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Integrating Z-scheme heterojunction of Co_1 - $C_3N_4@\alpha$ - Fe_2O_3 for efficient visible-light-driven photocatalytic CO_2 reduction†

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Photocatalytic CO_2 reduction coupled with water oxidation provides a fascinating approach to mitigating the issues of global warming and energy shortage. Herein, a direct Z-scheme heterojunction of Co_1 - $C_3N_4@\alpha$ - Fe_2O_3 comprising a g- C_3N_4 -supported single-atomic Co site catalyst (denoted as Co_1 - C_3N_4) and α - Fe_2O_3 nanorod arrays is fabricated for efficient CO_2 reduction. A CO production rate of 14.9 μ mol g^{-1} h⁻¹ with a high CO selectivity (>99%) is achieved under visible-light irradiation without any sacrificial agents other than water. Time-resolved photoluminescence (TRPL) analysis reveals that both the Z-scheme mechanism and the single-atomic Co sites contribute to the prolonged lifetime of the photo-induced excitons. Moreover, the formation of the Z-scheme heterojunction would lead to an altered charge density of the single-atomic Co sites. *In situ* diffuse reflectance infrared Fourier-transform spectroscopy and anion adsorption measurements reveal that the key intermediate CO_2 -could be efficiently stabilized by the positively charged Co sites in Co_1 - C_3N_4 @ α - Fe_2O_3 , thus enhancing the CO_2 reduction performance. This work offers a new direction for the rational design of single-atomic site catalysts in artificial photosynthesis.

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Introduction

The rapidly growing consumption of fossil fuels with excessive emission of CO₂ has been contributing to the severe global warming problem and the potential energy shortage. 1,2 Utilizing solar energy to convert CO2 into fuels provides a promising approach to solving the above problems, and scientists have devoted tremendous attention to developing various photocatalysts for CO₂ reduction.³⁻⁹ Recently, graphitic carbon nitride (g-C₃N₄)-supported single-atomic site catalysts have emerged as remarkable photocatalysts. 10-13 By virtue of the lone pair electrons, the N atoms in the framework can capture various transition metal ions, thus forming single-atomic metal sites on g-C₃N₄. In addition, the charge densities of the coordinated metal atoms would be altered by the neighboring N atoms, which may in turn change the adsorption strength and reaction barriers. Density functional theory (DFT) calculations have suggested that single-atomic Pd or Pt loaded on g-C₃N₄ can act as effective catalytic sites for photocatalytic CO₂

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reduction, leading to two different preferential products, HCOOH and CH₄, respectively. 14 With the aid of triethylamine (TEA), single-atomic Co²⁺ sites on C₃N₄ with different loadings have been successfully synthesized, and the optimized sample with a cobalt loading of 0.128 $\mu mol\ mg^{-1}$ exhibits a CO production rate of approximately 25.5 µmol g⁻¹ h⁻¹ under 60 mW cm⁻² incident light in the presence of triethanolamine (TEOA) as a sacrificial electron donor. 15 Recently, we have developed an efficient photocatalyst for CO2 reduction by implanting single titanium oxide species on g-C₃N₄. In the presence of the Co(bpy)₃Cl₂ co-catalyst and TEOA, a CO production rate of 283.9 μ mol g⁻¹ h⁻¹ has been achieved under visible light irradiation. These results strongly demonstrate the viability of g-C₃N₄-supported single-atomic site catalysts for photocatalytic CO₂ reduction. However, the use of TEOA makes these catalysts less attractive since TEOA is much more expensive than CO. Therefore, it still remains a great challenge to develop low-cost and robust g-C₃N₄-based photocatalysts with high efficiency for CO₂ conversion using water as an electron source.

Owing to the wide band gap (\sim 2.7 eV), g-C₃N₄ can only utilize a marginal portion of visible light (λ < 460 nm). Moreover, the water oxidation capacity of g-C₃N₄ is poor due to the high energy level of the valence band. ^{18–20} In this situation, integrating g-C₃N₄ with an appropriate semiconductor possessing a narrower band gap and a more positive valence band to establish a Z-scheme heterojunction has been acknowledged

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as an effective strategy, because the Z-scheme heterojunction not only facilitates the spatial separation of the photo-induced electron-hole pairs, but also preserves the maximum capacities for reduction and oxidation of the composites. ^{20–23}

Herein, we construct a direct Z-scheme heterojunction of Co₁-C₃N₄(aα-Fe₂O₃, which composes by single-atomic Co sites loaded on g-C₃N₄ (Co₁-C₃N₄) integrated with α -Fe₂O₃ nanorod arrays, for efficient visible-light-driven CO2 reduction coupled with water oxidation. The light-absorption range of Co₁-C₃N₄ is greatly extended to the entire visible-light region and the lifetime of photo-induced charge carriers is significantly prolonged by the successful incorporation of α-Fe₂O₃. Moreover, benefiting from the charge transfer induced by the different Fermi levels between α-Fe₂O₃ and Co₁-C₃N₄, the charge density of single-atomic Co can be further regulated. The results of anion adsorption measurements imply that the stabilization of the critical intermediate CO₂ is more efficient on the singleatomic Co sites with a higher positive charge. Compared with Co₁-C₃N₄, the constructed Z-scheme heterojunction shows a substantial improvement for photocatalytic CO2 conversion to CO, with 2.8 times higher than that of Co₁-C₃N₄ under visible light irradiation and almost 100% CO selectivity.

Experimental

Materials

FeCl₃·6H₂O (99%, AR) and CoCl₂·6H₂O (99%, AR) were purchased from Aladdin. Urea (99%, AR), NaOH (96%, AR) and Na₂SO₄ (99%, AR) were purchased from FuChen Chemical Reagent Factory. Nafion 117 solution (\sim 5% in alcohol/water) was purchased from Sigma-Aldrich. CO₂ (99.999%) and Ar (99.999%) were purchased from Tianjin Huanyu Gas company. 13 CO₂ (99%) was purchased from Sigma-Aldrich and H₂ 18 O (99%) was purchased from Energy Chemical. All chemicals were used as received without further purification. The ultrapure water (Milli-Q water) with an electrical resistivity of 18.2 MΩ cm was used in all experiments.

Synthetic procedures

The α -Fe₂O₃ nanorod arrays were fabricated by a modified strategy reported previously.^{24,25} In brief, a piece of fluorinedoped tin oxide (FTO) glass (1 cm × 2.5 cm) was sonicated in acetone, ethanol and water, respectively. Then the FTO glass was leant on the inner side of a Teflon liner with the FTO side facing down. Subsequently, an aqueous solution (15 mL) containing FeCl₃·6H₂O (0.51 g) and urea (0.17 g) was added, and the liner was sealed in a stainless steel autoclave, and then heated at 100 °C for 4 h. The as-prepared sample was washed with water and dried by N2 flow to remove redundant sediment. The film was annealed at 550 °C for 2 h and subsequently at 660 °C for 20 min in a muffle furnace with a ramping rate of 2 °C min⁻¹, and the α-Fe₂O₃ nanorod arrays were finally obtained. The loading amount of the α-Fe₂O₃ nanorod arrays was determined to be 0.3 mg by weighing the FTO glass before and after the synthesis.

The g-C₃N₄-supported Co single-atom catalyst was prepared by using a two-step strategy.²⁶ Specifically, urea (15 g) was put into a crucible with a cover, and calcined at 550 °C for 4 h with a ramping rate of 10 °C min⁻¹. After cooling down naturally, the product was heated again at 500 °C for 2 h to obtain exfoliated g-C₃N₄. For the synthesis of g-C₃N₄-supported singleatomic Co site catalyst (Co₁-C₃N₄), g-C₃N₄ (10 mg) was well dispersed in water (10 mL) by vigorous sonication for 30 min. Next, an aqueous solution (500 μL) containing CoCl₂·6H₂O (0.336 mM) was dropped into the g-C₃N₄ suspension under magnetic stirring. Subsequently, the suspension was stirred for 12 h at 80 °C in an oil bath. The above mixture was then frozen by liquid nitrogen and further dried in vacuum for 48 h by using a lyophilizer. The obtained sample was placed in a porcelain boat and heated to 400 °C for 2 h with a ramping rate of 5 °C min⁻¹ under Ar atmosphere. Similar procedures were applied for the synthesis of the g-C₃N₄-supported CoO nanoparticle catalyst (CoNP-C3N4), except that the concentration of CoCl₂·6H₂O was increased to 3.36 mM.

To fabricate the Z-scheme system, a well-dispersed aqueous suspension (300 μ L) of Co₁-C₃N₄ (1 mg mL⁻¹, 0.3 mg in total) was first drop-coated onto the α -Fe₂O₃ nanorod arrays under 60 °C. To strengthen the contact between α -Fe₂O₃ and Co₁-C₃N₄, the sample was transferred to a tube furnace and calcined at 200 °C for 2 h, with a ramping rate of 5 °C min⁻¹ under Ar atmosphere. The obtained sample was denoted as Co₁-C₃N₄@ α -Fe₂O₃. C₃N₄@ α -Fe₂O₃ and CoNP-C₃N₄@ α -Fe₂O₃ were fabricated according to the same method as that of Co₁-C₃N₄@ α -Fe₂O₃, except that Co₁-C₃N₄ was replaced by g-C₃N₄ and CoNP-C₃N₄, respectively.

Characterization

The powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku SmartLab 9 kW with Cu-K α radiation (λ = 1.5418 Å). A Thermo scientific iCAP RQ inductively coupled plasma-mass spectrometer (ICP-MS) was used to determine the Co content. Scanning electron microscopy (SEM) was performed using a FEI Verios 460L scanning electron microscope. Transmission electron microscopy (TEM) images and High-Resolution Transmission Electron Microscopy (HRTEM) images were obtained on FEI Tecnai G2 Spirit Twin and FEI Talos F200X transmission electron microscopes, respectively. Atomic-resolution aberration-corrected high-angle annular scanning transmission electron microscopy dark-field (HAADF-STEM) images and elemental mapping were obtained by using a FEI Titan Themis Cubed G2 60-300 transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a Thermo Scientific ESCALAB250Xi photoelectron spectrometer equipped with Mg Kα (1253.6 eV) as the X-ray source. Ultraviolet-visible (UV-vis) spectroscopic measurements were performed by using a PerkinElmer Lambda 750 UV/VIS/NIR spectrometer. A PerkinElmer Frontier Mid-IR FTIR spectrometer was employed to obtain Fourier-transform infrared spectra. The steady-state photoluminescence spectra (PL) were recorded on a Hitachi F-4600 fluorescence spectrometer. The time-resolved photo**Paper** Green Chemistry

luminescence (TRPL) curves were recorded using a PicoOuant MicroTime 200 time-resolved confocal fluorescence instrument. The electron spin resonance (ESR) analysis was conducted on an electron paramagnetic resonance spectrometer (Bruker EMXplus-6/1) with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the trapping agent at 298 K. CO₂ adsorption was tested by using a MicrotracBEL BELSORP-Max gas adsorption instrument at 298 K. A Hansatech Chlorolab-2 liquid-phase oxygen measurement system was employed to detect the oxygen evolution during the photocatalytic CO₂ reduction.

Photocatalytic CO₂ reduction measurements

Photocatalytic CO2 reduction tests were conducted in a gassolid setup. A piece of the sample was placed in a 35 mL quartz tube. High-purity CO2 (99.999%) was first passed through water to carry H₂O vapor and then introduced into the quartz tube. The quartz tube was purged with the CO₂/H₂O gas mixture for 30 min and sealed by using a rubber stopper. A 300 W xenon lamp (CEL-HXF300, CEAULIGHT) with a 400 nm cutoff filter was positioned above the sample as the light source. Gaseous products (CO, CH₄, and H₂) were analysed by using a SHIMADZU GC-2014 gas chromatograph equipped with TCD and FID dual detectors. The products of the ¹³CO₂ and H₂¹⁸O isotopic experiments were analysed by using a Hiden Analytical HPR20 mass spectrometer.

Photoelectrochemical measurements

All measurements were performed on a CHI 760E electrochemical workstation with a three-electrode setup (working electrode: FTO glass-supported sample; reference electrode: Ag/AgCl electrode; counter electrode: Pt foil) in 0.1 M Na₂SO₄ aqueous solution. To measure the photo-current responses, a 300 W Xe lamp (CEL-HXF300, CEAULIGHT) with a 400 nm cutoff filter was used as the light source. A potential of 0.5 V vs. Ag/AgCl was applied on the sample and the light was chopped every 10 s to simulate light/dark conditions during the test. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 0.1 MHz to 0.1 Hz with an AC voltage amplitude of 5 mV at an open-circuit potential under visible-light irradiation with a power density of 200 mW cm^{-2} .

In situ DRIFTS characterization

In situ diffuse reflectance infrared Fourier-transform spectra (DRIFTS) were recorded on a Bruker IFS 66v Fourier-transform spectrometer the Infrared Spectroscopy Microspectroscopy Endstation (BL01B) in the National Synchrotron Radiation Laboratory (NSRL), Hefei.²⁷ The sample was placed in a Harrick diffuse reflectance reaction chamber fixed in the light path. The chamber was equipped with two ZnSe windows and two gas channels. Each spectrum was recorded by 128 scans with a resolution of 4 cm⁻¹. The spectrum recorded under Ar atmosphere was set as the background signal.

Results and discussion

The composite structure comprising α-Fe₂O₃ and Co₁-C₃N₄ was fabricated by a multi-step strategy (Fig. 1a). Co₁-C₃N₄ exhibits a two-dimensional morphology without any distinguishable clusters, as shown in Fig. 1b and Fig. S1.† The results of elemental mapping indicate the uniform dispersion of Co species on g-C₃N₄ (Fig. 1c). The XRD pattern for Co₁-C₃N₄ also shows no peaks other than those corresponding to g-C₃N₄ (Fig. S2†). The atomic dispersion of Co sites was further verified by using a HAADF-STEM image, in which the bright spots represent Co atoms and no aggregation of the bright spots was observed (Fig. 1d).28 The line-scan profiles also confirm that the Co atoms are well isolated (Fig. S3†). ICP-MS was employed to determine the actual loading of Co. As listed in Table S1,† the mass loading of Co is 0.07% for Co₁-C₃N₄. A sample comprising CoO nanoparticles on g-C₃N₄ was also prepared, with a Co mass loading of 0.81% (denoted as CoNP-C₃N₄, Fig. S4†). SEM and TEM images (Fig. 1e and Fig. S5†) show that the α-Fe₂O₃ nanorods grown on fluorine-doped tin oxide (FTO) glass have an average length of ~500 nm and an average diameter of ~50 nm. The HRTEM image (Fig. 1f) displays lattice fringes with a lattice spacing of 0.25 nm, which can be assigned to the (110) planes of crystalline α -Fe₂O₃. The top view for the composite photocatalyst clearly shows that the α-Fe₂O₃ nanorod arrays are covered by highly corrugated Co₁-C₃N₄ nanosheets (Fig. S6†). Fourier-transform infrared spectrum for Co₁-C₃N₄ shows a series of characteristic peaks of g-C₃N₄ as those reported in the literature (Fig. 1g). Notably, the peak at 806 cm⁻¹, which is assigned to the breathing mode of the triazine unit in carbon nitride, is blue-shifted to 808 cm⁻¹ when Co₁-C₃N₄ is integrated with α-Fe₂O₃ nanorods.²⁹ Similar shifts are also found for the peaks at 1200 to 1650 cm⁻¹, which correspond to the stretching vibration modes characteristic of aromatic g-C₃N₄ heterocycles.³⁰ The blue shift can be attributed to the charge transfer between Co₁-C₃N₄ and α-Fe₂O₃, which strongly evidences the successful formation of heterojunctions.21

UV-vis diffuse reflectance spectroscopy was employed to explore the light-harvesting ability of the as-prepared photocatalysts (Fig. S7†). The absorption edge for Co₁-C₃N₄@α-Fe₂O₃ is significantly extended to 700 nm, covering almost the entire visible region. On the basis of the Tauc plots (Fig. S8†), the band gaps of the α-Fe₂O₃ nanorod and Co₁-C₃N₄ were determined to be 2.12 eV and 2.66 eV, respectively. The energy band structures were further resolved by Mott-Schottky plots (Fig. S9†). The positive slopes of the Mott-Schottky plots indicate the n-type characteristics for both the α-Fe₂O₃ nanorod and Co₁-C₃N₄.³¹ The flat band potentials of α-Fe₂O₃ and Co₁- C_3N_4 were calculated to be 0.36 V and -0.94 V versus the normal hydrogen electrode (NHE), respectively. For the n-type semiconductor, the flat band potential is close to the bottom of the conduction band (CB).31,32 Now we are able to draw a clear band diagram for the composite structure, as shown in Fig. 2c. To validate the Z-scheme route for the photo-induced charge carriers, ESR spectroscopy was employed to detect 'OH

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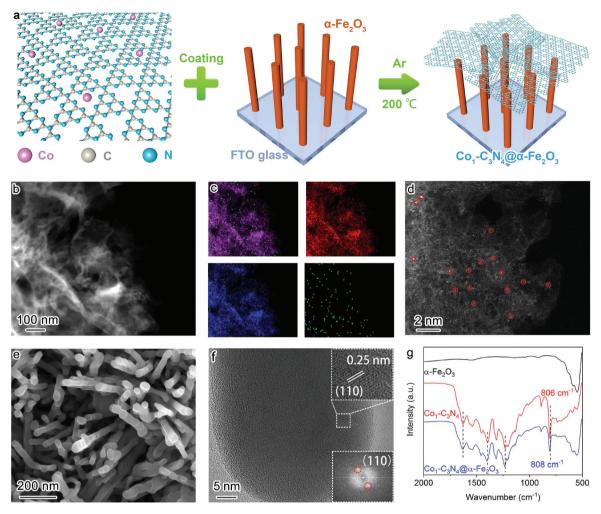


Fig. 1 (a) Schematic illustration of the fabrication strategy for $Co_1-C_3N_4@\alpha$ -Fe₂O₃. (b) Low-resolution HAADF-STEM image for $Co_1-C_3N_4$ and (c) the corresponding elemental mapping images of C (red), N (blue), and Co (green). (d) Atomic-resolution HAADF-STEM image for $Co_1-C_7N_4$. The atomically dispersed Co sites are marked in red circles. (e) SEM image and (f) HRTEM image for the α-Fe₂O₃ nanorod arrays; insets: lattice fringes of a single α -Fe₂O₃ nanorod (top) and the selected area electron diffraction (SAED) pattern (bottom). (g) Fourier-transform infrared spectra for α -Fe₂O₃, Co_1 - C_3N_4 , and Co_1 - C_3N_4 @ α - Fe_2O_3 .

and 'O2 species with DMPO as the trapping agent (Fig. 2a and b). For pristine α-Fe₂O₃, only a weak signal attributed to 'OH was observed under visible-light irradiation; for pristine Co₁-C₃N₄, only the signal attributed to 'O₂ was detected with four identical peaks. These results are understandable by comparing the energy band positions with the reaction potentials of O_2 / $^{\bullet}O_2$ and H_2O / $^{\bullet}OH$ (OH $^{-}$ / $^{\bullet}OH$). When Co_1 - $C_3N_4@\alpha$ - Fe_2O_3 was employed as the photocatalyst, the signals of both 'OH and 'O2 were observed with much stronger intensities than that for each single component. In addition, neither of the two species was observed for Co₁-C₃N₄@α-Fe₂O₃ under dark conditions (Fig. S10†), suggesting that the reactive oxygen species mentioned above were generated upon incident light. Therefore, we can conclude that the photo-induced charge carriers follow a Z-scheme mechanism rather than a Type II mechanism (Fig. 2c).8,33

With the Z-scheme mechanism for Co₁-C₃N₄@α-Fe₂O₃ validated, now we are in a position to investigate the efficacy of the composite structure in promoting photocatalytic CO₂ reduction. Fig. 3a shows the average CO evolution rates in CO₂ overall splitting for the as-prepared catalysts under visible light $(\lambda > 400 \text{ nm})$. No product was detected for α -Fe₂O₃ nanorod arrays, as the potential of the conduction band is too positive to trigger the reduction of CO2. The CO production rate for Co₁-C₃N₄(a)α-Fe₂O₃ was substantially elevated to 14.9 μmol g⁻¹ h^{-1} , 2.9 times as high as that for Co_1 - C_3N_4 (5.2 μ mol g^{-1} h^{-1}) and 6.5 times as that for $C_3N_4@\alpha$ -Fe₂O₃ (2.3 µmol g⁻¹ h⁻¹). These results imply that the construction of the Z-scheme heterojunction and the introduction of Co favor the photocatalytic reduction of CO2 under visible light. When ultraviolet light was also introduced to the photocatalytic system (by the removal of the cut-off filter), a CO production rate as high as 25.2 μmol g⁻¹ h⁻¹ was achieved, demonstrating the excellent CO₂ reduction capability for Co₁-C₃N₄@α-Fe₂O₃ under full spectrum. To evaluate the utilization efficiency of the solar energy, apparent quantum efficiencies (AQEs) for CO genePaper Green Chemistry

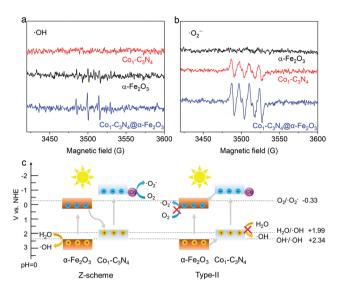


Fig. 2 (a and b) DMPO spin-trapping ESR spectra for α -Fe₂O₃, Co₁- C_3N_4 , and $Co_1-C_3N_4@\alpha-Fe_2O_3$ under visible-light irradiation. (c) Schematic illustration for the validation of the Z-scheme mechanism rather than Type-II.

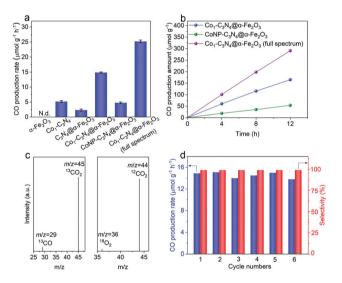


Fig. 3 (a) CO production rates of α -Fe₂O₃, Co₁-C₃N₄, C₃N₄@ α -Fe₂O₃, $Co_1-C_3N_4@\alpha-Fe_2O_3$, and $CoNP-C_3N_4@\alpha-Fe_2O_3$; N.d.: not detected. (b) Time-dependent production of CO by CoNP-C $_3$ N $_4$ @ α -Fe $_2$ O $_3$ and Co $_1$ - $C_3N_4@\alpha-Fe_2O_3$. (c) Mass spectra of ¹³CO (m/z=29) and ¹⁸O₂ (m/z=36) produced by Co_1 - C_3N_4 @ α - Fe_2O_3 in the isotopic experiments. (d) Cycling production of CO for Co_1 - C_3N_4 @ α - Fe_2O_3 in photocatalytic CO_2 reduction with pure water.

ration were determined under different monochromatic light irradiation (Fig. S11†). The AQEs at 365 nm and 405 nm were determined to be 0.52% and 0.42%, respectively. In addition, it is noteworthy that neither H2 nor CH4 was detected in the gaseous products for a continuous 12-hour photocatalytic test, suggesting the high selectivity for CO (Fig. 3b). To the best of our knowledge, the performance of Co₁-C₃N₄(a)α-Fe₂O₃ here is among the top levels in comparison with other g-C₃N₄-based

and single-atomic site catalysts in photocatalytic CO₂ coupled with water oxidation (Table S5†). To further examine the essentialness of the single-atomic character of Co in CO2 reduction, CoNP-C₃N₄@α-Fe₂O₃ was employed for comparison. The result shows that the CO production rate for CoNP-C₃N₄@α-Fe₂O₃ is much lower (4.8 µmol g⁻¹ h⁻¹), suggesting the critical role of single-atomic Co sites in photocatalytic CO2 reduction. A similar irradiation test under Ar atmosphere was conducted on Co₁-C₃N₄(a)α-Fe₂O₃, and no CO was detected. To further identify the origin of CO, we traced the carbon source in the reduction process using a ¹³C isotopic label. Fig. 3c shows the mass spectrum of CO obtained with ¹³CO₂ as a substrate under identical photocatalytic reaction conditions; a distinct 13 CO peak (m/z = 29) was observed, indicating that the CO indeed originates from CO2. H218O, instead of H216O, was also adopted to verify the water oxidation half-reaction, and a clear $^{18}O_2$ peak (m/z = 36) was observed in the mass spectrum. Moreover, molecular oxygen was detected as the product by liquid-phase oxygen measurement system, further confirming that the CO2 reduction is coupled with water oxidation (Fig. S12†). As shown in Fig. 3d and S13,† the production rate and selectivity of CO for Co₁-C₃N₄@α-Fe₂O₃ remained almost unchanged during the six consecutive cycles (4 h each), and no aggregation of Co species appeared after the stability test, validating the excellent stability for the Z-scheme system under visible light.

Given the above results, a question naturally arises: What role does the Z-scheme play in enhancing the photocatalytic CO2 reduction? In addition to the significantly broadened light-absorption range, the dynamic behaviors of the photoinduced charge carriers are also effectively regulated. The photocurrent responses were recorded under intermittent visible-light irradiation in 0.1 M Na₂SO₄ aqueous solution (Fig. S14†). The photocurrent density for Co₁-C₃N₄@α-Fe₂O₃ is higher than those for α-Fe₂O₃ and Co₁-C₃N₄, suggesting the more efficient photo-induced electron-hole separation for improved CO₂ reduction.³⁴ Electrochemical impedance spectroscopy (EIS) was conducted to reflect the charge transfer resistance (Fig. S15†). The Nyquist plots reveal that Co₁- $C_3N_4@\alpha$ -Fe₂O₃ has the lowest charge transfer resistance, which is beneficial for the separation and migration of the photoinduced charge carriers. 24,35 To investigate the lifetime of the electron-hole pairs, we employed PL spectroscopy. As shown in Fig. S16,† the main emission peak located at 442 nm can be ascribed to the inter-band recombination of photo-induced charge carriers. The dramatically quenched PL intensity for Co₁-C₃N₄(a)α-Fe₂O₃ indicates the faster electron migration and the efficient suppression of the carrier recombination.²⁹ To gain in-depth information for the carrier dynamics, TRPL decay curves for the as-prepared photocatalysts were recorded. As revealed in Fig. 4a and S17,† Co₁-C₃N₄(aα-Fe₂O₃ shows a significantly slower decay kinetics than α-Fe₂O₃ and Co₁-C₃N₄. The PL lifetimes are listed in Table S2.† The shorter lifetime τ_1 is related to the non-radiative relaxation, and the longer lifetime τ_2 is attributed to the inter-band recombination of the photo-induced excitons, which mainly contributes to the

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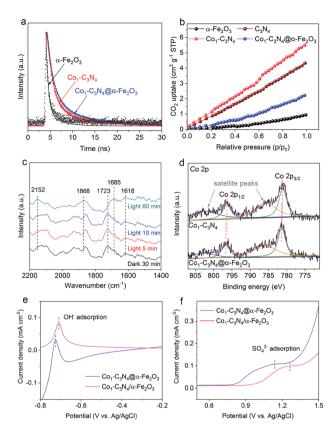


Fig. 4 (a) TRPL decay curves for $\alpha\text{-Fe}_2\text{O}_3$, $\text{Co}_1\text{-C}_3\text{N}_4$, and $\text{Co}_1\text{-}$ $C_3N_4@\alpha\text{-Fe}_2O_3.$ (b) CO_2 adsorption isotherms for $\alpha\text{-Fe}_2O_3,$ $g\text{-}C_3N_4,$ $Co_1\text{-}$ C_3N_4 , and Co_1 - C_3N_4 @ α -Fe₂O₃. (c) In situ DRIFTS spectra for Co₁- $C_3N_4@\alpha$ -Fe₂O₃ under different irradiation conditions with the existence of CO₂ and H₂O. (d) X-ray photoelectron spectroscopy spectra of the Co 2p core levels for $Co_1-C_3N_4$ and $Co_1-C_3N_4$ @ α -Fe₂O₃. Single oxidative LSV scans at 100 mV s⁻¹ in (e) Ar-bubbled 0.5 M NaOH and (f) Arbubbled 0.1 M Na₂SO₄ for Co₁-C₃N₄@ α -Fe₂O₃ and Co₁-C₃N₄/ α -Fe₂O₃, respectively.

photoluminescence. ²¹ Notably, the average lifetime (τ) of Co₁-C₃N₄@α-Fe₂O₃ is prolonged to 5.17 ns, suggesting the high efficacy of the Z-scheme heterojunction. Specifically, the photo-induced electrons in the conduction band of α-Fe₂O₃ can efficiently annihilate the holes in the valence band of Co₁-C₃N₄, thus suppressing the recombination of photo-induced excitons inside each component. As a consequence, more photo-induced electrons would be preserved on the conduction band of Co₁-C₃N₄, and more photo-induced holes would be preserved on the valence band of α-Fe₂O₃, thus leading to superior photocatalytic performances. Furthermore, the incorporation of single-atomic Co sites also results in prolonged average lifetimes with significantly altered τ_1 and τ_2 . The atomically dispersed Co can act as effective trap sites to capture the photo-induced electrons from the conduction band of g-C₃N₄, thereby inhibiting the recombination of the electrons with the VB holes. ^{36,37} Therefore, for Co₁-C₃N₄(a)α-Fe₂O₃, the Z-scheme structure and the single-atomic Co sites collaboratively contribute to the efficient separation of the photo-induced excitons.

To shed light on the role of single-atomic Co sites at the catalytic interface during photocatalytic CO2 reduction, CO2 adsorption was employed to determine the chemisorption capacities of these catalysts. As depicted in Fig. 4b, Co₁-C₃N₄ adsorbs a much larger amount of CO2 than bare g-C3N4, suggesting the efficacy of the single-atomic Co sites. It is also worth pointing out that the integration of α-Fe₂O₃ significantly reduces the CO₂ uptake, which can be attributed to the poor CO₂ adsorption ability of α-Fe₂O₃ nanorod arrays. To unravel the possible reaction pathway that occurs on Co₁- $C_3N_4@\alpha$ -Fe₂O₃, we carried out in situ DRIFTS measurements to explore the key intermediates in photocatalytic CO₂ reduction. As illustrated in Fig. 4c, the peaks at 1618 cm⁻¹, 1723 cm⁻¹, and 1868 cm⁻¹ can be assigned to bidentate carbonate (b-CO₃²⁻), chelating bridged carbonate (c-CO₃²⁻), and multibonded CO (m-CO) on the g-C₃N₄ substrate, respectively. 38,39 The carbonate species are formed by the interaction of the surface O atoms of g-C₃N₄ with adsorbed CO₂. 38 During the 60 min irradiation, the peak intensity of b-CO₃²⁻ remained unchanged, whereas the peak intensity of c-CO₃²⁻ significantly decreased. Meanwhile, an obvious increase was observed in the m-CO peak. These results can be explained by the catalytic effect that c-CO₃²⁻ is converted into m-CO during the photocatalytic CO₂ reduction. More importantly, a peak at 2152 cm⁻¹ emerged and the intensity of the peak gradually increased with the irradiation time. This peak can be assigned to the stretching vibration of CO adsorbed on an isolated Co site. 40,41 This result further highlights the key role of the single-atomic Co sites in CO evolution. Moreover, another peak at 1685 cm⁻¹ attributed to CO₂⁻ adsorbed on Co sites was observed, the intensity of which noticeably increased after 60 min irradiation. 38,42 Therefore, it can be inferred that the CO₂-to-CO conversion on the isolated Co sites proceeds via the formation of CO2-, which is generally regarded as the ratedetermining step in CO₂ reduction. 4,43-45 The stabilization of CO₂ has a great impact on the overall performance of the photocatalytic CO2 reduction, and largely depends on the local charge density of the active sites. 46-48 In our Z-scheme heterojunction, the electrons in Co₁-C₃N₄ with a relatively high Fermi level would spontaneously migrate to α-Fe₂O₃ to eliminate the disparity between the Fermi levels,³⁴ which was verified by XPS analysis in Fig. S18† and Fig. 4c. The N 1s spectrum for Co₁-C₃N₄ can be deconvoluted into three peaks located at 398.3 eV (C-N=C), 400 eV (N-(C)₃) and 401.3 eV (C-N-H_x), respectively. 13,49 Notably, these peaks shift to higher binding energies after assembly with α-Fe₂O₃ (Table S3†). Moreover, distinguishable shifts in similar trend were also observed for Co $2p_{3/2}$ peaks (Table S3†). ^{13,50} In contrast, in terms of the binding energy of Fe, the Fe 2p peaks of the Z-scheme heterojunction downshift by 0.2 eV relative to those of pristine α -Fe₂O₃ (Fig. S19 and Table S4†).⁵¹ This result is indicative of a partial electron transfer from N and Co to Fe, confirming the electron migration direction between the two components. 52,53 Accordingly, the Co species in Co₁-C₃N₄@α-Fe₂O₃ exhibits a higher oxidation state than that in Co₁-C₃N₄. In this case, the negatively charged CO2 can be better stabilized by the electro**Paper** Green Chemistry

static interaction with the more positively charged Co sites.⁴⁵ To confirm the superiority of Co₁-C₃N₄@α-Fe₂O₃ in CO₂⁻ stabilization, the adsorption of OH- and SO₄²⁻ (as proper surrogates for CO₂⁻) was conducted. ⁵⁴⁻⁵⁶ In order to eliminate any possible disturbance, we prepared a non-heterojunction mixture comprising α-Fe₂O₃ nanorod arrays and Co₁-C₃N₄ with the assistance of Nafion solution rather than via the subsequent thermal treatment (denoted as Co_1 - C_3N_4/α - Fe_2O_3). The oxidative linear sweep voltammograms (LSV) in NaOH aqueous solution reveal that the potential of OH adsorption for Co₁-C₃N₄(a)α-Fe₂O₃ is 19 mV lower than that for Co₁-C₃N₄/ α-Fe₂O₃ (Fig. 4e). This difference becomes more prominent in the adsorption of SO_4^{2-} . As shown in Fig. 4f, a potential of 1.14 V vs. Ag/AgCl is required for the adsorption of SO_4^{2-} on Co₁-C₃N₄(a)α-Fe₂O₃, 120 mV lower than that on Co₁-C₃N₄/ α-Fe₂O₃ (1.26 V vs. Ag/AgCl). Since the lower potential implies a stronger binding of the anion, these results strongly indicate that the Z-scheme Co₁-C₃N₄@α-Fe₂O₃ can efficiently stabilize the key intermediate CO₂⁻, thereby facilitating CO evolution.

Conclusions

In summary, we have constructed a Z-scheme heterojunction of Co₁-C₃N₄@α-Fe₂O₃ comprising Co₁-C₃N₄ and α-Fe₂O₃ nanorod arrays for efficient visible-light-driven CO2 reduction coupled with water oxidation. The introduction of the Z-scheme heterojunction into a single-atomic catalyst of Co₁-C₃N₄ not only promotes the separation of the photo-induced charge carriers for benefiting CO2 reduction, but also enhances the capability of water oxidation. XPS analysis reveals that the single-atomic Co sites in Co₁-C₃N₄ become more positively charged after the formation of the heterojunction, which contributes to the efficient stabilization of CO₂ and hence facilitates the CO2 reduction, as verified by the in situ DRIFTS spectra and anion adsorption test. As a result, a CO generation rate of 14.9 µmol g⁻¹ h⁻¹ with over 99% CO selectivity is achieved under visible-light irradiation using water as an electron source. Our findings here underline the importance of the charge regulation on single-atomic sites by the Z-scheme heterojunction for enhancing catalytic performances, and offer a new approach to developing high-efficiency single-atomic site catalysts for artificial photosynthesis.

Conflicts of interest

There are no conflicts to declare.

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