV) measurements were also carried out with a three-electrode system, in which 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was used as electrolyte in DMF solvent.

3. Results and discussion

3.1. Crystal structure and characterization

Co-CP was obtained by the mild reaction of Co(NO₃)₂·6H₂O and H₄L

(2'-amino-[1,1':4',1''-terphenyl]-3,3",5,5"-tetracarboxylic acid) ligand in DMF-Methanol-H₂O mixed solvent at 85 °C for 24 h. Single-crystal Xray crystallography shows a 3D framework crystallized in a chiral monoclinic space group $P2_1$ (Table S1). As shown in Fig. 1a, there are two different coordination environments for Co²⁺ ions. Co1 is hexacoordinated by six oxygen atoms, four of which are from chelating coordination carboxylate groups, and the other two are from monodentate coordinated carboxylate groups. Co2 is also hexa-coordinated by six oxygen atoms, while one of them comes from a coordinated water molecule, two from DMF, and the remaining three oxygen atoms are from monodentate coordinated carboxylate groups. The thus formed $\{Co_2O_6\}$ clusters are linked by the tetrapodal organic ligands (Fig. 1b). In general, a chiral network is formed in the crystal structure (Fig. 1c). However, since crystals with opposite chirality are co-existed, the bulk samples are racemic as a whole. Meanwhile, as calculated by PLATON software [22], after removing solvent, the total potential solvent accessible void volume is 1029.1 Å, which accounts for about 40.2% of the total crystal volume. To investigate the phase purity of Co-CP, powder X-ray diffraction (PXRD) experiment was performed, whose diffraction peaks matched well with the simulated one (Fig. S1).

Fourier transform infrared (FT-IR) spectrum was measured to prove the coordination effect between cobalt ions and organic ligands. Compared with the free ligand, the hydroxyl vibration peak of - COOH ranging from 2500 to 3200 cm^{-1} disappears in the Co-CP, and the stretching vibration peak of the carbonyl group shifts to a low wave number at around $1663 \sim 1623 \,\mathrm{cm}^{-1}$ (Fig. S2). According to the thermogravimetric analysis curve, the first weight loss peak appeared at around 100 °C due to the loss of the coordinated and free water molecules in the framework. The second weight loss peak appeared at around 150 °C should be attributed to the departure of DMF molecules. And the framework collapse of Co-CP occurred up to 450 °C, revealing the excellent thermal stability (Fig. S3). Co-CP also exhibited good solvent stability. There was no significant change in the powder diffraction peaks after soaking for 12h in DMF, acetonitrile, acetone, ethanol, trimethylamine, and DMF/H2O mixed solvent (v/v 4/1) (Fig. S4).

3.2. Optical and electrochemical properties

As shown in UV-vis diffuse reflectance spectra (Fig. 2a), H₄L owns an absorption band edge at 450 nm, which can be attributed to the K and B bands of aromatic group. Compared with the ligand, Co-CP possess a broad absorption in the visible region ranging from 420 to 650 nm due to the typical d-d transition absorption of Co²⁺ ions. Also, the introduction of the amino groups in the ligand also results in the strong visible-light absorption [23]. Calculated by the Kubelka-Munk method, the bandgap is about 2.65 eV for Co-CP, as shown in the Tauc plot curve (Fig. S5). For photocatalytic hydrogen production, in addition to having a suitable bandgap to separate photo-generated electrons and holes, the matching positions of the conduction band (CB) and valence band (VB) are critical. Mott-Schottky measurements were used to confirm the energy levels, which indicated the n-type property of the Co-CP and the flat band position was determined to be -0.90 V vs. Ag/ AgCl (-0.70 V vs. NHE, Fig. 2b). In general, the bottom of the conduction band of a n-type semiconductor is 0.10 V more negative than the flat band position [24], therefore the bottom of the conduction band of Co-CP is estimated to be -0.80 V, which is more negative than the redox potential of H^+/H_2 . Combining the bandgap of 2.65 eV obtained by UV-vis diffuse reflectance spectra and the CB, the valence band position should be 1.85 eV, which was well corroborated from the XPS spectra (Fig. S6). Considering the remarkable light absorption and suitable band position like semiconductors, Co-CP is a kind of potential catalyst for photocatalytic hydrogen evolution.



Fig. 2. a) UV–vis diffuse reflectance spectra of Co-CP and H₄L ligand; b) Mott-Schottky plots of the Co-CP. The illustration shows the predicted band edge positions. c) Photocatalytic hydrogen production efficiencies of Co-CP. Reaction conditions: Solvent, 4 mL DMF and 1 mL H₂O; 1 mL TEOA as sacrificial reagent; 4 mg Co-CP as photocatalyst, 4 mg Ru(bpy)₃Cl₂ as photosensitizer, irradiated by white-light LED lamp with a power of 100 mW·cm⁻².

3.3. Visible-light photocatalytic hydrogen production and proposed mechanism

The Co-CP powder was evaluated for visible-light driven photocatalytic water splitting to produce hydrogen at room temperature in the presence of TEOA serving as sacrificial agent and $\text{Ru}(\text{bpy})_3\text{Cl}_2$ as photosensitizer under a white-light LED lamp (100 mw·cm⁻²). As shown in Fig. 3c, comparative tests manifest that without light, photosensitizer, or sacrificial agent, there was no hydrogen product detected. Without water or catalyst, only traces of hydrogen was observed, which was ascribed to proton reduction from the sacrificial agent. It can be seen that the Co-CP, light irradiation, photosensitizer, sacrificial agent and water all play decisive role in the hydrogen production process. Furthermore, the solvent ratio of DMF to H₂O was adjusted to investigated the photocatalytic hydrogen production efficiencies, in which Co-CP showed the best catalytic performance in the



Fig. 3. a) PL emission spectra of Co-CP and H₄L ligand. b) XPS spectra of Co-CP. c) CW EPR spectra of pristine Co-CP and the Co-CP after photocatalytic hydrogen production. d) The Cyclic voltammogram of Co-CP. Measured conditions: Ag/AgCl was used as the reference electrode, indium-tin oxide (ITO) glass electrode was used as the working electrode, and a platinum plate was used as counter electrode; electrolyte, a DMF solution of Bu_4NPF_6 (0.1 M); scan rate, 0.1 V/s.

DMF/H₂O (4/1, v/v) mixed solvent (Fig. S7). Through a series of control experiments, it was found that triethanolamine (TEOA) worked best as a sacrificial agent (Fig. S8). Screening the above conditions, 4 mg Co-CP, 4 mg Ru(bpy)₃Cl₂, and 1 mL TEOA were added into 5 mL of DMF/H₂O (4/1, v/v) pre-mixed solvent and exposed to visible light for photocatalytic hydrogen evolution, which could reach an activity of 1778 µmol g⁻¹ h⁻¹ at 3 h. The Co-CP-catalyzed HER reaction was further investigated by recycling experiments, in which Co-CP was centrifuged from the catalytic reaction solution, washed with DMF for 3 times, and redistributed in the fresh solvent after every 2 h illumination. As shown in Fig. S9, Co-CP maintained catalytic activity within three cycles, indicating that the catalyst is recyclable and stable for photocatalytic hydrogen.

In attempt to study the separation and recombination of photo-induced electron-hole pairs in the catalyst, photoluminescence (PL) measurements were performed on Co-CP and H₄L ligand. Both excited by 460 nm, H₄L ligand presented a maximum emission peak at 575 nm, while the PL of the Co-CP was almost quenched, showing the rapid transfer of photo-generated electrons and lower recombination rate of the photo-induced electron-hole (Fig. 3a). Furthermore, the photocurrent response of Co-CP was recorded versus Ag/AgCl under visible light. As soon as the light was turn on, a fast and apparent current signal was observed, while the signal decayed rapidly with the light turned off. The fast, uniform and invertible photocurrent response shown in Fig. S10 suggested the efficient separation of photo-generated charge carriers in Co-CP.

High-resolution X-ray photoelectron spectroscopy (XPS) measurement was used to probe the surface chemical state of cobalt in Co-CP. As shown in Fig. 3b, the peaks at 781.3 and 797.5 eV were attributed to Co $2p_{3/2}$ and Co $2p_{1/2}$ core level photo emission. And the two adjacent satellite peaks at 785.8 and 801.9 eV were originated from Co²⁺ shake up excitation [25,26], which indicating the existence of Co²⁺ species in Co-CP. To elucidate the mechanism of the photocatalytic process, continuous wave (CW) EPR spectroscopy was used to determine the active intermediates formed during visible-light irradiation over the Co-CP at 100 K. Recorded at X-band microwave frequency (9.85 GHz), the CW EPR spectra of pristine Co-CP in the dark and after visible-light driven photocatalytic hydrogen production were presented in Fig. 3c. According to literature, the downfield signal at g = 2.04 both occurred to the pristine Co-CP and the catalyzed sample can be attributed to the spatially confined amino-groups in the Co-CP [27,28]. Furthermore,

there was no signal of the low spin (S = 1/2) Co^{II} species occurred to both two samples, disclosing the weak 6-coordination in Co-CP. While exposing Co-CP to visible light for photocatalysis, an intense new signal with a g value of 3.49 (at around 120 m T) was observed, which is characteristic of an octahedral high-spin (S = 3/2) Co^{II} species. The photo-induced EPR signal indicated that there was charge transfer in the Co-CP during photocatalysis [29].

The cyclic voltammetry (CV) measurement was performed on a DMF solution of 0.1 M Bu₄NPF₆ and the Co-CP coated electrode, which revealed the photo-induced electron transition inside the catalyst. As shown in Fig. 3d, there was two irreversible reduction peaks at -2.21 V and -1.47 V, respectively, which could be ascribed to the signal electron transfer from $[Co^{II}Co^{II}]$ to $[Co^{I}Co^{II}]$ and then $[Co^{I}Co^{II}]$ to $[Co^{I}Co^{II}]$ [16]. It was generally believed that in the photocatalytic process, the photosensitizer $[Ru(bpy)_3]^{2+}$ underwent an excited state $[Ru(bpy)_3]^{2+*}$ to quenching process, possibly by oxidative quenching or reduction quenching pathway [18]. In particular, the excited state $[Ru(bpy)_3]^{2+*}$ might be oxidized by the Co-CP catalyst, forming [Ru(bpy)₃]³⁺ species, or might be reduced by the sacrificial agent TEOA to form [Ru(bpy)₃]¹⁺ species, both of which accompanied with an electron-transfer (ET) process. In attempt to verify the quenching pathway of $[Ru(bpy)_3]^{2+*}$, the photoluminescence measurements of original Ru(bpy)₃Cl₂ solution and the solution with added 1 mL of TEOA were carried out (Fig. S11). There was no fluorescence quenching but a fluorescence enhancement occurred while adding 1 mL of TEOA into original mixed solution, indicating an oxidatively quenching pathway for the excited state [Ru $(bpy)_3]^{2+*}$. Additionally, comparing the UV-vis diffuse reflectance spectra of Co-CP and the emission spectrum of $[Ru(bpy)_3]^{2+}$, partial spectra overlap illustrated a feasible energy-transfer (EnT) from [Ru $(bpy)_3$ ²⁺ to the catalyst Co-CP (Fig. S12) [18].

Taking into account the above factors, we propose the possible mechanism of Co-CP photocatalytic hydrogen production as following. In the presence of the visible light, the photosensitizer $[Ru(bpy)_3]^2$ was excited to from photoactive [Ru(bpy)₃]^{2+*}, which then underwent an oxidatively quenching pathway accompanied by the generation of $[Ru(bpy)_3]^{3+}$ species. The excited photoelectron formed from the LUMO state of Ru(bpy)₃Cl₂ transfer to the unsaturated Co^{II} sites. The Co^{2+} in the catalyst Co-CP was reduced from the $[Ru(bpy)_3]^{2+*}$ to form an intermediate state [Co^{II}Co^I] or [Co^{II}Co^I], and the [Ru(bpy)₃]³⁺ immediately obtained electron from sacrificial agent TEOA, achieving a loop. Finally, the protons gathered on the catalyst surface by hydrogen bonding react with the photoelectrons on the unsaturated Co^{II} cites to continuously generate hydrogen. In general, Co-CP provides a good platform to promote the transfer of photoelectrons and inhibit the combination of photo-generated electron-holes of the Ru(bpy)₃Cl₂. The photocatalytic process is shown in Scheme 1.



Scheme 1. Plausible mechanism for visible-light driven photocatalytic hydrogen production by Co-CP.

4. Conclusion

To sum up, we synthesized a new amino-functionalized 3D cobalt coordination polymer (Co-CP) with efficient photocatalytic hydrogen production ability under visible-light irradiation. Benefiting from the appropriate bandgap of the framework and the rapid charge transfer as well as the efficient suppression of electron-hole recombination, Co-CP exhibits a photocatalytic activity of $1778 \,\mu$ mol g⁻¹ h⁻¹. This study might promote further exploration for the design and application of noble-metal-free coordination polymers in artificial photosynthesis.

Declaration of Competing Interest

No conflict of interests are reported.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2019. 112137.

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