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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 $\text{CO}_2$ reduction†

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Photocatalytic  $\text{CO}_2$  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- $\text{C}_3\text{N}_4$ -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  $\text{CO}_2$  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  $\text{CO}_2^-$  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  $\text{CO}_2$  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  $\text{CO}_2$  has been contributing to the severe global warming problem and the potential energy shortage.<sup>1,2</sup> Utilizing solar energy to convert  $\text{CO}_2$  into fuels provides a promising approach to solving the above problems, and scientists have devoted tremendous attention to developing various photocatalysts for  $\text{CO}_2$  reduction.<sup>3–9</sup> Recently, graphitic carbon nitride (g- $\text{C}_3\text{N}_4$ )-supported single-atomic site catalysts have emerged as remarkable photocatalysts.<sup>10–13</sup> 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- $\text{C}_3\text{N}_4$ . 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- $\text{C}_3\text{N}_4$  can act as effective catalytic sites for photocatalytic  $\text{CO}_2$

reduction, leading to two different preferential products, HCOOH and  $\text{CH}_4$ , respectively.<sup>14</sup> With the aid of triethylamine (TEA), single-atomic  $\text{Co}^{2+}$  sites on  $\text{C}_3\text{N}_4$  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  $60 \text{ mW cm}^{-2}$  incident light in the presence of triethanolamine (TEOA) as a sacrificial electron donor.<sup>15</sup> Recently, we have developed an efficient photocatalyst for  $\text{CO}_2$  reduction by implanting single titanium oxide species on g- $\text{C}_3\text{N}_4$ .<sup>16</sup> 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- $\text{C}_3\text{N}_4$ -supported single-atomic site catalysts for photocatalytic  $\text{CO}_2$  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- $\text{C}_3\text{N}_4$ -based photocatalysts with high efficiency for  $\text{CO}_2$  conversion using water as an electron source.

Owing to the wide band gap ( $\sim 2.7 \text{ eV}$ ), g- $\text{C}_3\text{N}_4$  can only utilize a marginal portion of visible light ( $\lambda < 460 \text{ nm}$ ).<sup>17</sup> Moreover, the water oxidation capacity of g- $\text{C}_3\text{N}_4$  is poor due to the high energy level of the valence band.<sup>18–20</sup> In this situation, integrating g- $\text{C}_3\text{N}_4$  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.<sup>20–23</sup>

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  $\text{CO}_2$  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  $\text{CO}_2^-$  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  $\text{CO}_2$  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  $\text{Na}_2\text{SO}_4$  (99%, AR) were purchased from FuChen Chemical Reagent Factory. Nafion 117 solution (~5% in alcohol/water) was purchased from Sigma-Aldrich.  $\text{CO}_2$  (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  $\text{H}_2^{18}\text{O}$  (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 $\Omega$  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.<sup>24,25</sup> 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  $\text{N}_2$  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.<sup>26</sup> 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  $\mu\text{L}$ ) 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  $\mu\text{L}$ ) of  $\text{Co}_1\text{-C}_3\text{N}_4$  (1 mg  $\text{mL}^{-1}$ , 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 $\alpha$  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 $\alpha$  (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. CO<sub>2</sub> 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 CO<sub>2</sub> reduction.

### Photocatalytic CO<sub>2</sub> reduction measurements

Photocatalytic CO<sub>2</sub> reduction tests were conducted in a gas-solid setup. A piece of the sample was placed in a 35 mL quartz tube. High-purity CO<sub>2</sub> (99.999%) was first passed through water to carry H<sub>2</sub>O vapor and then introduced into the quartz tube. The quartz tube was purged with the CO<sub>2</sub>/H<sub>2</sub>O 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, CH<sub>4</sub>, and H<sub>2</sub>) were analysed by using a SHIMADZU GC-2014 gas chromatograph equipped with TCD and FID dual detectors. The products of the <sup>13</sup>CO<sub>2</sub> and H<sub>2</sub><sup>18</sup>O 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 Na<sub>2</sub>SO<sub>4</sub> 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<sup>-2</sup>.

### *In situ* DRIFTS characterization

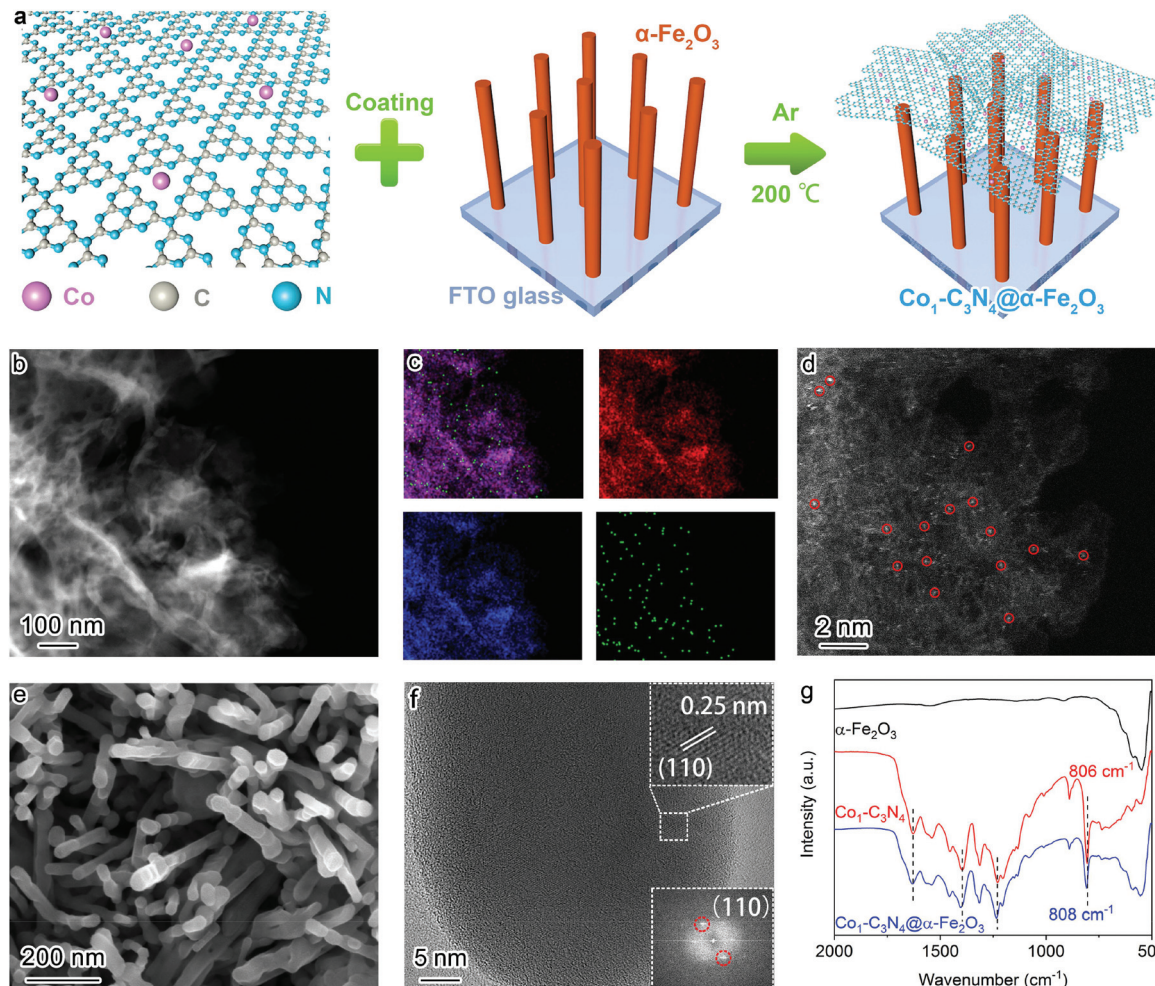
*In situ* diffuse reflectance infrared Fourier-transform spectra (DRIFTS) were recorded on a Bruker IFS 66v Fourier-transform spectrometer at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) in the National Synchrotron Radiation Laboratory (NSRL), Hefei.<sup>27</sup> The sample was 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<sup>-1</sup>. The spectrum recorded under Ar atmosphere was set as the background signal.

## Results and discussion

The composite structure comprising  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> was fabricated by a multi-step strategy (Fig. 1a). Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> 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-C<sub>3</sub>N<sub>4</sub> (Fig. 1c). The XRD pattern for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> also shows no peaks other than those corresponding to g-C<sub>3</sub>N<sub>4</sub> (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).<sup>28</sup> 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 Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>. A sample comprising CoO nanoparticles on g-C<sub>3</sub>N<sub>4</sub> was also prepared, with a Co mass loading of 0.81% (denoted as CoNP-C<sub>3</sub>N<sub>4</sub>, Fig. S4†). SEM and TEM images (Fig. 1e and Fig. S5†) show that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 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  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The top view for the composite photocatalyst clearly shows that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorod arrays are covered by highly corrugated Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> nanosheets (Fig. S6†). Fourier-transform infrared spectrum for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> shows a series of characteristic peaks of g-C<sub>3</sub>N<sub>4</sub> as those reported in the literature (Fig. 1g). Notably, the peak at 806 cm<sup>-1</sup>, which is assigned to the breathing mode of the triazine unit in carbon nitride, is blue-shifted to 808 cm<sup>-1</sup> when Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> is integrated with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorods.<sup>29</sup> Similar shifts are also found for the peaks at 1200 to 1650 cm<sup>-1</sup>, which correspond to the stretching vibration modes characteristic of aromatic g-C<sub>3</sub>N<sub>4</sub> heterocycles.<sup>30</sup> The blue shift can be attributed to the charge transfer between Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which strongly evidences the successful formation of heterojunctions.<sup>21</sup>

UV-vis diffuse reflectance spectroscopy was employed to explore the light-harvesting ability of the as-prepared photocatalysts (Fig. S7†). The absorption edge for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 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  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorod and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> 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  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorod and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>.<sup>31</sup> The flat band potentials of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> 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).<sup>31,32</sup> 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



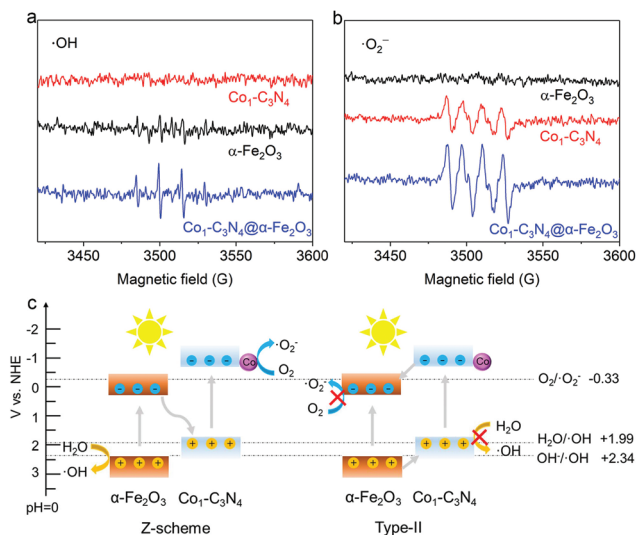


**Fig. 1** (a) Schematic illustration of the fabrication strategy for  $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ . (b) Low-resolution HAADF-STEM image for  $\text{Co}_1\text{-C}_3\text{N}_4$  and (c) the corresponding elemental mapping images of C (red), N (blue), and Co (green). (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  $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ .

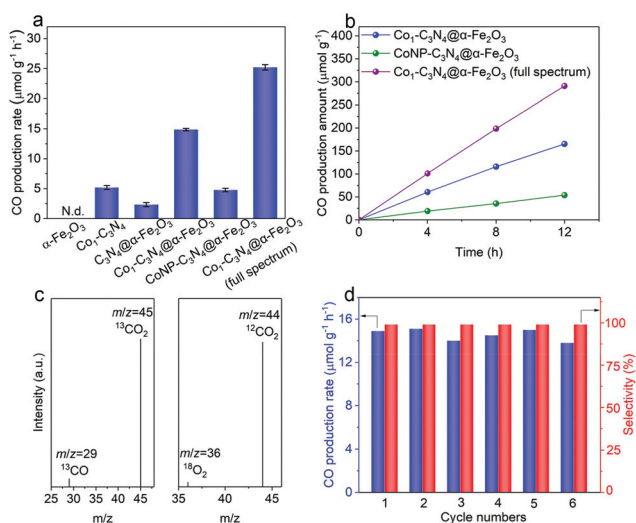
and  $\cdot\text{O}_2^-$  species with DMPO as the trapping agent (Fig. 2a and b). For pristine  $\alpha\text{-Fe}_2\text{O}_3$ , only a weak signal attributed to  $\cdot\text{OH}$  was observed under visible-light irradiation; for pristine  $\text{Co}_1\text{-C}_3\text{N}_4$ , only the signal attributed 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  $\text{O}_2/\text{O}_2^-$  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<sup>†</sup>), 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).<sup>8,33</sup>

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  $\text{CO}_2$  reduction. Fig. 3a shows the average CO evolution rates in  $\text{CO}_2$  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  $\text{CO}_2$ . 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  $\text{CO}_2$  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  $\text{CO}_2$  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.



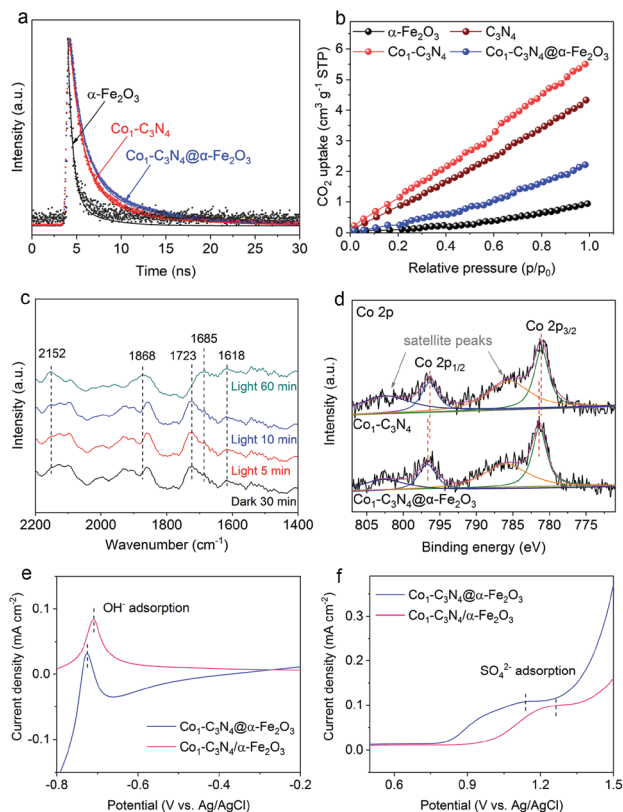
**Fig. 3** (a) CO production rates of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Co}_1\text{-C}_3\text{N}_4$ ,  $\text{C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ , and  $\text{CoNP-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$ ; N.d.: 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  $^{13}\text{CO}$  ( $m/z = 29$ ) 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  $\text{CO}_2$  reduction with pure water.

ration were determined under different monochromatic light irradiation (Fig. S11<sup>†</sup>). 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  $\text{H}_2$  nor  $\text{CH}_4$  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- $\text{C}_3\text{N}_4$ -based

and single-atomic site catalysts in photocatalytic  $\text{CO}_2$  coupled with water oxidation (Table S5<sup>†</sup>). To further examine the essentialness of the single-atomic character of Co in  $\text{CO}_2$  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  $\text{CO}_2$  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  $^{13}\text{C}$  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  $^{13}\text{CO}$  peak ( $m/z = 29$ ) was observed, indicating that the CO indeed originates from  $\text{CO}_2$ .  $\text{H}_2^{18}\text{O}$ , instead of  $\text{H}_2^{16}\text{O}$ , 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  $\text{CO}_2$  reduction is coupled with water oxidation (Fig. S12<sup>†</sup>). As shown in Fig. 3d and S13,<sup>†</sup> 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  $\text{CO}_2$  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  $\text{Na}_2\text{SO}_4$  aqueous solution (Fig. S14<sup>†</sup>). 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  $\text{CO}_2$  reduction.<sup>34</sup> Electrochemical impedance spectroscopy (EIS) was conducted to reflect the charge transfer resistance (Fig. S15<sup>†</sup>). 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.<sup>24,35</sup> To investigate the lifetime of the electron-hole pairs, we employed PL spectroscopy. As shown in Fig. S16,<sup>†</sup> 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.<sup>29</sup> 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,<sup>†</sup>  $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$  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.<sup>†</sup> The shorter lifetime  $\tau_1$  is related to the non-radiative relaxation, and the longer lifetime  $\tau_2$  is attributed to the inter-band recombination of the photo-induced excitons, which mainly contributes to the





**Fig. 4** (a) TRPL decay curves for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>, and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (b) CO<sub>2</sub> adsorption isotherms for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>, and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. (c) *In situ* DRIFTS spectra for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> under different irradiation conditions with the existence of CO<sub>2</sub> and H<sub>2</sub>O. (d) X-ray photoelectron spectroscopy spectra of the Co 2p core levels for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Single oxidative LSV scans at 100 mV s<sup>-1</sup> in (e) Ar-bubbled 0.5 M NaOH and (f) Ar-bubbled 0.1 M Na<sub>2</sub>SO<sub>4</sub> for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, respectively.

photoluminescence.<sup>21</sup> Notably, the average lifetime ( $\tau$ ) of Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 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  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can efficiently annihilate the holes in the valence band of Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>, 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 Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>, and more photo-induced holes would be preserved on the valence band of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, thus leading to superior photocatalytic performances. Furthermore, the incorporation of single-atomic Co sites also results in prolonged average lifetimes with significantly altered  $\tau_1$  and  $\tau_2$ . The atomically dispersed Co can act as effective trap sites to capture the photo-induced electrons from the conduction band of g-C<sub>3</sub>N<sub>4</sub>, thereby inhibiting the recombination of the electrons with the VB holes.<sup>36,37</sup> Therefore, for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 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 CO<sub>2</sub> reduction, CO<sub>2</sub> adsorption was employed to determine the chemisorption capacities of these catalysts. As depicted in Fig. 4b, Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> adsorbs a much larger amount of CO<sub>2</sub> than bare g-C<sub>3</sub>N<sub>4</sub>, suggesting the efficacy of the single-atomic Co sites. It is also worth pointing out that the integration of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> significantly reduces the CO<sub>2</sub> uptake, which can be attributed to the poor CO<sub>2</sub> adsorption ability of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorod arrays. To unravel the possible reaction pathway that occurs on Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, we carried out *in situ* DRIFTS measurements to explore the key intermediates in photocatalytic CO<sub>2</sub> reduction. As illustrated in Fig. 4c, the peaks at 1618 cm<sup>-1</sup>, 1723 cm<sup>-1</sup>, and 1868 cm<sup>-1</sup> can be assigned to bidentate carbonate (b-CO<sub>3</sub><sup>2-</sup>), chelating bridged carbonate (c-CO<sub>3</sub><sup>2-</sup>), and multi-bonded CO (m-CO) on the g-C<sub>3</sub>N<sub>4</sub> substrate, respectively.<sup>38,39</sup> The carbonate species are formed by the interaction of the surface O atoms of g-C<sub>3</sub>N<sub>4</sub> with adsorbed CO<sub>2</sub>.<sup>38</sup> During the 60 min irradiation, the peak intensity of b-CO<sub>3</sub><sup>2-</sup> remained unchanged, whereas the peak intensity of c-CO<sub>3</sub><sup>2-</sup> significantly decreased. Meanwhile, an obvious increase was observed in the m-CO peak. These results can be explained by the catalytic effect that c-CO<sub>3</sub><sup>2-</sup> is converted into m-CO during the photocatalytic CO<sub>2</sub> reduction. More importantly, a peak at 2152 cm<sup>-1</sup> 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.<sup>40,41</sup> This result further highlights the key role of the single-atomic Co sites in CO evolution. Moreover, another peak at 1685 cm<sup>-1</sup> attributed to CO<sub>2</sub><sup>-</sup> adsorbed on Co sites was observed, the intensity of which noticeably increased after 60 min irradiation.<sup>38,42</sup> Therefore, it can be inferred that the CO<sub>2</sub>-to-CO conversion on the isolated Co sites proceeds *via* the formation of CO<sub>2</sub><sup>-</sup>, which is generally regarded as the rate-determining step in CO<sub>2</sub> reduction.<sup>4,43-45</sup> The stabilization of CO<sub>2</sub><sup>-</sup> has a great impact on the overall performance of the photocatalytic CO<sub>2</sub> reduction, and largely depends on the local charge density of the active sites.<sup>46-48</sup> In our Z-scheme heterojunction, the electrons in Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> with a relatively high Fermi level would spontaneously migrate to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to eliminate the disparity between the Fermi levels,<sup>34</sup> which was verified by XPS analysis in Fig. S18† and Fig. 4c. The N 1s spectrum for Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub> can be deconvoluted into three peaks located at 398.3 eV (C-N=C), 400 eV (N-(C)<sub>3</sub>) and 401.3 eV (C-N-H<sub>x</sub>), respectively.<sup>13,49</sup> Notably, these peaks shift to higher binding energies after assembly with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Table S3†). Moreover, distinguishable shifts in similar trend were also observed for Co 2p<sub>3/2</sub> peaks (Table S3†).<sup>13,50</sup> 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  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fig. S19 and Table S4†).<sup>51</sup> This result is indicative of a partial electron transfer from N and Co to Fe, confirming the electron migration direction between the two components.<sup>52,53</sup> Accordingly, the Co species in Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>@ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibits a higher oxidation state than that in Co<sub>1</sub>-C<sub>3</sub>N<sub>4</sub>. In this case, the negatively charged CO<sub>2</sub><sup>-</sup> can be better stabilized by the electro-

static interaction with the more positively charged Co sites.<sup>45</sup> To confirm the superiority of  $\text{Co}_1\text{-C}_3\text{N}_4@\alpha\text{-Fe}_2\text{O}_3$  in  $\text{CO}_2^-$  stabilization, the adsorption of  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  (as proper surrogates for  $\text{CO}_2^-$ ) was conducted.<sup>54–56</sup> 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  $\text{OH}^-$  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  $\text{SO}_4^{2-}$ . As shown in Fig. 4f, a potential of 1.14 V *vs.* Ag/AgCl is required for the adsorption of  $\text{SO}_4^{2-}$  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  $\text{CO}_2^-$ , 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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2^-$  and hence facilitates the  $\text{CO}_2$  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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