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Photocatalyst based on a transition metal-Schiff base ligand and V-doped Keggin-type polyoxometalate for efficient and stable CO₂ reduction†

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In order to simultaneously control the greenhouse effect and solve the problem of energy depletion, the strategy of converting CO₂ into other forms of energy can be used. In this work, two Keggin-type polyoxometalate-based compounds were synthesized *via* the hydrothermal method: [Co(C₁₁H₁₅N₇O₂)(H₂O)]₂([Co(C₁₁H₁₅N₇O₂)(H₂O)]₂(PW₁₁^{VI}V^{IV}O₄₀))(PW₉^{VI}W^V₂V^{IV}O₄₀)·14.5H₂O (**1**) and [Fe(C₁₁H₁₅N₇O₂)(H₂O)]₂([Fe(C₁₁H₁₅N₇O₂)(H₂O)]₂(BW₁₂O₄₀))(BW₁₂O₄₀)·11H₂O (**2**). The structural analysis of compound **1** indicated that an interesting V-doped Keggin-type (PW₁₁^{VI}V^{IV}O₄₀)⁵⁻ anion is successfully bonded to the two [Co(C₁₁H₁₅N₇O₂)(H₂O)]²⁺ cations to generate a hybrid [Co(C₁₁H₁₅N₇O₂)(H₂O)]₂(PW₁₁^{VI}V^{IV}O₄₀) unit. Through a series of photocatalytic CO₂ reduction reaction (CO₂RR) experiments, it was found that compound **1** exhibits good photocatalytic performance. The CO generation rate can reach 7081.4 μmol g⁻¹ h⁻¹, and the selectivity was 83.8%. In addition, the stable and efficient photocatalytic activity of compound **1** was verified after four-cycle photocatalytic experiments, which provided a new idea for CO₂ photoreduction to CO. Comparatively, the CO production rates was 103.5 μmol g⁻¹ h⁻¹ for compound **2**. This is because the adsorption energy of CO on Co is lower than that on Fe. Furthermore, V-modified compound **1** enhances CO₂ adsorption to promote CO₂ conversion.

Received 8th May 2025,
Accepted 27th May 2025

DOI: 10.1039/d5dt01081k

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Introduction

In recent years, it has triggered negative environmental impacts such as increased consumption of fossil fuel and rising greenhouse gas emissions as the country's industrialisation has progressed smoothly.^{1–4} Therefore, there is an urgent need to think about how we can simultaneously address the dual challenge of the depletion of non-renewable resources and global warming. One immediate solution is to utilize renewable solar energy for photocatalysis to convert greenhouse gases such as carbon dioxide into needed chemicals or other forms of renewable energy.⁵ This approach would contribute to the alleviation of the prevailing energy crisis and align with the development of a greener society.

Polyoxometalates (POMs) are anionic forms of transition metal oxides with a variety of structures. Different redox potentials and intramolecular charge transfer capabilities can be achieved by selecting POMs with different structures and transition metals (TMs). POMs as a unique organic-inorganic hybrid material have been applied in photocatalysis, electrocatalysis, and magnetic materials.^{6–16} Nowadays, the development of heterogeneous POM-based photocatalysts with high activity, selectivity, and stability has become a research topic in the field of catalysis.^{17–20} POM-based hybrid materials were modified by organic ligands during POM self-assembly owing to their limitations such as poor stability and strong solubility. Notably, organic ligands enhanced the stability, light adsorption and hydrophobicity of POM-based hybrid materials.^{21–23} Moreover, the introduction of TM into POMs can modulate their electronic structure and improve their physicochemical properties to facilitate the reaction. Among numerous POMs, Keggin-type POMs are typical representatives of the most commonly synthesized and well-studied POMs, which stand out for their easy-to-manufacture, economic, green and non-corrosive properties.^{24–29} In 2006, Prof. Francis Sécheresse's group synthesized the mixed clusters of V-doped Keggin-type heteropolytungstates for the first time. Then, the study on these materials

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† Electronic supplementary information (ESI) available: Synthesis, details of crystallographic data, structural figures, PXRD patterns, IR spectra, and TGA characterization. CCDC 2449245 2449246. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5dt01081k>

began to enter the public vision. The introduction of V atoms enhanced the adsorption of CO₂.^{30–33} Given that the Schiff base ligand 2,6-diacetylpyridinedicarbazide (DAPSC) was employed for the modification of two Keggin-type POMs because it has a similar structure to chlorophyll's, which possesses a planar conjugate structure. The conjugated structures formed by DAPSC and metal coordination accelerate the ligand-to-metal charge transfer (LMCT) process. Therefore, two different Keggin-type POMs with different TM (Co, Fe) serving as catalytic sites were synthesized by hydrothermal method in this work: [Co(C₁₁H₁₅N₇O₂)(H₂O)₂]₄{[Co(C₁₁H₁₅N₇O₂)(H₂O)₂]₂(PW₁₁^{VI}V^{IV}O₄₀)}₂{PW₉^{VI}W^V₂V^{IV}O₄₀}·14.5H₂O (**1**), [Fe(C₁₁H₁₅N₇O₂)(H₂O)₂]₃{[Fe(C₁₁H₁₅N₇O₂)(H₂O)₂]₂(BW₁₂O₄₀)}₂(BW₁₂O₄₀)·11H₂O (**2**). In particular, compound **1** was successfully V-modified. Compounds **1–2** formed 3D supramolecular structures through hydrogen bonding interactions. Notably, compound **1** exhibits higher activity than compound **2** because the adsorption energy of CO on Co is lower than that on Fe.³⁴ Furthermore, the V-modified derivative of compound **1** enhances CO₂ adsorption, thereby promoting CO₂ conversion. The experimental results demonstrated that the optimum dosage of compound **1** (3 mg) resulted in the production of 169.9 μmol of CO after eight hours of visible light irradiation. The results show an average CO generation rate of 7081.4 μmol g^{−1} h^{−1} and 83.8% selectivity. The maximum rate was found to be 8690.1 μmol g^{−1} h^{−1}. Compound **1**, as a heterogeneous catalyst, maintained its photocatalytic activity after four cycle experiments. The results prove that compound **1** exhibits remarkable photocatalytic performance and structural stability.

Experimental section

Synthesis of the compounds

[Co(C₁₁H₁₅N₇O₂)(H₂O)₂]₄{[Co(C₁₁H₁₅N₇O₂)(H₂O)₂]₂(PW₁₁^{VI}V^{IV}O₄₀)}₂{PW₉^{VI}W^V₂V^{IV}O₄₀}·14.5H₂O (**1**). A solution prepared from H₃PW₁₂O₄₀ (0.1 g, 0.035 mmol), CoCl₂·6H₂O (0.12 g, 0.5 mmol), VOSO₄ (0.041 g, 0.25 mmol) and DAPSC (0.025 g, 0.09 mmol) was added to deionized water (10 mL) in a Teflon-lined autoclave under stirring with a magnetic stirrer for twenty minutes. The autoclave was then transferred to the oven, kept at 90 °C for 3 days, and then cooled to room temperature. The resulting precipitate was washed with deionized water, and black shuttle crystals (Fig. S1a†) were obtained (yield: 47% calculated as DAPSC). Experimental value of elemental analysis: C: 9.97%, N: 7.40%, H: 1.75% (theoretical value: C: 9.65%, N: 7.14%, H: 1.70%).

[Fe(C₁₁H₁₅N₇O₂)(H₂O)₂]₃{[Fe(C₁₁H₁₅N₇O₂)(H₂O)₂]₂(BW₁₂O₄₀)}₂(BW₁₂O₄₀)·11H₂O (**2**). The synthetic procedure for **2** was the same as that for **1**, except that K₅(α-BW₁₂O₄₀)·11.4H₂O (0.1 g, 0.03 mmol) was used instead of H₃PW₁₂O₄₀ and that Fe(CH₃COO)₂ (0.087 g, 0.5 mmol) was used instead of CoCl₂·6H₂O. Black block crystals (Fig. S1b†) were obtained (yield: 41% calculated as K₅BW₁₂O₄₀). Experimental value of

elemental analysis: C: 8.56%, N: 6.35%, H: 1.36% (theoretical value: C: 8.30%, N: 6.67%, H: 1.39%).

Results and discussion

Crystal structure

The crystal structures of compounds **1** and **2** were examined by single-crystal X-ray diffraction. Compound **1** belongs to the monoclinic crystal system and crystallizes in the *P*2₁/*m* space group (Table S1†). Two Keggin-type POMs clusters formed by W and V atoms partially in disorder are present in compound **1** as {PW₁₁^{VI}V^{IV}} and {PW₉^{VI}W^V₂V^{IV}}. The doping of V atoms enhances the adsorption of CO₂ on {PW₁₁^{VI}V^{IV}} as well as {PW₉^{VI}W^V₂V^{IV}}. The structure of compound **1** (Fig. 1a) consists of two parts. The first part is a typical double-cap structure composed of two cationic fragments [Co(C₁₁H₁₅N₇O₂)(H₂O)]²⁺ connected to the POMs [PW₁₁^{VI}V^{IV}O₄₀]^{5−} clusters (Fig. 1b). The [Co(C₁₁H₁₅N₇O₂)(H₂O)]²⁺ fragment consists of Co²⁺, a DAPSC ligand and a coordinated water molecule. The other part is the Keggin-type heteropolytungstate [PW₉^{VI}W^V₂V^{IV}O₄₀]^{7−} clusters surrounded by four free [Co(C₁₁H₁₅N₇O₂)(H₂O)]²⁺ fragments, forming a flower-like cluster (Fig. 1c). The [Co(C₁₁H₁₅N₇O₂)(H₂O)]²⁺ fragment consists of Co²⁺, a DAPSC ligand and two coordinated water molecules. The Co atoms in compound **1** have two coordination environments, both in the seven-coordination pattern, forming a typical double pentagonal cone structure (Fig. S2†). Co1 is described as an example, which is connected to two O atoms (O1W, O2W) on two coordinated water molecules in addition to three N (N3, N4, N3) atoms and two O atoms (O13, O13) from the DAPSC (Fig. S3a†). The Co ions attached to the [PW₁₁^{VI}V^{IV}O₄₀]^{5−} bind three N atoms (N7, N8, N9) and two O atoms (O12, O45) originating from the same DAPSC, an O atom (O8) on [PW₁₁^{VI}V^{IV}O₄₀]^{5−} and an O

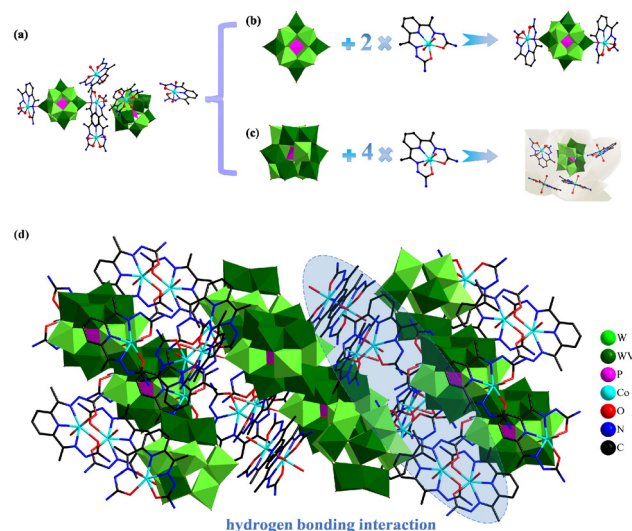


Fig. 1 (a) Asymmetric unit of compound **1**. (b) Double-cap structure of compound **1**. (c) Floral structure of compound **1** (ball-and-stick model). (d) 3D supramolecular framework (polyhedral) of compound **1**.

atom (O3W) in the coordinated water molecule (Fig. S3b†). The hydrogen bonding interactions between these two parts form the isolated structural unit. The Co–O bond lengths (2.111–2.192 Å) and Co–N bond lengths (2.155–2.201 Å) are indicated in Table S2.† In addition, the neighboring isolated structural units through hydrogen bonding formed a 3D supramolecular structure that maintained the stability of the crystal structure (Fig. 1d).

Compound **2** belongs to the triclinic crystal system and crystallizes in the $P\bar{1}$ space group. The individual structure unit (Fig. S5†) of compound **2** consists of a $\{BW_{12}\}$ cluster bridging two $[\text{Fe}(\text{C}_{11}\text{H}_{15}\text{N}_7\text{O}_2)(\text{H}_2\text{O})]^{2+}$, a free $\{BW_{12}\}$ cluster and three free $[\text{Fe}(\text{C}_{11}\text{H}_{15}\text{N}_7\text{O}_2)(\text{H}_2\text{O})_2]^{2+}$ clusters. The asymmetric unit of compound **2** formed a 3D structure through hydrogen bonding (Fig. S6 and S7†).

Characterization

Energy dispersive spectrometer (EDS) spectrum analyzed the elemental compositions of compounds **1** and **2** (Fig. S8 and S9†). All compounds were synthesized with the addition of V, but V was detected only in compound **1**. According to the mapping diagrams, the elements Co/Fe, C, W, O, N, and P were uniformly distributed in compound **1** (compound **2**), with the exception of V. Their PXRD experimental spectra are unanimity with the practical spectra, which prove that the above compounds are pure phases (Fig. S10 and S11†). The Fourier-transform infrared (FT-IR) spectrogram of compounds **1** and **2** was acquired in the range of 4000 to 400 cm^{-1} (Fig. S12 and S13†). For example, the broad peak at 3418–3433 cm^{-1} corresponds to the O–H stretching vibration of free water molecules in compound **1**. The peak at 2922 cm^{-1}

indicates the asymmetric stretching vibration of the C–H bond in DAPSC. Peaks at 1627–1664 cm^{-1} , 1445–1533 cm^{-1} , and 1200–1272 cm^{-1} suggest the presence of C=N, C=O, C=C, and C–N bonds,^{35,36} confirming the successful coordination of DAPSC. The absorption near 1053 cm^{-1} is attributed to the unique P–O bond in the main structural unit of compound **1**, while peaks around 955 cm^{-1} and 792–812 cm^{-1} correspond to M=O (M=W, V) and M–O–M bonds^{37,38} in heteropolytungstate. In compound **2**, the peak near 1050 cm^{-1} is associated with the B–O bond in its primary structure. Bond valence sum (BVS) calculations for the two POM-based anions in compound **1** confirmed the presence of W^{5+} in the free Keggin-type heteropolytungstate (Tables S4 and S5†). X-ray photoelectron spectroscopy (XPS) was used to characterize the elemental composition of compounds **1** and **2** and their chemical valence states (Fig. 2 and S14†). The experimental XPS spectrum of compound **1** confirmed the presence of Co, W, V, P, C, O and N elements in compound **1** (Fig. 2a). The W 4f XPS spectrum of compound **1** forms four classically overlapping peaks (Fig. 2b). The peaks with binding energies around 35.3 and 37.3 eV are attributed to W^{6+} , while the peaks at 34.6 and 36.7 eV can be assigned to W^{5+} in compound **1**.³⁹ As shown in Fig. 2c, the XPS of V 2p spectra indicate that the V^{4+} valence in compound **1**. In the XPS spectrum of Co (Fig. 2d), the deconvolution peaks with binding energies of 782.6 eV and 798.7 eV are attributed to the $2p_{3/2}$ and $2p_{1/2}$ of the Co^{2+} oxidation state, respectively. The XPS spectrum of Fe 2p (Fig. S14b†) indicated that the $2p_{3/2}$ and $2p_{1/2}$ regions of Fe^{2+} were at 710.7 and 724.0 eV. In addition, the crystal structures and thermal stability of compounds **1** and **2** were explored by thermogravimetric analysis (TGA) conducted at 25 °C–850 °C under N_2 atmosphere

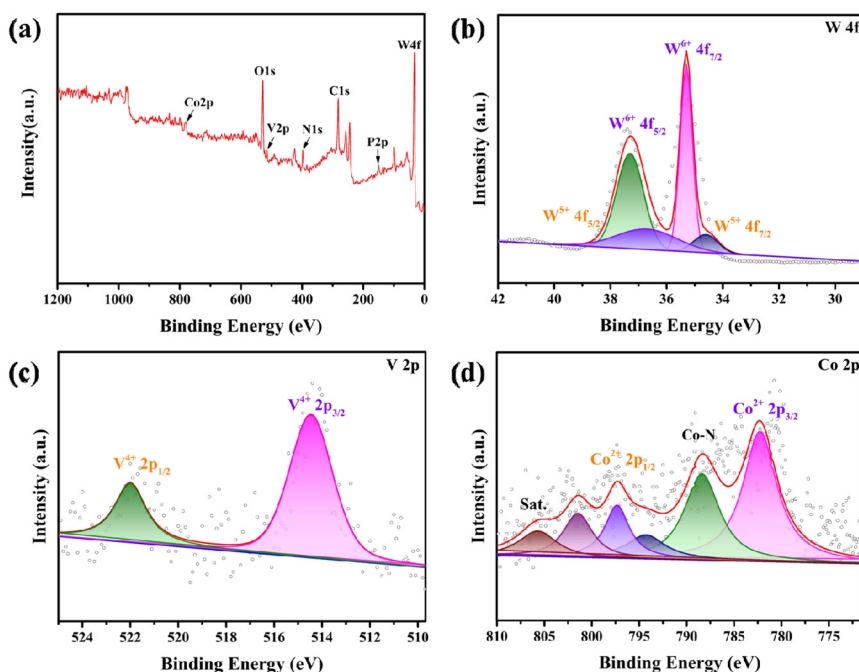


Fig. 2 (a) Full scan XPS spectrum, (b) W 4f, (c) V 2p, and (d) Co 2p XPS spectra of compound **1**.

(Fig. S15 and S16†). Both compounds **1** and **2** showed two weight loss phases. For compound **1** as an example, the weight loss of compound **1** was 3.57% (calcd 3.28%) at 25–240 °C, attributed to the loss of free and coordinated water molecules. The weight loss of compound **1** during 240–330 °C is attributed to the gradual decomposition of DAPSC.

Photocatalytic CO₂ reduction

These two compounds were evaluated through a series of photoelectronic experiments to assess their potential for use in photocatalytic CO₂RR. The absorption of visible light by the photocatalyst has a significant impact on the performance. Consequently, compounds **1** and **2** were characterized by solid-state ultraviolet-visible absorption spectroscopy (UV-vis). The results (Fig. 3a) show that compounds **1** and **2** exhibit strong absorption in the visible region. Tauc plots were constructed using the Kubelka–Munk equation ($ah\nu = C(h\nu - E)^2$) based on the measured UV-vis spectra, and the bandgap values (E_g) of compounds **1** and **2** were calculated to be 2.02 and 1.73 eV (Fig. 3b and S17†). Subsequently, Mott–Schottky curves were performed at 1000, 1500 and 2000 Hz to explore the energy-band structure and semiconducting properties of compounds **1** and **2**. As shown in Fig. 3c and S18,† the positive slopes exhibited indicate that compounds **1** and **2** have n-type semiconductor characteristics. Their flat band potentials (E_{FB}) were –1.36 and –1.09 V vs. Ag/AgCl. The conduction band potentials (E_{CB}) of compounds **1** and **2** were converted to –1.16 and –0.89 V vs. NHE. Their valence band potentials (E_{VB}) were cal-

culated to be 0.86 and 0.84 V vs. NHE in accordance with the equation $E_g = E_{VB} - E_{CB}$. Then, the band structure diagram^{40,41} of compound **1** was derived from the above data (Fig. 3d). It can be seen that the lowest unoccupied molecular orbital (LUMO) positions of these two compounds are lower than those of photocatalytic CO₂RR (CO₂/CO = –0.53 V vs. NHE), which proves that both are theoretically possible for photocatalytic CO₂RR.

A saturated mixture solution (MeCN : TEOA = 4 : 1, v/v) was designed with [Ru(bpy)₃]Cl₂·6H₂O as photosensitizer (PS) to investigate their catalytic activities in a photocatalytic CO₂RR system. The reduction product CO was produced when the two compounds were used separately. As shown in Fig. 4a, compound **1** produced 199.6 μmol of CO, 53.7 μmol of H₂, and 0.5 μmol of CH₄ after 8 h. The CO, H₂, and CH₄ yields were 4.48, 5.9, and 0.5 μmol when compound **2** was used. The properties of compounds **1** and **2** are quite different; thus, several factors were considered. First, from the initial step of CO₂RR, CO₂ + H⁺ + e[–] → COOH*, it can determine the ability of the catalysts to activate CO₂.⁴² Research shows that the compounds formed by Co with organic matter have a lower free energy barrier for activation of CO₂ molecules than Fe.

Second, CO can poison the metal active sites; thus, the adsorption barrier of TM for CO also affects the catalytic performance of the catalyst. It was found that CO molecules are more likely to be adsorbed at the TM center through the TM–C bond. The moderate interaction between Co and CO is weaker than Fe. Hence, the CO adsorption energy is lower, and the catalytic performance of Co-POM is improved. Considering the

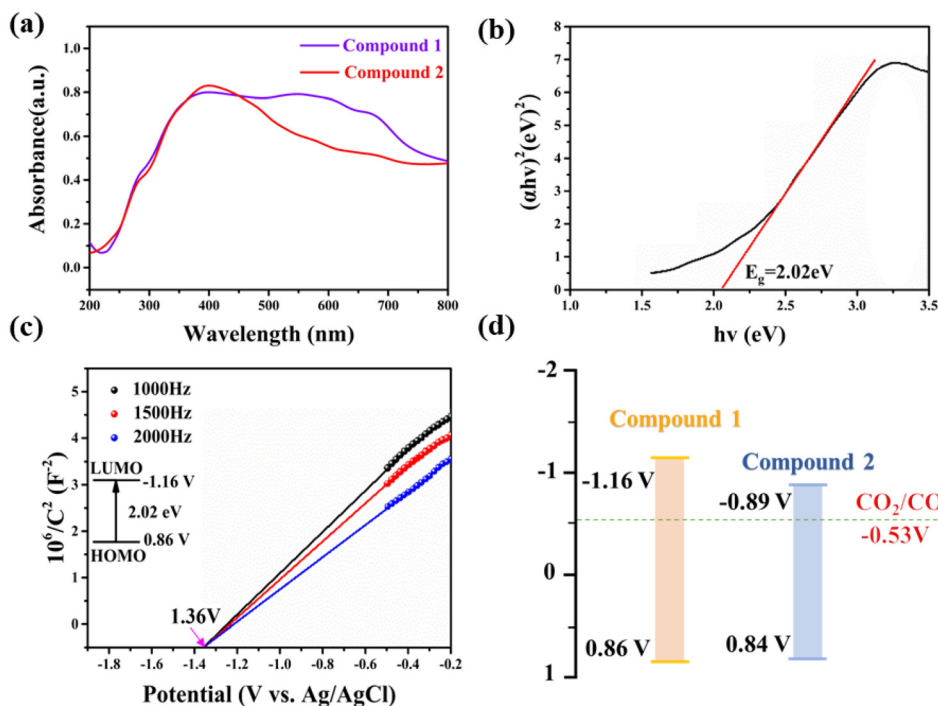


Fig. 3 (a) UV-vis spectra of compounds **1** and **2**. (b) Tauc plot of $(ah\nu)^2$ vs. $h\nu$ for compound **1**. (c) Mott–Schottky plot for compound **1**. (d) Band-structure diagrams of compound **1**.

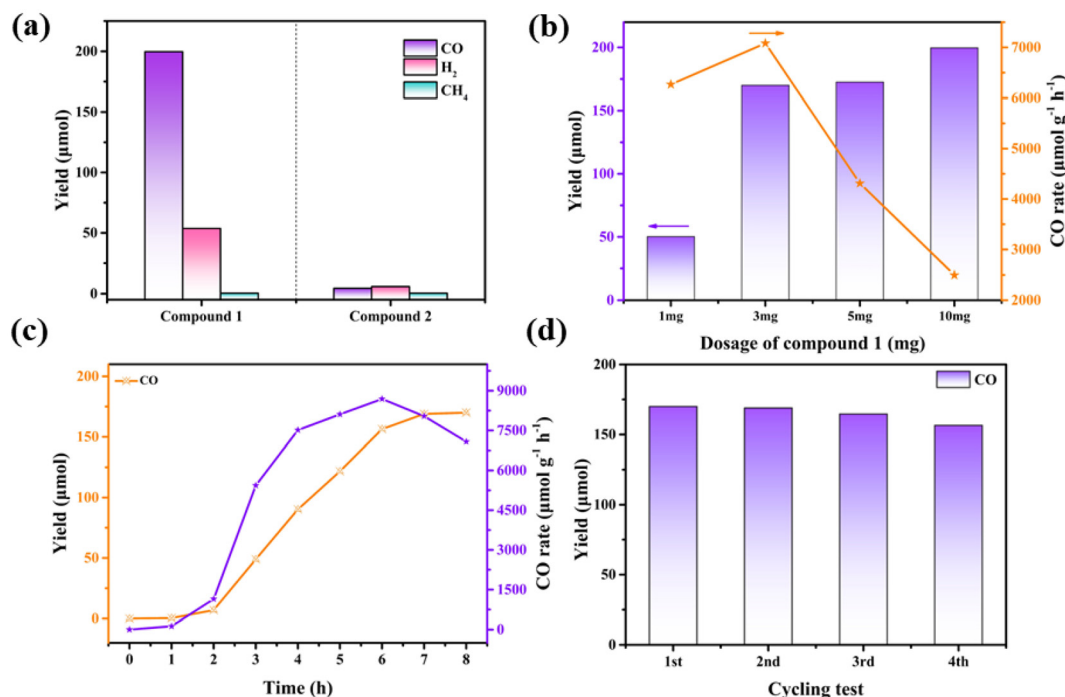


Fig. 4 (a) Yields of CO, H₂, and CH₄ for compounds 1 and 2. (b) Effect of the dose of compound 1 on the yield of CO. (c) Yield and rate of CO for compound 1 (3 mg). (d) Yield of CO after four cycles of compound 1.

above experimental results, the optimal dosage of compound 1 was investigated in detail. As the catalyst dosage increased, the CO production rate increased and then decreased with time. The CO rate reached a maximum of $7081.4 \mu\text{mol g}^{-1} \text{h}^{-1}$ with 3 mg compound 1 (Fig. 4b). When it reached 5 mg, the CO increased to $172.5 \mu\text{mol}$. Conversely, the rate dropped sharply to $4311.5 \mu\text{mol g}^{-1} \text{h}^{-1}$, which could only reach a little more than half of 3 mg. It was speculated that this phenomenon was attributed to the limitation of the electron transfer dynamics, resulting in too much of the catalyst not being fully utilized. When 3 mg of compound 1 was introduced, the yields of the reduction products CO can reach $169.9 \mu\text{mol}$ after 8 h. Additionally, the rate of CO reached its highest value of $8690.1 \mu\text{mol g}^{-1} \text{h}^{-1}$ and the turnover number (TON) of CO was 450.1 at 6 h (Fig. 4c). The speculation is that the consumption of PS results in not enough photogenerated electrons being transferred to the catalyst to maintain the catalytic reaction. Next, control experiments were performed on compound 1 to demonstrate the indispensability of each reaction component to the CO₂RR. According to Fig. S19,[†] it was found that there was no CO production from the reaction system in the dark and almost no gas production when no PS or catalyst was added.⁴³

Photocatalytic cycling test experiments were conducted to investigate the durability and recyclability to assess the practical application potential of compound 1 (Fig. 4d). The used catalysts were recovered from the reaction solution by centrifugation and dried at 80 °C for 12 h. Four cycles of experiments were carried out over 8 h, with a slight decrease possibly due

to a small amount of catalyst loss in the recycling process. In addition, thermal filtration experiments were performed on compound 1, and it was found that the reaction system did not continue to produce CO after filtering it out (Fig. S20[†]).⁴⁴ It was found that there was no significant change in their PXRD pattern and IR spectrogram after the cycling experiments (Fig. S21 and S22[†]), which proved that compound 1 had excellent structural stability and could be reused in at least four cycles.⁴⁵

Mechanistic study

Photoluminescence (PL) quenching experiments were conducted to investigate the differences in the catalytic properties of the two compounds. The PL spectra of PS and the catalysts (Fig. 5a) revealed that compound 1 possesses a distinct fluorescence quenching effect. This result demonstrates that compound 1 exhibits higher charge transport efficiency than compound 2. Furthermore, compound 1 exhibits a higher transient

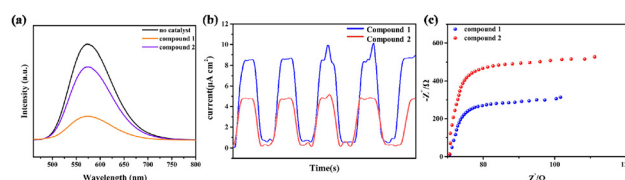


Fig. 5 (a) [Ru(bpy)₃]Cl₂ in MeCN solutions containing catalyst compounds 1 and 2. (b) Transient photocurrent response of compounds 1 and 2. (c) EIS of compounds 1 and 2.

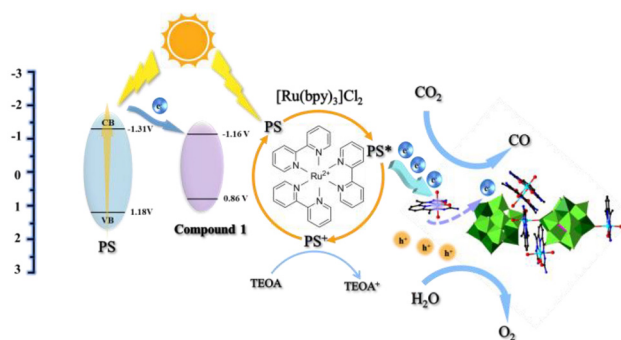


Fig. 6 Schematic of the electron transfer energy levels for the proposed mechanism of photocatalytic CO₂ reduction over compound 1.

photocurrent intensity, proving its effective inhibition of photogenerated electron-hole pairs recombination (Fig. 5b). The photoelectrochemical properties of compounds 1 and 2 were further investigated by electrochemical impedance spectroscopy (EIS). The Nyquist plots (Fig. 5c) denote that compound 1 has the smallest arc radius, proving that it has the least charge transfer resistance and higher photocatalytic efficiency.⁴⁶ The summarized photoelectrochemical experiments have demonstrated the superior charge transfer rate and charge separation ability of compound 1.

The proposed rational mechanism for the photocatalysis^{47–49} of CO₂RR by compound 1 is based on the described characterizations and experimental results (Fig. 6). Since the conduction band energy level of compound 1 is lower than that of PS, the photoelectrons in the excited state are spontaneously transferred from PS to compound 1. These electrons are transferred to Co-DAPSC, where CO₂ is subsequently reduced. Meanwhile, H₂O consumes the photo-induced holes and undergoes an oxygen evolution reaction. Finally, TEOA as a sacrificial agent eliminates the photogenerated holes in PS and maintains the catalytic reaction.

Conclusions

In summary, we successfully synthesized two novel Keggin-type POM-based hybrid materials modified with two different transition metals and Schiff base ligands in this work. Various characteristic methods have demonstrated the presence of V atoms in the structure of compound 1. Photocatalytic CO₂RR experiments showed that compound 1 exhibits exceptional photocatalytic activity, achieving a CO rate of 7081.4 μmol g^{−1} h^{−1} and selectivity of 83.8% after 8 hours. Cycle tests demonstrated that compound 1 exhibits good structural stability and maintains activity for at least four cycles. The introduction of V atoms into Keggin-type POM may enhance CO₂ adsorption. Likewise, the use of DAPSC with the same structure as chlorophyll increased the visible light absorption of the compounds. This innovative approach provides a new perspective for the development of highly efficient photocatalytic CO₂RR catalysts.

Author contributions

Xiao-Yu Bai: writing – original draft, methodology, data curation, and conceptualization. Pin-Fang Yan: writing – original draft, validation, methodology, formal analysis, and data curation. Jiu-Lin Zhou: software, methodology, and investigation. Yu Lv: review and editing of the manuscript. Ji-Lei Wang: writing – original draft and supervision. Hua Mei: writing, reviewing and editing of the manuscript. Yan Xu: formal analysis, writing, review and editing of the manuscript.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (92161109).

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