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Integrating Z-scheme heterojunction of $\text{Co}_1\text{-C}_3\text{N}_4@ \alpha\text{-Fe}_2\text{O}_3$ 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 $\text{Co}_1\text{-C}_3\text{N}_4@ \alpha\text{-Fe}_2\text{O}_3$ comprising a g- C_3N_4 -supported single-atomic Co site catalyst (denoted as $\text{Co}_1\text{-C}_3\text{N}_4$) and $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays is fabricated for efficient CO_2 reduction. A CO production rate of $14.9 \mu\text{mol g}^{-1} \text{h}^{-1}$ 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 $\text{Co}_1\text{-C}_3\text{N}_4@ \alpha\text{-Fe}_2\text{O}_3$, 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 CO_2 has been contributing to the severe global warming problem and the potential energy shortage.^{1,2} Utilizing solar energy to convert CO_2 into fuels provides a promising approach to solving the above problems, and scientists have devoted tremendous attention to developing various photocatalysts for CO_2 reduction.^{3–9} Recently, graphitic carbon nitride (g- C_3N_4)-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- C_3N_4 . 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- C_3N_4 can act as effective catalytic sites for photocatalytic CO_2

reduction, leading to two different preferential products, HCOOH and CH_4 , respectively.¹⁴ With the aid of triethylamine (TEA), single-atomic Co^{2+} sites on C_3N_4 with different loadings have been successfully synthesized, and the optimized sample with a cobalt loading of $0.128 \mu\text{mol mg}^{-1}$ exhibits a CO production rate of approximately $25.5 \mu\text{mol g}^{-1} \text{h}^{-1}$ 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 CO_2 reduction by implanting single titanium oxide species on g- C_3N_4 .¹⁶ In the presence of the $\text{Co}(\text{bpy})_3\text{Cl}_2$ co-catalyst and TEOA, a CO production rate of $283.9 \mu\text{mol g}^{-1} \text{h}^{-1}$ has been achieved under visible light irradiation. These results strongly demonstrate the viability of g- C_3N_4 -supported single-atomic site catalysts for photocatalytic CO_2 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- C_3N_4 -based photocatalysts with high efficiency for CO_2 conversion using water as an electron source.

Owing to the wide band gap ($\sim 2.7 \text{ eV}$), g- C_3N_4 can only utilize a marginal portion of visible light ($\lambda < 460 \text{ nm}$).¹⁷ Moreover, the water oxidation capacity of g- C_3N_4 is poor due to the high energy level of the valence band.^{18–20} In this situation, integrating g- C_3N_4 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 $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$, which composes by single-atomic Co sites loaded on $\text{g-C}_3\text{N}_4$ ($\text{Co}_1\text{-C}_3\text{N}_4$) integrated with $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays, for efficient visible-light-driven CO_2 reduction coupled with water oxidation. The light-absorption range of $\text{Co}_1\text{-C}_3\text{N}_4$ 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 $\alpha\text{-Fe}_2\text{O}_3$. Moreover, benefiting from the charge transfer induced by the different Fermi levels between $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Co}_1\text{-C}_3\text{N}_4$, 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 CO_2^- is more efficient on the single-atomic Co sites with a higher positive charge. Compared with $\text{Co}_1\text{-C}_3\text{N}_4$, the constructed Z-scheme heterojunction shows a substantial improvement for photocatalytic CO_2 conversion to CO, with 2.8 times higher than that of $\text{Co}_1\text{-C}_3\text{N}_4$ under visible light irradiation and almost 100% CO selectivity.

Experimental

Materials

$\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (99%, AR) and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (99%, AR) were purchased from Aladdin. Urea (99%, AR), NaOH (96%, AR) and Na_2SO_4 (99%, AR) were purchased from FuChen Chemical Reagent Factory. Nafion 117 solution (~5% in alcohol/water) was purchased from Sigma-Aldrich. CO_2 (99.999%) and Ar (99.999%) were purchased from Tianjin Huanyu Gas company. $^{13}\text{C}\text{O}_2$ (99%) was purchased from Sigma-Aldrich and H_2^{18}O (99%) was purchased from Energy Chemical. All chemicals were used as received without further purification. The ultra-pure water (Milli-Q water) with an electrical resistivity of 18.2 M Ω cm was used in all experiments.

Synthetic procedures

The $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays were fabricated by a modified strategy reported previously.^{24,25} In brief, a piece of fluorine-doped tin oxide (FTO) glass (1 cm \times 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 $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (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 $^\circ\text{C}$ for 4 h. The as-prepared sample was washed with water and dried by N_2 flow to remove redundant sediment. The film was annealed at 550 $^\circ\text{C}$ for 2 h and subsequently at 660 $^\circ\text{C}$ for 20 min in a muffle furnace with a ramping rate of 2 $^\circ\text{C min}^{-1}$, and the $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays were finally obtained. The loading amount of the $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays was determined to be 0.3 mg by weighing the FTO glass before and after the synthesis.

The $\text{g-C}_3\text{N}_4$ -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 $^\circ\text{C}$ for 4 h with a ramping rate of 10 $^\circ\text{C min}^{-1}$. After cooling down naturally, the product was heated again at 500 $^\circ\text{C}$ for 2 h to obtain exfoliated $\text{g-C}_3\text{N}_4$. For the synthesis of $\text{g-C}_3\text{N}_4$ -supported single-atomic Co site catalyst ($\text{Co}_1\text{-C}_3\text{N}_4$), $\text{g-C}_3\text{N}_4$ (10 mg) was well dispersed in water (10 mL) by vigorous sonication for 30 min. Next, an aqueous solution (500 μL) containing $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.336 mM) was dropped into the $\text{g-C}_3\text{N}_4$ suspension under magnetic stirring. Subsequently, the suspension was stirred for 12 h at 80 $^\circ\text{C}$ 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 $^\circ\text{C}$ for 2 h with a ramping rate of 5 $^\circ\text{C min}^{-1}$ under Ar atmosphere. Similar procedures were applied for the synthesis of the $\text{g-C}_3\text{N}_4$ -supported CoO nanoparticle catalyst ($\text{CoNP-C}_3\text{N}_4$), except that the concentration of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ was increased to 3.36 mM.

To fabricate the Z-scheme system, a well-dispersed aqueous suspension (300 μL) of $\text{Co}_1\text{-C}_3\text{N}_4$ (1 mg mL^{-1} , 0.3 mg in total) was first drop-coated onto the $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays under 60 $^\circ\text{C}$. To strengthen the contact between $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Co}_1\text{-C}_3\text{N}_4$, the sample was transferred to a tube furnace and calcined at 200 $^\circ\text{C}$ for 2 h, with a ramping rate of 5 $^\circ\text{C min}^{-1}$ under Ar atmosphere. The obtained sample was denoted as $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$. $\text{C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ and $\text{CoNP-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ were fabricated according to the same method as that of $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$, except that $\text{Co}_1\text{-C}_3\text{N}_4$ was replaced by $\text{g-C}_3\text{N}_4$ and $\text{CoNP-C}_3\text{N}_4$, respectively.

Characterization

The powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku SmartLab 9 kW with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). 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 dark-field scanning transmission electron microscopy (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 K α (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-

luminescence (TRPL) curves were recorded using a PicoQuant 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 gas-solid 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 at the Infrared Spectroscopy and 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-C₃N₄ 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 \cdot OH

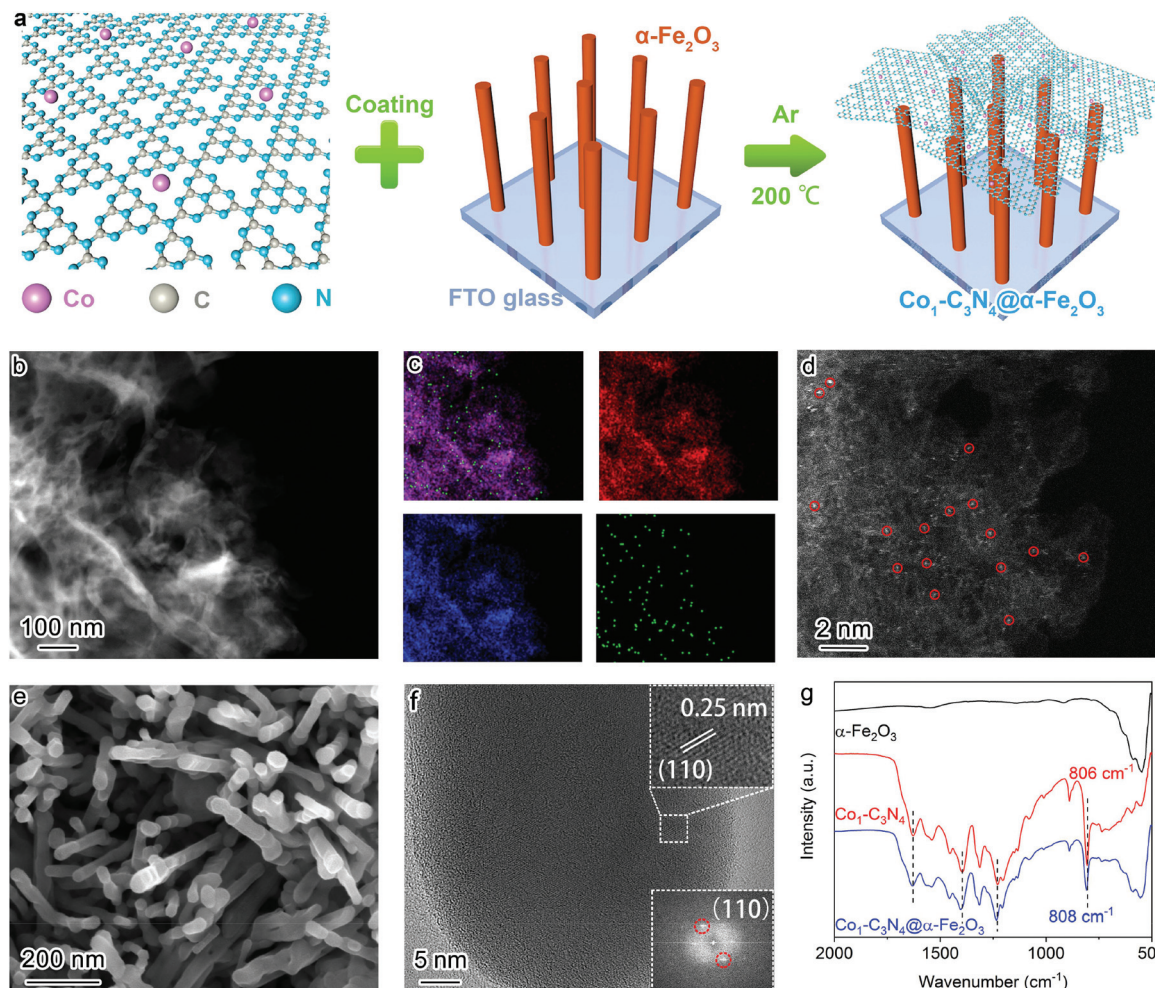


Fig. 1 (a) Schematic illustration of the fabrication strategy for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$. (b) Low-resolution HAADF-STEM image for $\text{Co}_1\text{-C}_3\text{N}_4$ and (c) the corresponding elemental mapping images of C (red), N (blue), and Co (green). (d) Atomic-resolution HAADF-STEM image for $\text{Co}_1\text{-C}_3\text{N}_4$. The atomically dispersed Co sites are marked in red circles. (e) SEM image and (f) HRTEM image for the $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays; insets: lattice fringes of a single $\alpha\text{-Fe}_2\text{O}_3$ nanorod (top) and the selected area electron diffraction (SAED) pattern (bottom). (g) Fourier-transform infrared spectra for $\alpha\text{-Fe}_2\text{O}_3$, $\text{Co}_1\text{-C}_3\text{N}_4$, and $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$.

and $\cdot\text{O}_2^-$ species with DMPO as the trapping agent (Fig. 2a and b). For pristine $\alpha\text{-Fe}_2\text{O}_3$, only a weak signal attributed to $\cdot\text{OH}$ was observed under visible-light irradiation; for pristine $\text{Co}_1\text{-C}_3\text{N}_4$, only the signal attributed to $\cdot\text{O}_2^-$ was detected with four identical peaks. These results are understandable by comparing the energy band positions with the reaction potentials of O_2/O_2^- and $\text{H}_2\text{O}/\cdot\text{OH}$ ($\text{OH}^-/\cdot\text{OH}$). When $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ was employed as the photocatalyst, the signals of both $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ were observed with much stronger intensities than that for each single component. In addition, neither of the two species was observed for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ 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 $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ validated, now we are in a position to investigate the efficacy of

the composite structure in promoting photocatalytic CO_2 reduction. Fig. 3a shows the average CO evolution rates in CO_2 overall splitting for the as-prepared catalysts under visible light ($\lambda > 400$ nm). No product was detected for $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays, as the potential of the conduction band is too positive to trigger the reduction of CO_2 . The CO production rate for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ was substantially elevated to $14.9 \mu\text{mol g}^{-1} \text{h}^{-1}$, 2.9 times as high as that for $\text{Co}_1\text{-C}_3\text{N}_4$ ($5.2 \mu\text{mol g}^{-1} \text{h}^{-1}$) and 6.5 times as that for $\text{C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ ($2.3 \mu\text{mol g}^{-1} \text{h}^{-1}$). These results imply that the construction of the Z-scheme heterojunction and the introduction of Co favor the photocatalytic reduction of CO_2 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 $25.2 \mu\text{mol g}^{-1} \text{h}^{-1}$ was achieved, demonstrating the excellent CO_2 reduction capability for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ under full spectrum. To evaluate the utilization efficiency of the solar energy, apparent quantum efficiencies (AQEs) for CO gene-

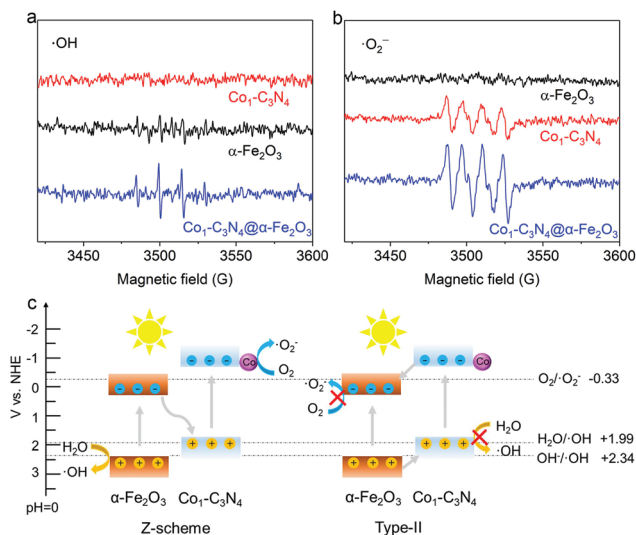


Fig. 2 (a and b) DMPO spin-trapping ESR spectra for $\alpha\text{-Fe}_2\text{O}_3$, $\text{Co}_1\text{-C}_3\text{N}_4$, and $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ under visible-light irradiation. (c) Schematic illustration for the validation of the Z-scheme mechanism rather than Type-II.

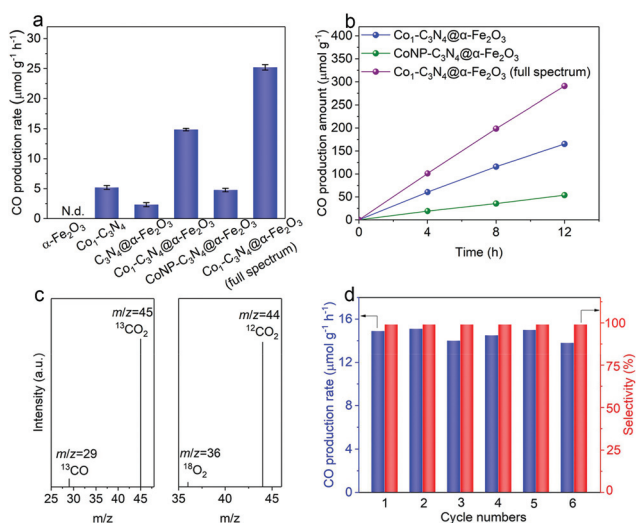


Fig. 3 (a) CO production rates of $\alpha\text{-Fe}_2\text{O}_3$, $\text{Co}_1\text{-C}_3\text{N}_4$, $\text{C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$, $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$, and $\text{CoNP-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$; N.d.: not detected. (b) Time-dependent production of CO by $\text{CoNP-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ and $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$. (c) Mass spectra of ^{13}CO ($m/z = 29$) and $^{18}\text{O}_2$ ($m/z = 36$) produced by $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ in the isotopic experiments. (d) Cycling production of CO for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ 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 H_2 nor CH_4 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 $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ here is among the top levels in comparison with other g- C_3N_4 -based

and single-atomic site catalysts in photocatalytic CO_2 coupled with water oxidation (Table S5[†]). To further examine the essentialness of the single-atomic character of Co in CO_2 reduction, $\text{CoNP-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ was employed for comparison. The result shows that the CO production rate for $\text{CoNP-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ is much lower ($4.8 \mu\text{mol g}^{-1} \text{h}^{-1}$), suggesting the critical role of single-atomic Co sites in photocatalytic CO_2 reduction. A similar irradiation test under Ar atmosphere was conducted on $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$, and no CO was detected. To further identify the origin of CO, we traced the carbon source in the reduction process using a ^{13}C isotopic label. Fig. 3c shows the mass spectrum of CO obtained with $^{13}\text{CO}_2$ 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 CO_2 . H_2^{18}O , instead of H_2^{16}O , was also adopted to verify the water oxidation half-reaction, and a clear $^{18}\text{O}_2$ 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 CO_2 reduction is coupled with water oxidation (Fig. S12[†]). As shown in Fig. 3d and S13,[†] the production rate and selectivity of CO for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ 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 CO_2 reduction? In addition to the significantly broadened light-absorption range, the dynamic behaviors of the photo-induced charge carriers are also effectively regulated. The photocurrent responses were recorded under intermittent visible-light irradiation in 0.1 M Na_2SO_4 aqueous solution (Fig. S14[†]). The photocurrent density for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ is higher than those for $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Co}_1\text{-C}_3\text{N}_4$, suggesting the more efficient photo-induced electron-hole separation for improved CO_2 reduction.³⁴ Electrochemical impedance spectroscopy (EIS) was conducted to reflect the charge transfer resistance (Fig. S15[†]). The Nyquist plots reveal that $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ has the lowest charge transfer resistance, which is beneficial for the separation and migration of the photo-induced 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 $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ 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,[†] $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ shows a significantly slower decay kinetics than $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Co}_1\text{-C}_3\text{N}_4$. 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

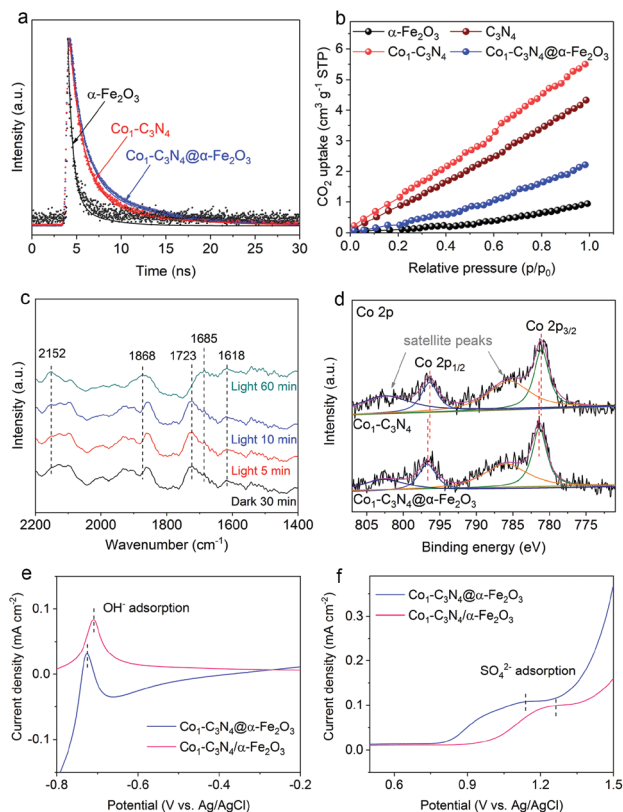


Fig. 4 (a) TRPL decay curves for α -Fe₂O₃, Co₁-C₃N₄, and Co₁-C₃N₄@ α -Fe₂O₃. (b) CO₂ adsorption isotherms for α -Fe₂O₃, g-C₃N₄, Co₁-C₃N₄, and Co₁-C₃N₄@ α -Fe₂O₃. (c) *In situ* DRIFTS spectra for Co₁-C₃N₄@ α -Fe₂O₃ under different irradiation conditions with the existence of CO₂ and H₂O. (d) X-ray photoelectron spectroscopy spectra of the Co 2p core levels for Co₁-C₃N₄ and Co₁-C₃N₄@ α -Fe₂O₃. Single oxidative LSV scans at 100 mV s⁻¹ in (e) Ar-bubbled 0.5 M NaOH and (f) Ar-bubbled 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@ 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-C₃N₄@ α -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 multi-bonded 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 rate-determining 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-

static interaction with the more positively charged Co sites.⁴⁵ To confirm the superiority of $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ in CO_2^- stabilization, the adsorption of OH^- and SO_4^{2-} (as proper surrogates for CO_2^-) was conducted.^{54–56} In order to eliminate any possible disturbance, we prepared a non-heterojunction mixture comprising $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays and $\text{Co}_1\text{-C}_3\text{N}_4$ with the assistance of Nafion solution rather than *via* the subsequent thermal treatment (denoted as $\text{Co}_1\text{-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3$). The oxidative linear sweep voltammograms (LSV) in NaOH aqueous solution reveal that the potential of OH^- adsorption for $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ is 19 mV lower than that for $\text{Co}_1\text{-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3$ (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 $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$, 120 mV lower than that on $\text{Co}_1\text{-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3$ (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 $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ can efficiently stabilize the key intermediate CO_2^- , thereby facilitating CO evolution.

Conclusions

In summary, we have constructed a Z-scheme heterojunction of $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ comprising $\text{Co}_1\text{-C}_3\text{N}_4$ and $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays for efficient visible-light-driven CO_2 reduction coupled with water oxidation. The introduction of the Z-scheme heterojunction into a single-atomic catalyst of $\text{Co}_1\text{-C}_3\text{N}_4$ not only promotes the separation of the photo-induced charge carriers for benefiting CO_2 reduction, but also enhances the capability of water oxidation. XPS analysis reveals that the single-atomic Co sites in $\text{Co}_1\text{-C}_3\text{N}_4$ become more positively charged after the formation of the heterojunction, which contributes to the efficient stabilization of CO_2^- and hence facilitates the CO_2 reduction, as verified by the *in situ* DRIFTS spectra and anion adsorption test. As a result, a CO generation rate of $14.9 \mu\text{mol g}^{-1} \text{h}^{-1}$ 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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