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Article

Encapsulation of Co single sites in covalent triazine frameworks for photocatalytic production of syngas

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ABSTRACT

The photocatalytic production of syngas using a noble-metal-free catalytic system is a promising approach for renewable energy and environmental sustainability. In this study, we demonstrate an efficient catalytic system formed by integrating Co single sites, which act as the active sites, in covalent triazine frameworks (CTFs), which act as the photoabsorber, for the photocatalytic production of syngas from CO₂ in aqueous solution. The enhanced light absorption of the CTFs, which contain intramolecular heterojunctions, in conjunction with 0.8 mmol L⁻¹ of the Co complex enables excellent syngas production with a yield of 3303 μmol g⁻¹ (CO:H₂ = 1.4:1) in 10 h, which is about three times greater than that achieved using CTF without a heterojunction. In the photocatalytic reaction, the coordinated single Co centers accept the photogenerated electrons from the CTF, and serve as active sites for CO₂ conversion through an adsorption-activation-reaction mechanism. Theoretical calculations further reveal that the intramolecular heterojunctions highly promote photogenerated charge separation, thus boosting photocatalytic syngas production. This work reveals the promising potential of CTFs for single-metal-site-based photocatalysis.

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1. Introduction

Syngas (a mixture of CO and H₂) is a key precursor for the production of bulk chemicals by Fischer-Tropsch processing [1,2]. Currently, syngas is mainly prepared by the reforming of natural gas or coal gasification, which requires harsh synthesis conditions [3,4]. The simultaneous photocatalytic reduction of CO₂ and H₂ evolution from water is one of the sustainable strategies for the production of syngas for chemical production [5]. So far, many photocatalytic systems have been developed for the production of syngas [6–10]. However, most of these systems use expensive metals such as Re and Ru as photosensi-

tizers and/or catalysts with high efficiency [11]. Thus, developing efficient catalytic systems utilizing earth-abundant but highly active metal catalysts for photocatalytic syngas production is highly desirable, but remains challenging [12].

Molecular-metal-complex-based photocatalytic systems have shown promising catalytic performance in the photoreduction of CO₂ [13]. The coordinated metal centers serve as single active sites in the catalytic reaction [14,15]. Their coordinative versatility endows metal active sites with tailorable electronic properties [16–19], which are favorable for optimization of the catalytic efficiency. However, most of these systems suffer from insufficient stability and separation of the

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expensive metal catalysts. Thus, the heterogenization of metal complexes that convert CO₂ in a semiconductor may combine their high catalytic activity with the classic advantages of heterogeneous catalysis [20–23]. To maximize the atom utilization efficiency, the selection of a semiconductor with the porosity to accommodate metal single sites is required [24]. Additionally, to readily control the catalytic activity, a semiconductor possessing a tunable energy band structure is also needed.

Covalent triazine frameworks (CTFs) have recently emerged as a new class of photoactive materials due to their tunable light-harvesting properties and adjustable electronic structures at the molecular level [25–29]. Their high surface area and nitrogen-rich structure endow CTFs with distinct advantages for the accommodation of guest molecules [30] and very importantly, the guest molecules are accessible to the reactants in catalysis [31–33]. In spite of their merits, there have been only a few reports of the use of CTFs in the field of photocatalytic production of syngas so far [34]. Herein, we demonstrate the utilization of CTFs for the production of syngas via the photo-reduction of CO₂ in aqueous solution. CTFs containing triphenylamine and triazine units as intramolecular heterojunctions are employed for the accommodation of molecular Co complexes, which serve as active single sites for CO₂ conversion. The resultant catalytic system exhibits excellent photocatalytic performance, which is ascribed to the efficient transfer of the photogenerated carriers due to the intramolecular heterojunctions in the CTFs and the well-stabilized single Co active sites in the framework.

2. Experimental

2.1. Synthesis of CTFs

The CTFs prepared from 1,4-benzene-dialdehyde and 4,4'-biphenyldicarboxaldehyde with 4,4',4''-nitrilotribenzimidamide trihydrochloride are referred to as CTF-TPN and CTF-TDPN, respectively.

Synthesis of CTF-TPN. A mixture of 4,4',4''-nitrilotribenzimidamide trihydrochloride (336 mg, 0.69 mmol), 1,4-phthalaldehyde (69.9 mg, 0.52 mmol), and cesium carbonate (752.6 mg, 2.31 mmol) in DMSO (5.5 mL) and H₂O (0.2 mL) was heated at 60 °C, 80 °C, and 100 °C for 12 h respectively, and at 120 °C for 72 h. The resulting product was filtered and washed three times with water, acetone, and tetrahydrofuran individually, and then dried at 60 °C for 12 h under vacuum to yield CTF-TPN as a yellow powder.

Synthesis of CTF-TDPN. Following the same procedures as in the synthesis of CTF-TPN, CTF-TDPN was obtained by the polycondensation of 4,4',4''-nitrilotribenzimidamide trihydrochloride and 4,4'-biphenyldicarboxaldehyde as a yellow powder.

2.2. Characterization

All the starting materials were used without further purification. The FTIR spectra of the as-synthesized CTFs were recorded with a Nicolet 5700 instrument. The ¹H and ¹³C NMR

spectra were recorded on a Bruker AVANCE III NMR. High performance liquid phase chromatography (HPLC) was performed on an Agilent 1260 Infinity II. Powder X-ray diffraction (PXRD) patterns were obtained in the range of $2\theta = 3^\circ\text{--}40^\circ$ on a DY5261/Xpert3 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449C instrument over the temperature range 30°–800 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{−1}. X-ray photoelectron spectrometry (XPS) was performed on a Thermo ESCALAB 250 spectrometer using nonmonochromatic Al K α X-rays as the excitation source and choosing C 1s (284.6 eV) as the reference line. Nitrogen adsorption and desorption isotherms were measured at 77 K using an ASAP 2460 system. The samples were degassed at 80 °C for 12 h before the measurements. The surface areas were calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) equation. Solid-state UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded at room temperature with a UV-vis spectrophotometer (Agilent Cary 5000 spectrometer) using powder samples. Field-emission scanning electron microscopy (SEM) was performed on a JEOL JSM-7500F operated at an accelerating voltage of 3.0 kV. Transmission electron microscopy (TEM) images were obtained with a TECNAI G² F20. The photoluminescence (PL) spectra were obtained using an Edinburgh FL/FS900 spectrophotometer with an excitation wavelength at 365 nm. Time-resolved fluorescence emission decay spectra were recorded with a FLS1000. The content of Co was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; iCAP 7000, Thermo Fisher Scientific Inc.). Gas chromatographic analysis (GC) was conducted using an Agilent Technologies-7890B instrument equipped with a flame ionization detector (FID), a thermal conductivity detector (TCD), and a TD-01 packed column. The CO gas produced in the ¹³CO₂ isotope experiments was analyzed using a gas chromatograph-mass spectrometer (GC-MS, Agilent 7890B-5977B).

2.3. Photocatalytic CO₂ reduction performance

The photocatalytic reactions were performed in a Schlenk flask containing cobalt(II) acetate tetrahydrate (0.8 mmol L^{−1}), 2,2'-bipyridine (15.6 mg, 0.1 mmol), and CTF (10 mg) in 5 mL of an acetonitrile/triethanolamine/H₂O (v/v/v = 3:1:1) solution. The Schlenk flask was purged with CO₂ gas three times and charged with CO₂ (1.0 bar) for 10 min until the solution reached CO₂ saturation. The mixture was then irradiated under a Xe lamp (300 W) with a $\lambda \geq 420 \text{ nm}$ cutoff filter. After the reaction, the gases were analyzed by GC. The recycling experiments were carried out for 2 h under visible light irradiation ($\lambda \geq 420 \text{ nm}$) as described above. CTF was recovered by centrifugation and washed with acetonitrile (10 mL $\times$ 3) after the reaction was completed. The recovered CTF was then reused in the subsequent cycle experiment with fresh 2,2'-bipyridine and Co salt. The apparent quantum yield (AQY) at 420 nm was calculated using the following equation: $\text{AQY} = [(2 \times \text{amount of CO and H}_2 \text{ molecules evolved in 2 h}) / (\text{number of incident photons in 2 h})] \times 100\%$. The single Co sites were formed in-situ by the coordination of 2,2'-bipyridine and Co ions, and were encapsu-

lated within the CTFs in the photocatalytic reaction.

2.4. Theoretical calculations

The DFT calculation utilized the B3LYP hybrid functional basis sets. The DMOL3 program was employed. All molecules were optimized using the DNP basis set. The maximum tolerances for force and atom displacements along any Cartesian component were $0.002 \text{ Ha } \text{\AA}^{-1}$ and $5 \times 10^{-3} \text{ \AA}$, respectively, and the SCF tolerance was 1×10^{-6} . The final morphology was determined from the model when the lowest total energy was reached.

3. Results and discussion

3.1. Structure characterization

CTF-TPN and CTF-TDPN were synthesized by reacting 4,4',4''-nitrilotriphenylbenzimidamide trihydrochloride with either 1,4-phthalaldehyde or 4,4'-biphenyldicarboxaldehyde, respectively (Fig. 1). The Fourier transform infrared spectra (FT-IR) of the CTFs show the typical peaks for the triazine ring at 1508 and 1370 cm^{-1} (Fig. 2a), revealing the success of the trimerization reactions [35]. The characteristic signal at 170 ppm in the solid state ^{13}C NMR spectrum was attributed to the carbon atoms in the triazine rings (Fig. 2b). The additional signals at 149.1, 138.1, and 128.9 ppm were assigned to the carbon atoms in the aromatic rings. The X-ray photoelectron spectroscopy (XPS) survey scan showed that the elements C, N, and O coexisted in CTF-TPN and CTF-TDPN (Fig. S1). The N 1s peak can be resolved into two peaks. The peak at 398.6 eV was ascribed to the N atom of the triazine moieties, and the other

Fig. 1. Schematic of the synthesis of CTF-TPN and CTF-TDPN and their application in the photocatalytic reduction of CO_2 under visible light.

peak at 399.9 eV corresponds to the N atom in the triphenylamine moiety (Fig. 2c) [36,37], further verifying the coexistence of triphenylamine and triazine moieties in the frameworks. The PXRD patterns show that CTF-TPN and CTF-TDPN were amorphous (Fig. 2d), mainly owing to the fast nucleation rates [38].

The porosities of CTF-TPN and CTF-TDPN were investigated using N_2 adsorption-desorption experiments at 77 K (Fig. 3a). The initial N_2 uptake in CTF-TPN and CTF-TDPN demonstrated the existence of micropores. The Brunauer-Emmett-Teller (BET) surface areas of CTF-TPN and CTF-TDPN were $206 \text{ m}^2 \text{ g}^{-1}$ and $310 \text{ m}^2 \text{ g}^{-1}$, respectively. Interestingly, appreciable amounts of CO_2 adsorption were also observed. The CO_2 uptakes of CTF-TPN and CTF-TDPN at 273 K and 1 atm were 64 mg g^{-1} and 40 mg g^{-1} (Fig. 3b and S2), which may be attributed to their nitrogen-rich microporous structures. The isosteric heat of adsorption (Q_{st}) values of CTF-TPN and CTF-TDPN for CO_2 sorption at zero coverage were $31.74 \text{ kJ mol}^{-1}$ and $33.48 \text{ kJ mol}^{-1}$ (inset in Fig. 3b), respectively, confirming their affinity for CO_2 . Scanning electron microscopy (SEM) images show that CTF-TPN and CTF-TDPN were composed of granular particles

Fig. 2. (a) FTIR spectra of the monomers and CTFs; (b) Solid state ^{13}C NMR spectra, (c) N 1s XPS profiles, and (d) XRD patterns of CTF-TPN and CTF-TDPN.

Fig. 3. (a) N_2 adsorption-desorption isotherms at 77 K (inset: pore size distribution); (b) CO_2 adsorption-desorption isotherms at 273 K (inset: isotherms of the heat of adsorption for CO_2) of CTF-TPN and CTF-TDPN; (c) TEM image of CTF-TDPN; (d) UV-vis DRS spectra; (e) band gaps of the CTFs; (f) band structures of the CTFs.

(Fig. S3). The high-resolution transmission electron microscopy (HR-TEM) images indicate that the particles consisted of stacked nanosheets (Fig. 3c). Thermal gravimetric analysis (TGA) measurements of CTF-TPN and CTF-TDPN show their high thermal stability, with stability up to 350 °C (Fig. S4). The slight mass loss below 200 °C can be attributed to the residual solvent or organic oligomers in the pores of the CTFs.

The optical properties of CTF-TPN and CTF-TDPN were further characterized. The UV-visible diffuse-reflectance spectra (UV-Vis DRS) show that CTF-TPN and CTF-TDPN could strongly harvest visible light over a wide range (Fig. 3d). The red shift of their absorption edges in comparison to the monomers was attributed to the increased π -electron delocalization in the conjugated framework [39]. For comparison, CTF-HUST-1, which lacks triphenylamine moieties, was synthesized [40], as shown in the experimental section of the supporting information. CTF-TPN and CTF-TDPN displayed broader absorption edges and narrower band gaps than CTF-HUST-1, showing that introduction of triphenylamine units into the framework efficiently enhanced visible light harvesting [41]. The energy band structures obtained from the UV-Vis DRS (Fig. 3e) and Mott-Schottky analyses (Fig. S5) reveal that the reduction potentials of CTF-TPN and CTF-TDPN energetically favored CO_2 reduction (Fig. 3f), making them attractive for the photocatalytic reduction of CO_2 .

3.2. Photocatalytic activity

In light of their suitable band structure and CO_2 adsorption capacity, the photocatalytic performances of CTF-TPN and

CTF-TDPN for CO_2 reduction were evaluated using the in situ formed $[Co(bpy)_3]^{2+}$ ($bpy = 2,2'$ -bipyridine) as a cocatalyst and triethanolamine (TEOA) as an electron donor. Under the optimized reaction conditions, the kinetic profiles show that CO and H_2 evolved simultaneously under visible light irradiation and increased with reaction time (Fig. 4a and 4b). The gas production of CTF-TPN and CTF-TDPN reached 3368 $\mu mol\ g^{-1}$ and 3303 $\mu mol\ g^{-1}$ ($CO:H_2 = 1.4:1$) in 10 h of irradiation, respectively. The apparent quantum yield (AQY) of CO and H_2 evolution at 420 nm was calculated to be 0.14%. For comparison, CTF-HUST-1 was employed in the reaction under identical conditions and showed much lower activity than CTF-TPN and CTF-TDPN (Fig. 4c and S6), suggesting the importance of the triphenylamine units in the framework for the photocatalytic reduction of CO_2 to CO.

Control experiments showed no activity in the absence of Co^{2+} or 2,2'-bipyridine, while a considerable amount of CO and H_2 was detected in the presence of $[Co(bpy)_3]^{2+}$ (Fig. 4d), which proved that the activity resulted from the in situ formed $[Co(bpy)_3]^{2+}$. An isotope experiment was carried out using $^{13}CO_2$ as the carbon source to confirm the source of the produced CO. As shown in Fig. S7, the peaks at $m/z = 29$ and $m/z = 13$ confirmed that the source of the produced CO was $^{13}CO_2$ gas rather than other organic species in the photocatalytic system. No by-products of CO_2 reduction such as CH_4 , CH_3OH , or $HCOOH$ were detected in solution NMR spectrum (Fig. S8) or HPLC spectrum (Fig. S9). The yield of CO matched well with the UV-vis DRS spectrum of CTF-TDPN (Fig. S10). As the amount of CTF in the reaction was increased from 1 to 10 mg, the production of syngas increased (Fig. S11), proving that the photocata-

Fig. 4. Photocatalytic evolution of CO and H₂ by (a) CTF-TPN and (b) CTF-TDPN; (c) comparison of the average CO and H₂ evolution efficiencies of the CTFs; (d) control experiments using CTF-TDPN; (e) experiments using different solvents; (f) experiments with different H₂O contents in the reaction. MeCN, DMF, DMC, and Diox are acetonitrile, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and 1,4-dioxane, respectively.

lytic reduction of CO₂ to CO was indeed induced by light irradiation of the CTFs. Increasing the concentration of [Co(bpy)₃]²⁺ in the reaction led to an increase in H₂ production with a slight decrease in CO production (Fig. S12). When the concentration of [Co(bpy)₃]²⁺ was increased to 0.8 mmol L⁻¹, a CO/H₂ ratio of approximately 1:1 was obtained. The activity of CTF-TDPN in different organic solvents was correlated with its fluorescence intensity in the corresponding solvent (Fig. 4e). The content of H₂O in the reaction played an important role in the composition of the produced syngas (Fig. 4f). Only a small amount of CO was produced in the absence of H₂O. When the volume content of H₂O was increased from 2.5% to 20%, the ratio of CO/H₂ decreased from 2.4:1 to 1:1. Above all, the composition of the photocatalytic products could be changed facily by adjusting the reaction conditions. The reusability of CTF-TDPN for photocatalytic syngas production was studied. After each reaction, the photocatalyst was separated, washed with acetonitrile, and then added to the next reaction. A slight loss of activity for CO and H₂O production was observed after four cycles (Fig. S13). The FTIR spectrum of the recovered CTFs showed that the typ-

ical peaks of the triazine ring at 1508 and 1370 cm⁻¹ were retained in the chemical structure (Fig. S14). Inductively coupled plasma mass spectrometry (ICP) shows that only 0.85 wt% of Co was present in the recovered CTF-TDPN. The TEM image of recovered CTF-TDPN shows a remain of the nanosheet morphology (Fig. 5a), but no Co-related nanoparticles were observed. EDX elemental mapping shows only weak Co signals on the recovered CTF-TDPN, suggesting weak interaction between the CTF and Co single sites (Fig. 5b). The recovered CTF-TDPN did not generate syngas products in a subsequent reaction in the absence of the Co complex, further suggesting that the interactions between Co active sites and CTF were almost physical.

3.3. Photocatalytic mechanism

To investigate the photocatalytic mechanism of the as-prepared CTFs, the photoluminescence (PL) spectra of the CTFs were investigated. Upon excitation at 365 nm, CTF-TPN, CTF-TDPN and CTF-HUST-1 emit with maximum emission wavelengths at 553, 538, and 538 nm in solid state, respectively (Fig. 6a). The emission intensities of CTF-TPN and CTF-TDPN were much stronger than that of CTF-HUST-1, suggesting that the introduction of triphenylamine moieties could promote electron generation, but could also lead to quick recombination of the electron-hole pairs. The time-resolved fluorescence emission decay spectra for the CTFs were obtained and are shown in Fig. 6b. The decay kinetics for CTF-HUST-1, CTF-TPN, and CTF-TDPN show that their respective average fluorescence lifetimes were 2.11, 2.95, and 3.47 ns. The longer fluorescence lifetimes of CTF-TPN and CTF-TDPN compared to that of

Fig. 5. (a) TEM image and (b) EDX mapping of the recovered CTF-TDPN.

Fig. 6. (a) PL spectra under 365 nm excitation at room temperature (Inset: CTFs under 365 nm UV-light); (b) time-resolved fluorescence emission decay spectra; (c) transient photocurrents under visible light (≥ 420 nm) irradiation of CTF-TPN, CTF-TDPN, and CTF-HUST-1; (d) UV-vis absorption spectra of $[\text{Co}(\text{bpy})_3]^{2+}$ formed in situ by the consecutive addition of bpy to $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in $\text{MeCN}/\text{H}_2\text{O}$ ($v/v = 3:1$); (e) CV curves of the self-assembled $[\text{Co}(\text{bpy})_3]^{2+}$ under Ar and CO_2 atmospheres; (f) PL spectra of CTF-TDPN with $[\text{Co}(\text{bpy})_3]^{2+}$ in $\text{MeCN}/\text{H}_2\text{O}$ upon irradiation at 365 nm.

CTF-HUST-1 indicate the long lifetime of the photogenerated charge carriers in CTF-TPN and CTF-TDPN, further confirming that the presence of intramolecular heterojunctions could effectively facilitate the separation of photogenerated electrons and holes [42]. Photoelectrochemical measurements of the CTFs revealed that CTF-TPN and CTF-TDPN presented much higher photocurrent densities than CTF-HUST-1 (Fig. 6c). The electrochemical impedance spectroscopy (EIS) Nyquist plot shows smaller charge-transfer resistances in CTF-TPN and CTF-TDPN than in CTF-HUST-1 (Fig. S15). The above results evidenced that the intramolecular heterostructures were beneficial for the generation and separation of charge carriers [43,44].

The role of the Co complex in the photocatalytic CO_2 reduction process was also investigated. The UV-vis absorption spectra demonstrate the easy formation of the $[\text{Co}(\text{bpy})_3]^{2+}$ complex upon the addition of the bpy ligand and $\text{Co}(\text{II})$ salt to an aqueous solution. The remarkable red-shift of bpy in the UV-vis absorption spectra indicates the coordination of bpy to Co ions (Fig. 6d). Cyclic voltammetry (CV) analysis of the in-situ formed $[\text{Co}(\text{bpy})_3]^{2+}$ aqueous solution shows two primary reduction peaks at -0.83 and -1.45 V vs. NHE under an Ar atmosphere (Fig. 6e), which were assigned to the reduction of Co^{II} to Co^{I} and Co^{I} to Co^0 , respectively [45]. The catalytic current emerged after the Co^{II} to Co^{I} reduction wave under a CO_2 atmosphere, suggesting the reaction of Co^{I} with CO_2 in the electrochemical process [15]. Moreover, the fluorescence of CTF-TDPN in solution can be significantly quenched by the in-situ formed $[\text{Co}(\text{bpy})_3]^{2+}$ (Fig. 6f), indicating that the active Co single sites originated from the in-situ formed $[\text{Co}(\text{bpy})_3]^{2+}$,

which could accept photogenerated electrons from the CTF.

Density functional theory (DFT) calculations of the optimized structures of the building blocks were further performed to study the electronic details of the CTFs. For CTF-TPN, the HOMO was located on the triphenylamine unit, while the LUMO was distributed on the triazine ring (Fig. 7a). These orbital locations are conducive to the separation of photogenerated

Fig. 7. HOMOs and LUMOs of (a) CTF-TPN and (b) CTF-HUST-1; ESP maps of (c) CTF-TPN and (d) CTF-HUST-1; (e) proposed mechanism for the photocatalytic syngas production with $[\text{Co}(\text{bpy})_3]^{2+}$ as a catalyst under visible light irradiation.

electrons. For CTF-HUST-1, the HOMO and LUMO are symmetrically distributed across the framework (Fig. 7b), which would increase the probability of electron and hole recombination. The electrostatic potential (ESP) results show that the triphenylamine unit in CTF-TPN exhibits more positive charges than the triazine unit, again proving that electrons flow from the triphenylamine to the triazine unit (Fig. 7c and 7d). Moreover, the negative charges on the triazine unit are beneficial for the adsorption of the cationic Co complex on the triazine units, boosting the electron transport.

Based on the above studies and DFT calculations, a reasonable mechanism for the photocatalytic reduction of CO₂ by CTFs is proposed (Fig. 7e). Upon visible light irradiation, electrons are excited and transferred from the triphenylamine units to the triazine units. The holes on the triphenylamine units are captured by TEOA. The photogenerated electrons are transferred from the triazine unit to the cationic Co²⁺ complex, where [Co(bpy)₃]²⁺ is reduced to [Co(bpy)₂]⁺, which serves as the active site for the reduction of CO₂ and H₂O to CO and H₂.

4. Conclusions

In summary, we have demonstrated the integration of single Co active sites within covalent triazine frameworks for the photocatalytic production of syngas via the reduction of CO₂ in aqueous solution. The covalent triazine frameworks containing intramolecular heterojunctions narrow the bandgap and enhance visible light harvesting. DFT calculations revealed that the photogenerated electrons separated from the central triphenylamine units and migrated to the triazine units through intra-molecular charge-transfer, resulting in efficient carrier separation. The single Co sites in the pores of the CTFs accept electrons to reduce CO₂ and H₂O to syngas. Consequently, CTFs with heterojunction structures display considerable photocatalytic activity. This work not only shows the great potential of CTFs for the photocatalytic production of syngas, but also offers a deep understanding of the electron-transfer mechanism of organic semiconductor-based photocatalysis.

References

- [1] Y. F. Zhao, G. I. N. Waterhouse, G. B. Chen, X. Y. Xiong, L. Z. Wu, C. H. Tung, T. R. Zhang, *Chem. Soc. Rev.*, **2019**, 48, 1972–2010.
- [2] X. Li, J. Yu, M. Jaroniec, X. Chen, *Chem. Rev.*, **2019**, 119, 3962–4179.
- [3] J. M. Spurgeon, B. Kumar, *Energy Environ. Sci.*, **2018**, 11, 1536–1551.
- [4] M. D. Porosoff, B. H. Yan, J. G. Chen, *Energy Environ. Sci.*, **2016**, 9, 62–73.
- [5] H. Wang, Y. Wang, L. Guo, X. Zhang, C. Ribeiro, T. He, *Chin. J. Catal.*, **2020**, 41, 131–139.
- [6] M. Liu, Y. F. Mu, S. Yao, S. Guo, X. W. Guo, Z. M. Zhang, T. B. Lu, *Appl. Catal. B*, **2019**, 245, 496–501.
- [7] J. C. Hu, M. X. Gui, W. Xia, J. Wu, Y. N. Zhou, N. D. Feng, J. W. Xiao, H. F. Liu, C. H. Tung, L. Z. Wu, F. Wang, *J. Mater. Chem. A*, **2019**, 7, 10475–10482.
- [8] J. S. Lee, D. I. Won, W. J. Jung, H. J. Son, C. Pac, S. O. Kang, *Angew. Chem. Int. Ed.*, **2017**, 56, 976–980.
- [9] A. Li, T. Wang, X. Chang, Z. J. Zhao, C. Li, Z. Huang, P. Yang, G. Zhou, J. Gong, *Chem. Sci.*, **2018**, 9, 5334–5340.
- [10] M. Liu, S. Wageh, A. A. Al-Ghamdi, P. Xia, B. Cheng, L. Zhang, J. Yu, *Chem. Commun.*, **2019**, 55, 14023–14026.
- [11] X. Li, C. Liu, D. Wu, J. Li, P. Huo, H. Wang, *Chin. J. Catal.*, **2019**, 40, 928–939.
- [12] J. Low, B. Dai, T. Tong, C. Jiang, J. Yu, *Adv. Mater.*, **2019**, 31, 1802981.
- [13] J. Jiang, S. Cao, C. Hu, C. Chen, *Chin. J. Catal.*, **2017**, 38, 1981–1989.
- [14] B. P. Biswal, H. A. Vignolo-González, T. Banerjee, L. Grunenberg, G. Savasci, K. Gottschling, J. Nuss, C. Ochsenfeld, B. V. Lotsch, *J. Am. Chem. Soc.*, **2019**, 141, 11082–11092.
- [15] W. Zhong, R. Sa, L. Li, Y. He, L. Li, J. Bi, Z. Zhuang, Y. Yu, Z. Zou, *J. Am. Chem. Soc.*, **2019**, 141, 7615–7621.
- [16] W. T. Eckenhoff, *Coord. Chem. Rev.*, **2018**, 373, 295–316.
- [17] J. W. Wang, W. J. Liu, D. C. Zhong, T. B. Lu, *Coord. Chem. Rev.*, **2019**, 378, 237–261.
- [18] J. Xiao, W. Yang, S. Gao, C. Sun, Q. Li, *J. Mater. Sci. Technol.*, **2018**, 34, 2331–2336.
- [19] C. Bie, B. Zhu, F. Xu, L. Zhang, J. Yu, *Adv. Mater.*, **2019**, 31, e1902868.
- [20] D. T. Genna, A. G. Wong-Foy, A. J. Matzger, M. S. Sanford, *J. Am. Chem. Soc.*, **2013**, 135, 10586–10589.
- [21] Q. Xie, W. He, S. Liu, C. Li, J. Zhang, P. K. Wong, *Chin. J. Catal.*, **2020**,

Graphical Abstract

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Encapsulation of Co single sites in covalent triazine frameworks for photocatalytic production of syngas

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Encapsulation of Co single sites in covalent triazine frameworks with intramolecular heterojunctions boosts the efficiency of photocatalytic syngas production, revealing the promising potential of covalent triazine frameworks for single-site photocatalysis.

- 41, 140–153.
- [22] W. Yu, D. Xu, T. Peng, *J. Mater. Chem. A*, **2015**, 3, 19936–19947.
- [23] D. Li, Y. Huang, S. Li, C. Wang, Y. Li, X. Zhang, Y. Liu, *Chin. J. Catal.*, **2020**, 41, 154–160.
- [24] X. Liu, M. Ye, S. Zhang, G. Huang, C. Li, J. Yu, P. K. Wong, S. Liu, *J. Mater. Chem. A*, **2018**, 6, 24245–24255.
- [25] J. Bi, W. Fang, L. Li, J. Wang, S. Liang, Y. He, M. Liu, L. Wu, *Macromol. Rapid Commun.*, **2015**, 36, 1799–1805.
- [26] M. Liu, Q. Huang, S. Wang, Z. Li, B. Li, S. Jin, B. Tan, *Angew. Chem. Int. Ed.*, **2018**, 57, 11968–11972.
- [27] S. Kuecken, A. Acharyya, L. Zhi, M. Schwarze, R. Schomacker, A. Thomas, *Chem. Commun.*, **2017**, 53, 5854–5857.
- [28] Z. A. Lan, Y. Fang, Y. Zhang, X. Wang, *Angew. Chem., Int. Ed.*, **2018**, 57, 470–474.
- [29] K. Cui, W. Zhong, L. Li, Z. Zhuang, L. Li, J. Bi, Y. Yu, *Small*, **2019**, 15, 1804419.
- [30] W. Huang, B. C. Ma, H. Lu, R. Li, L. Wang, K. Landfester, K. A. I. Zhang, *ACS Catal.*, **2017**, 7, 5438–5442.
- [31] H. S. Jena, C. Krishnaraj, G. Wang, K. Leus, J. Schmidt, N. Chaoui, P. Van Der Voort, *Chem. Mater.*, **2018**, 30, 4102–4111.
- [32] S. Padmanaban, G. H. Gunasekar, M. Lee, S. Yoon, *ACS Sustain. Chem. Eng.*, **2019**, 7, 8893–8899.
- [33] Y. Ren, D. Zeng, W. J. Ong, *Chin. J. Catal.*, **2019**, 40, 289–319.
- [34] H. Zhong, Z. Hong, C. Yang, L. Li, Y. Xu, X. Wang, R. Wang, *ChemSusChem*, **2019**, 12, 4493–4499.
- [35] S. Hug, M. E. Tauchert, S. Li, U. E. Pachmayr, B. V. Lotsch, *J. Mater. Chem.*, **2012**, 22, 13956–13964.
- [36] H. Zhong, C. Yang, L. Li, Y. Xu, X. Wang, R. Wang, *ChemSusChem*, **2019**, 12, 4493–4499.
- [37] Q. Wang, W. Wang, L. Zhang, Y. Su, K. Wang, H. Wu, *J. Mater. Sci. Technol.*, **2018**, 34, 2337–2341.
- [38] M. Liu, Q. Huang, S. Wang, Z. Li, B. Li, S. Jin, B. Tan, *Angew. Chem. Int. Ed.*, **2018**, 57, 11968–11972.
- [39] Z. Zhou, W. Zhong, K. Cui, Z. Zhuang, L. Li, L. Li, J. Bi, Y. Yu, *Chem. Commun.*, **2018**, 54, 9977–9980.
- [40] K. Wang, L. Yang, X. Wang, L. Guo, G. Cheng, C. Zhang, S. Jin, B. Tan, A. Cooper, *Angew. Chem. Int. Ed.*, **2017**, 56, 14149–14153.
- [41] J. Low, B. Cheng, J. Yu, *Appl. Surf. Sci.*, **2017**, 392, 658–686.
- [42] Y. Xia, Z. Tian, T. Heil, A. Meng, B. Cheng, S. Cao, J. Yu, M. Antonietti, *Joule*, **2019**, 3, 2792–2805.
- [43] E. X. Han, Y. Y. Li, Q. H. Wang, W. Q. Huang, L. Luo, W. Hu, G. F. Huang, *J. Mater. Sci. Technol.*, **2019**, 35, 2288–2296.
- [44] J. Low, J. Yu, M. Jaroniec, S. Wageh, A. A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [45] Y. Xu, Y. Ye, T. Liu, X. Wang, B. Zhang, M. Wang, H. Han, C. Li, *J. Am. Chem. Soc.*, **2016**, 138, 10726–10729.

共价三嗪框架复合Co单活性位点光催化制合成气

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摘要: 合成气是费托合成的关键原料, 目前其主要是通过天然气重整或煤气化来制备, 但是该制备过程需要苛刻的合成条件. 光催化技术利用太阳能将CO₂还原制备合成气是未来能源开发的重要研究方向. 到目前为止, 已经开发了许多用于生产合成气的光催化系统. 然而, 大多数催化体系使用昂贵的金属如Re和Ru作为光敏剂和或催化剂, 利用非贵金属催化剂光催化还原CO₂制合成气是实现环境可持续发展的一种有效方法. 共价三嗪框架(CTF)由于具有可调节的光吸收性质、在分子水平上可调节的电子结构、高表面积和富氮结构, 因而在光催化体系中具有明显优势. 在此, 我们设计了一种基于分子内异质结的CTF光催化CO₂还原生成合成气体体系, 通过傅里叶变换红外光谱(FT-IR)、核磁共振波谱(NMR)和X射线光电子能谱(XPS)等表征证明了CTF内的分子内异质结, 采用X射线多晶衍射(XRD)、比表面积及孔隙度分析(BET)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和紫外-可见吸收光谱(UV-Vis DRS)等表征手段充分研究了CTF的组成、结构与光学性质. 将所制备的CTF光催化剂应用于可见光催化还原CO₂反应中, 实验结果表明, 基于分子内异质结的CTF在10 h内达到3303 μmol g⁻¹(CO:H₂ = 1.4:1)的合成气产率, 相对于不具有分子内异质结的CTF催化体系, 产率提高了3倍. 时间分辨荧光发射衰减光谱、荧光光谱和瞬时光电流图谱等测试结果表明, 分子内异质结极大提高了CTF内光生载流子的空间分离和转移效率. 反应体系中自组装形成的吡啶Co配合物作为Co单活性位点可有效吸附和配位活化CO₂分子. 理论计算进一步证明含有分子内异质结结构的CTF能极大地促进电荷分离效率, 从而实现催化性能的增强. 这项工作不仅显示了CTF在光催化等领域潜在的应用前景, 而且为合理设计基于CTF的光催化体系提供了新的见解.

关键词: 合成气; 光催化; 共价三嗪框架; 二氧化碳还原; 单点催化剂; 合成气

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