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Coordination Regulation of Cobalt in Covalent Organic Frameworks Enhances Syngas Production from CO_2 Photoreduction

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Abstract. Against the backdrop of energy conservation, emission reduction and green low-carbon development, traditional syngas production processes are plagued by high energy consumption and excessive greenhouse gas emissions. In contrast, the photocatalytic CO_2 reduction technology, driven by solar energy, enables the conversion of CO_2 into syngas. It combines the values of environmental protection and resource recycling, thus becoming a current research hotspot. In the design of high-efficiency single-atom catalysts (SACs) for photocatalytic CO_2 reduction, the microenvironment design of single-atom metal sites is of crucial importance. Based on this, in this work, a series of Co-coordinated COF catalysts named Triazine-COF-Co-Cl were synthesized to regulate the Co-coordination microenvironment for enhancing syngas production via photocatalytic CO_2 reduction. Among them, the Triazine-COF-Co-AA catalyst with the best performance achieved a syngas production rate of 381.7 mmol g^{-1} h^{-1}, and the H_2/CO molar ratio could be continuously adjusted in the range of 1-3, which is sufficient to cover the commonly used syngas ratio range in industry. This paper improves the performance of COF-based photocatalysts for syngas production via CO_2 reduction through the regulation of Co-coordination environment, and provides ideas and certain data support for the research on solving energy and environmental problems and reducing CO_2 emissions.

Keywords: Covalent Organic Frameworks, Single-Atom Catalysts, Photocatalysis, Carbon Dioxide Reduction

1. Introduction

Syngas is a mixture of hydrogen and carbon monoxide, which can be produced from natural gas, coal, petroleum, biomass and even organic waste. Therefore, syngas sources are ubiquitous in nature, and it also serves as a major and increasingly demanded feedstock for clean fuels and chemicals [1]. Syngas with different H_2/CO molar ratios has different industrial applications. For example, the required H_2/CO ratio for Fischer-Tropsch (FT) synthesis is 2, while that for oxo synthesis is 1 [2,3]. Traditional syngas production methods, such as steam methane reforming, consume a large amount of fossil energy and thermal energy [4]. Heterogeneous photocatalytic CO_2 reduction technology, driven by solar energy and with water as the hydrogen source, does not require additional thermal energy or high-pressure conditions, and is thus regarded as one of the most promising strategies for CO_2 conversion [5-7].

Two-dimensional covalent organic frameworks (2D-COFs) possess a π-conjugated structure with abundant functional groups, which is conducive to band gap control for enhanced visible light harvesting, as well as the separation and transfer of photogenerated charge carriers. They can also realize the mass transfer and adsorption of CO_2 by adjusting the one-dimensional pore structure and size, and regulate the photoelectrochemical activity through the design of customized skeletons and site functional groups, so as to improve the performance for photocatalytic CO_2 reduction. Therefore, 2D-COFs are ideal candidates for developing high-efficiency photocatalysts for CO_2 reduction [8]. Loading Co(II) on them to form single-atom catalysts (SACs) can further improve the catalytic performance, but it is still limited by the low separation efficiency of photogenerated carriers and insufficient activity of catalytic sites.

Based on this, in this work, a 2D-COF catalyst Triazine-COF-Co-Cl with Co coordination was synthesized, and on this basis, a variety of different additional ligands were introduced to coordinate with Co sites, including neutral ligand (2,2'-bipyridine, Bpy), oxygen-containing anionic ligand conducive to hydrogen bond formation (acetylacetone, AA), and nitrogen and sulfur-containing ligand simulating CO dehydrogenase (2-mercaptopyridine, PM). This realization of the regulation of Co-coordination microenvironment enhanced syngas production from photocatalytic CO_2 reduction. Among them, the Triazine-COF-Co-AA with the best performance achieved a syngas production rate of 381.7 mmol g^{-1} h^{-1}, and the H_2/CO molar ratio could be adjusted in the range of 1-3, which is sufficient to cover the commonly used syngas ratio range in industry.

2. Synthesis and characterization of four catalysts

Triazine-COF was synthesized using 2,5-dihydroxyterephthalaldehyde (DHTA) and 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (TAPT) according to the method reported previously [4], and Co and additional ligands were introduced on this basis. Powder X-ray diffraction (PXRD) patterns were used to reveal the crystal structures of COF and Co-containing COF catalysts. The experimental PXRD patterns of Triazine-COF and all four Co-containing COF catalysts are in good agreement with the simulation results based on the 2D layer AA stacking model, and no obvious changes in the PXRD patterns were observed before and after the loading of Co and additional ligands (Fig.1a). The diffraction peaks at $2\theta = 2.9$ °, 4.9 °, 5.7 ° and 7.5 ° correspond to the (100), (210), (200) and (320) crystal planes of COF or the catalysts, respectively. The PXRD results confirm the successful synthesis of highly crystalline Triazine-COF, the successful loading of Co and additional ligands, and the stability of Triazine-COF during the process. As shown in Fig.1b, ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) shows that there are slight differences in the absorption edges of the four Co-based Triazine-COF catalysts.

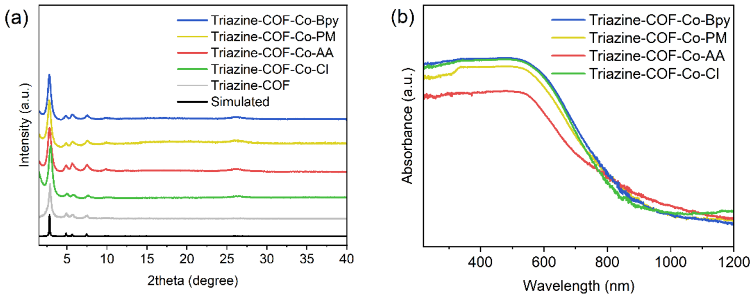

Figure 1. (a) PXRD patterns and (b) UV-V is spectra of Triazine-COF-Co-Cl (green), Triazine-COF-Co-AA (red), Triazine-COF-Co-PM (yellow) and Triazine-COF-Co-Bpy (blue).

3. Verification of thermodynamic feasibility for photocatalytic CO2 reduction to syngas

The Mott-Schottky plots with positive slopes (Fig.2a-d) indicate that all four catalysts are n-type semiconductors [9]. The conduction band minimum (CBM) of Triazine-COF-Co-Cl, Triazine-COF-Co-AA, Triazine-COF-Co-PM and Triazine-COF-Co-Bpy are approximately −0.89 V, −0.87 V, −0.73 V and −1.05 V relative to the standard hydrogen electrode (SHE), respectively. The Tauc plots were calculated according to their UV-Vis DRS spectra, as shown in Fig.3a. The band gaps of Triazine-COF-Co-Cl, Triazine-COF-Co-AA, Triazine-COF-Co-PM and Triazine-COF-Co-Bpy are 1.90 eV, 1.89 eV, 1.88 eV and 1.90 eV, respectively, and the schematic diagram of their energy band structures calculated from the above data is shown in Fig.3b. Notably, the CBM of all four catalysts are more negative than the reduction potentials of CO_2/CO (–0.53 V vs. SHE) and H_2O/H_2 (–0.41 V vs. SHE), but more positive than the lowest unoccupied molecular orbital (LUMO) of the photosensitizer $[Ru(bpy)_3]^{2+}$ (–1.31 V vs. SHE). Such an energy arrangement confirms the thermodynamic feasibility of electron transfer from the photosensitizer to the catalysts, as well as the thermodynamic feasibility of these four catalysts for photocatalytic syngas production [10].

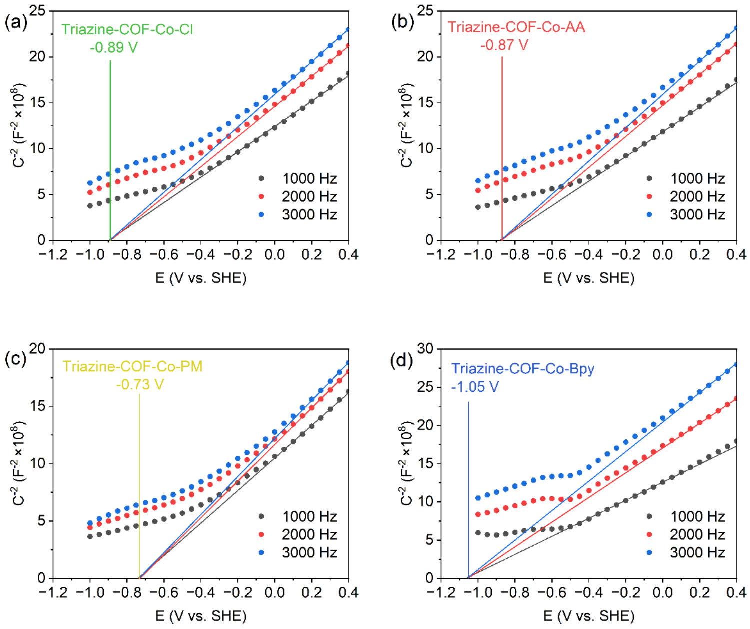

Figure 2. Mott-Schottky plots of (a) Triazine-COF-Co-Cl, (b) Triazine-COF-Co-AA, (c) Triazine-COF-Co-PM and (d) Triazine-COF-Co-Bpy.

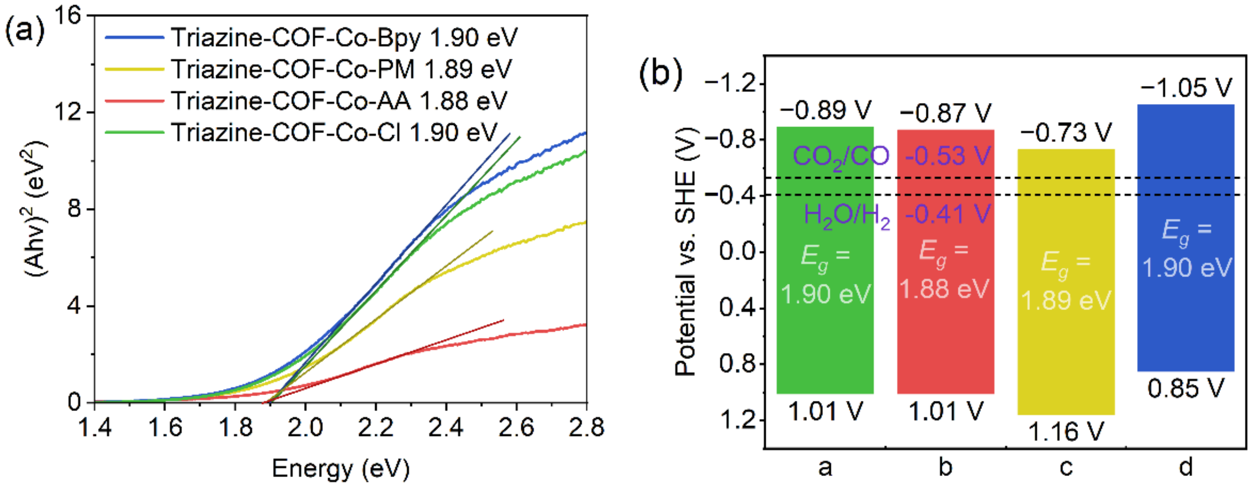

Figure 3. (a) Tauc plots and (b) schematic diagrams of energy band structures of Triazine-COF-Co-Cl (green), Triazine-COF-Co-AA (red), Triazine-COF-Co-PM (yellow) and Triazine-COF-Co-Bpy (blue).

4. Performance test of photocatalytic CO2 reduction for syngas production

The performance of the four catalysts with different additional ligands for photocatalytic CO_2 reduction to produce syngas was evaluated. The reaction was conducted at 5 °C under simulated sunlight with an intensity of 300 mW cm−2, using 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzimidazole (BIH, 100 mg) as the hole scavenger, $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (15 mg) as the photosensitizer, and a mixed solvent of water (5 mL) and acetonitrile (25 mL). As shown in Fig.4a, the CO production rates of Triazine-COF-Co-Cl, Triazine-COF-Co-AA, Triazine-COF-Co-PM and Triazine-COF-Co-Bpy are 101.7, 106.6, 87.4 and 100.0 mmol g^{-1} h^{-1}, respectively, while the H_2 production rates are 48.2, 105.0, 47.9 and 55.4 mmol g^{-1} h^{-1}, respectively. It can be observed that Triazine-COF-Co-AA has the highest CO and H_2 production rates, with the H_2 production rate being significantly superior. This may be due to the fact that the oxygen anions of the acetylacetonate (AA) ligand still have a high electron cloud density after coordinating with Co(II), which can form hydrogen bonds during the reaction and promote water dissociation and proton transfer [11].

The molar ratio of H_2/CO in the produced syngas can be altered by adjusting the reaction temperature of the photocatalytic reaction system. Triazine-COF-Co-AA, which exhibited the best syngas production rate under the previous 5 °C condition, was selected for the test. As shown in Fig.4b, with the increase of reaction temperature, Triazine-COF-Co-AA shows a decreased CO yield and a doubled H_2 yield. The H_2/CO ratio is observed to increase from 1 to 3 in the temperature range of 5 to 15 °C. The CO and H_2 yields at 5 °C are 110.2 and 105.0 mmol g^{-1} h^{-1}, respectively, with an H_2/CO molar ratio of 1. When the temperature rises to 10 °C, the CO and H_2 yields are 101.4 and 190.9 mmol g^{-1} h^{-1}, respectively, and the H_2/CO molar ratio is 2. When the temperature increases to 15 °C, the CO and H_2 yields are 98.3 and 283.4 mmol g^{-1} h^{-1}, respectively, with an H_2/CO molar ratio of 3. Such a continuously adjustable range is sufficient to cover the commonly used syngas ratio range in industry.

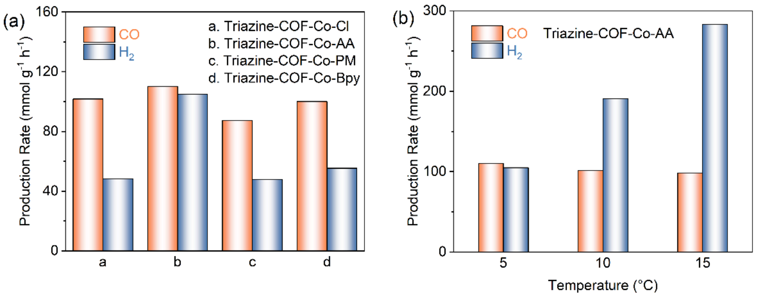

Figure 4. (a) Syngas production rates of the four catalysts and (b) syngas production rates of Triazine-COF-Co-AA at different temperatures.

5. Conclusion

In summary, a series of imine COFs immobilized with Co(II) atoms were designed and synthesized by loading additional ligands on the Co-loaded COF catalysts to coordinate with Co, which were used for the efficient photocatalytic reduction of CO_2 and H_2O to produce syngas. Among them, the optimal catalyst Triazine-COF-Co-AA achieved a continuous adjustment of the H_2/CO ratio in the range of 1 to 3 at the reaction temperature of 5 to 15 °C, with the maximum syngas production rate reaching 381.7 mmol g^{-1} h^{-1}, which reaches the top level in the industry.

Acknowledgement

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