Electronic Supplementary Information for

Highly dispersive and stable Fe^{3+} active sites on 2D graphitic carbon nitride nanosheets for efficient photocatalytic nitrogen fixation

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Exfoliation of g-C_3N_4 into CNNS

Colloidal suspension of CNNS was obtained by a simple alkali treatment at a reflux condition. Typically, 1 g g-C_3N_4 was dispersed into 50 mL NaOH aqueous solution (0.2 mol L^{-1}) and then heated at 100 ^oC for 12 h. After collecting the sediment by removal of the clear supernatant, it was re-dispersed into 50 mL deionized water. Centrifuging the mixture at 12,000 rpm for 5 min to remove precipitation, we obtained CNNS colloidal suspension. In addition, the solid residue could be further dispersed into water, and finally all of solids were dispersed to form CNNS suspension by repeated water washing.

Examination of the ammonia concentration using the Nessler's reagent spectrophotometry method

The collected solution (0.800 mL) in the photocatalytic process was diluted to 4.000 mL with deionized water, and then was followed with the addition of 150 μL Nessler reagent. After 10 min, the mixed solution was measured to obtain the absorbance at 420 nm by spectrophotometer, and the ammonia concentration was calculated according to the standard curve.

Examination of the ammonia concentration using the indophenol blue method

Typically, 2 mL of a sample solution was mixed with 2 mL of 1 M NaOH solution (containing 5 wt% salicylic acid). Then 1 mL 5 wt% sodium citrate was added followed by 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt.% $C_5FeN_6Na_2O$ (sodium nitroferricyanide) aqueous solution. After 2 h of incubation at room temperature, the absorption spectrum was measured

using UV–vis spectroscopy. The formation of indophenol blue was determined based on the absorbance at a wavelength of 655 nm. The value was related to the concentration by the concentration-absorbance curves which were calibrated using standard ammonium chloride solutions.

Measurements of hydrazine and nitrate species concentrations

The hydrazine presented was estimated by the method of Watt and Chrisp.[1] A mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. 5 mL of the treated products was removed from the reaction vessel. Then, 5 mL of above prepared color reagent was added to the solution and stirred for 10 min at room temperature. The absorbance of the resulting solution was measured at a wavelength of 455 nm. The concentration-absorbance curves were calibrated using standard hydrazine monohydrate solution with a series of concentrations.

And, the nitrate species (NO_x) was determined using N-(-1-naphthyl)-ethylenediamine dihydrochloride spectrophotometric method.[2] Detailedly, 0.5 g sulfanilic acid was dissolved in 90 mL H_2O and 5 mL acetic acid. Then, 5mg n-(1-naphthyl)-ethylenediamine dihydrochloride was added and the solution was filled to 100 mL to obtain chromogenic agent. 1 mL of the treated products was mixed with 4mL chromogenic agent and left in darkness for 15 min. The UV-Vis absorption spectrum was then measured at 540 nm. The concentration-absorbance curves were calibrated using standard sodium nitrite solution with a series of concentrations.

Characterized by the above methods, the generation of hydrazine hydrate is about 267 μmol L^{-1} h^{-1} g^{-1} and nitrate species is nearly 7 μmol L^{-1} h^{-1} g^{-1}, and the UV-vis absorption spectra of products and the standard curves of the above methods are shown in Figure S6.

[1] Q. Wang, L. Yu, Y. Liu, L. Lin, R. Lu, J. Zhu, L. He and Z. Lu. Talanta, 2017, 165, 709-720.

[2] G. W. Watt and J. D. Chrisp. Anal. Chem. 1952, 24, 2006-2008.

The calculation of apparent quantum efficiency

The apparent quantum efficiency (AQE) of the NH_4^+ production using 420 nm (±5 nm) band-pass filter is calculated as follows:

$$AQE = \frac{N_e}{N_p} = \frac{3N_{NH_4^+}}{N_p} = \frac{3n_{NH_4^+} \cdot N_A}{\frac{W \cdot A \cdot t}{h \cdot v}} \times 100\% = \frac{3 \cdot 1941.31 \times 10^{-6} \times 50 \times 1}{\frac{14 \cdot 3.847 \times}{6.626 \times 10}} \times 100\% = 0.86\%$$

where Ne, Np and N_{NH4^+} represent the number of reacted electrons, incident photons and generated NH_4^+, respectively; n_{NH4^+} represents the molar number of generated NH_4^+; ν, W, A and t are the incident light frequency, intensity, irradiation area and time, respectively; N_A and h are the Avogadro's constant and Planck constant, respectively.

The calculation of Ammonia selectivity (S_{NH4^+})

$$S_{NH_4^+} = \frac{N_{NH_4^+}}{N_r} = \frac{N_{NH_4^+}}{N_{NH_4^+} + N_{H_2}} = \frac{3 \cdot n_{NH_4^+} \cdot N_A}{(3 \cdot n_{NH_4^+} + 2 \cdot n_{H_2}) \cdot N_A} \cdot 100\% = \frac{}{(3 \cdot 50} \cdot 100\% = 78.13\%$$

where Nr, N_{NH4^+} and N_{H2} represent the number of all reacted electrons, the electrons for nitrogen fixation and the electrons for hydrogen production, respectively; n_{NH4^+} represents the molar number of generated NH_4^+; n_{H2} represents the molar number of generated H_2; N_A is the Avogadro's constant.

Titration of carbonate ions

The concentration of carbonate ions after the reaction is measured by acid-base titration. 0.28 mL of H_2SO_4 was added to 100 mL of deionized water, calibrated with a standard sodium carbonate solution, diluted 100 times and used as a titrant (about 1 mM). 1 g of

phenolphthalein was dissolved in a 50% water-ethanol solution (100 mL) as an indicator. Take 25.00 mL of the product solution, add 2 drops of the indicator, the solution turns red. And add the titrant until the red color disappears. The concentration of carbonate ions is calculated to be 0.31 mmol L^{-1} by the amount of titrant. And the balance coefficient of electron/hole can be calculated as follows:

$$balance\ coefficient = \frac{n_{electron}}{n_{hole}} = \frac{3c_{NH_4^+} + 2c_{H_2}}{4c_{CO_3^{2-}}} = \frac{3 \cdot 296\ \mu mol\ L^{-1} + 2 \cdot 127\ \mu mol\ L^{-1}}{4 \cdot 310\ \mu mol\ L^{-1}} = 0.92$$

where $n_{electron}$ and n_{hole} represent the number of reacted electrons and holes, respectively; c_{NH4^+}, c_{H2} and $c_{CO3^{2-}}$ represent the concentration of acquired NH_4^+, H_2 and CO_3^{2-}, respectively.

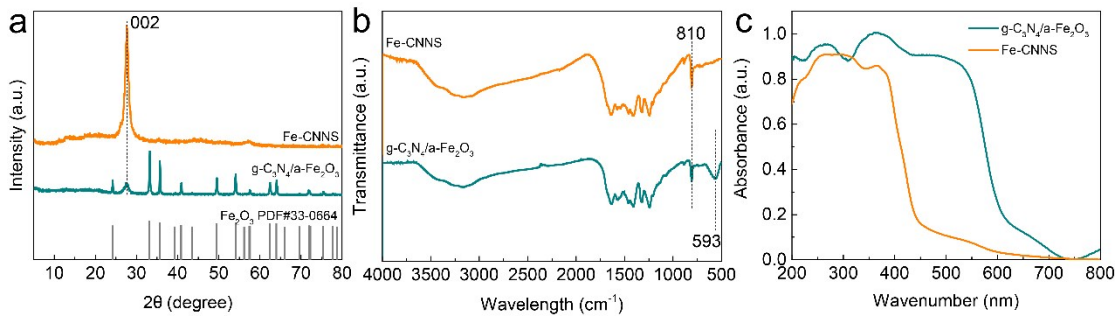

Figure S1. Characterization results of Fe-CNNS and g-C_3N_4/α-Fe_2O_3.

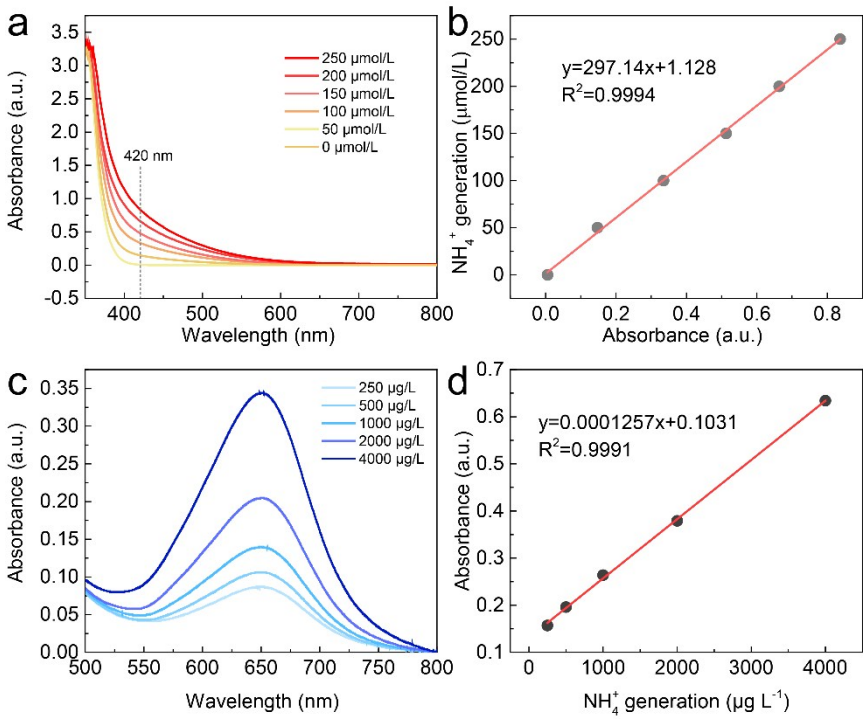

Figure S2. UV-vis absorption spectra and the standard curves using the Nessler's reagent spectrophotometry method (a,b) and the indophenol blue method (c,d).

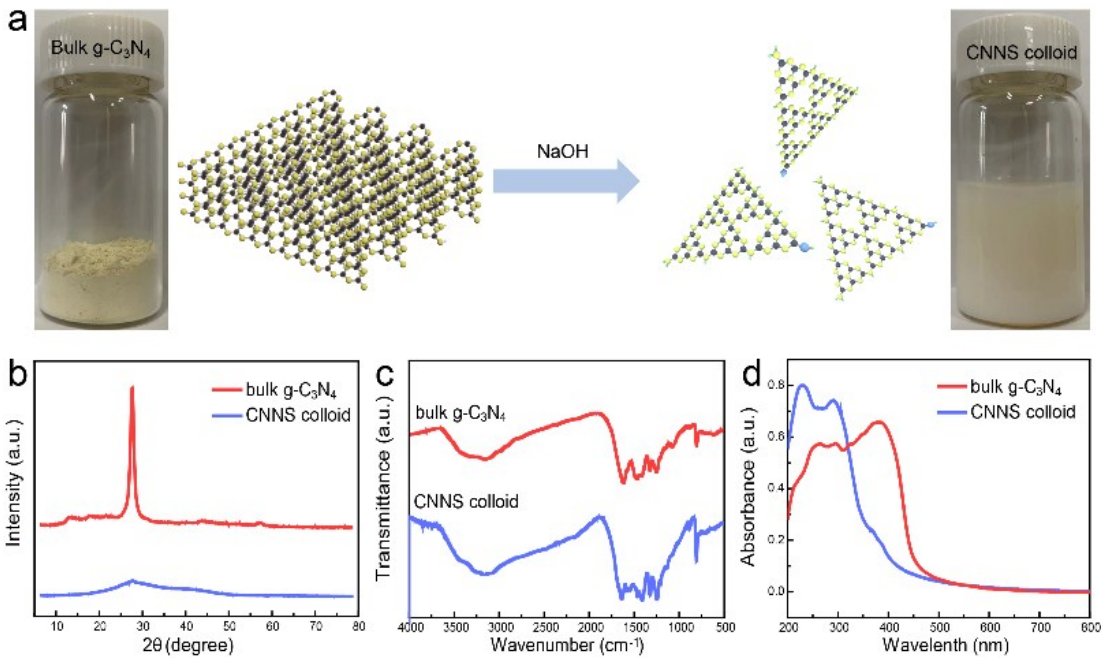

Figure S3. Characterization results of the obtained CNNS.

Figure S3a is the schematic illustration for formation of CNNS colloid from g-C_3N_4 by the alkali treatment. Figure S3b are XRD patterns of bulk g-C_3N_4 and CNNS colloid samples. The weakening interlayer diffraction of CNNS colloid at $2\theta \approx 27.7^{o}$ demonstrates that the ordered stacking of CN layers is broken. It is a good evidence to indicate the exfoliation of layered structures. As illustrated in Figure S3c, the FT-IR spectrum of g-C_3N_4 presents

multiple bands at 1200~1600 cm^{-1} and an intense peak at 810 cm^{-1}, which are related to the stretching vibrations of conjugated CN rings and the breathing mode of s-triazine, respectively. The well preservation of these absorptions suggests that the inplanar structure of CN layer was not destroyed by the alkali exfoliation process. The yellow bulky g-C_3N_4 shows absorption prolonging to visible light region. After exfoliation into nanosheets, the colloidal suspension of CNNS depicts a gigantic blue-shift of absorption edge. It should be attributed to the quantum confinement effect from ultrathin thickness of CNNS.

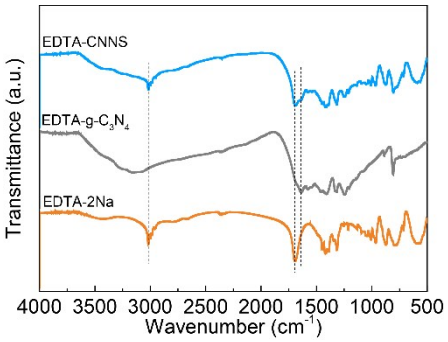

Figure S4. FTIR spectra of EDTA-CNNS, EDTA-g-C_3N_4 and EDTA-2Na.

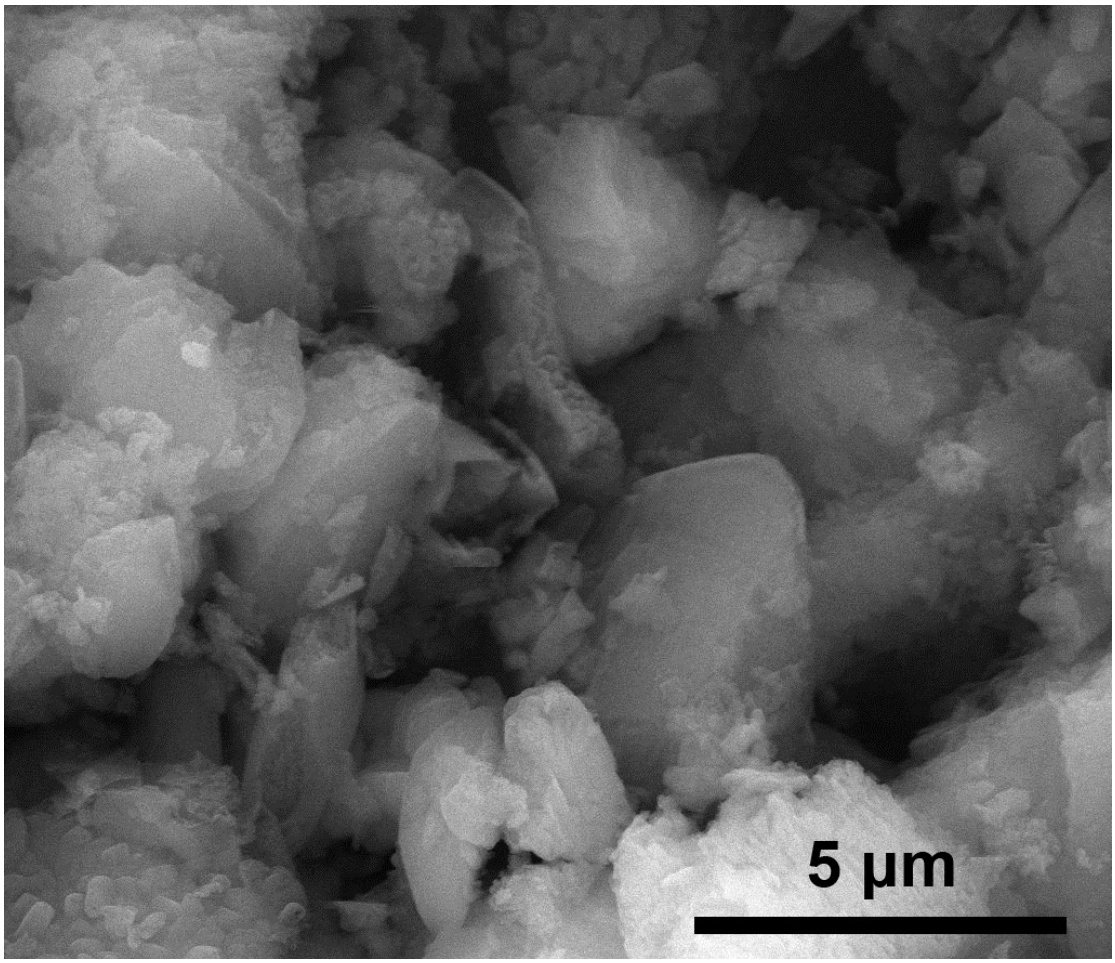

Figure S5. SEM images of bulk g-C_3N_4.

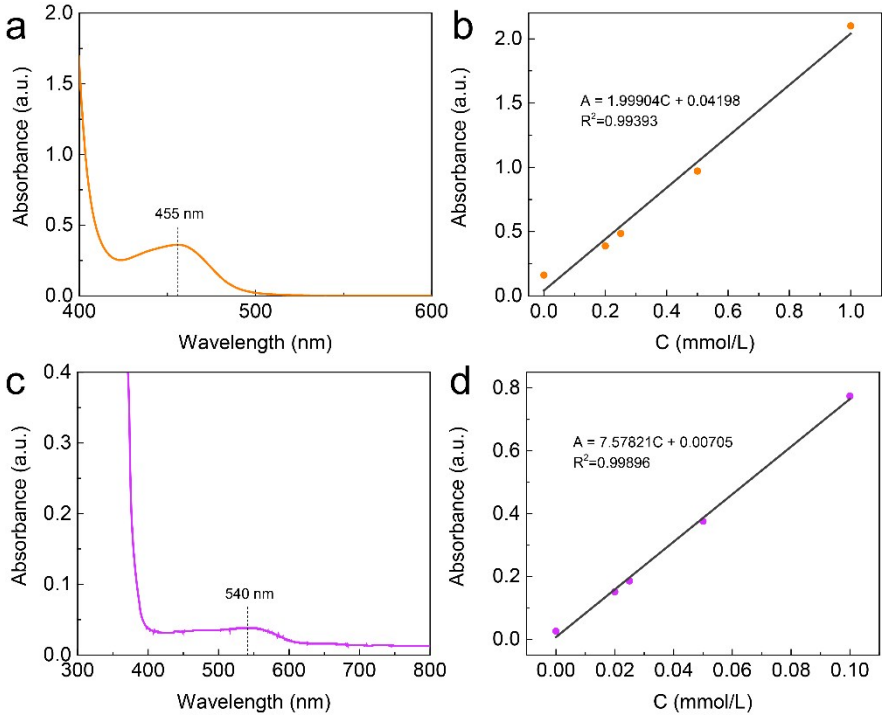

Figure S6. UV-vis absorption spectra of products and the standard curves using the method of Watt and Chrisp (a,b) and N-(-1-naphthyl)-ethylenediamine dihydrochloride spectrophotometric method (c,d).

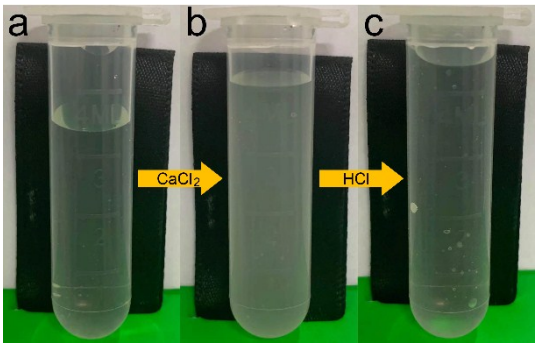

Figure S7. Identification of carbonate in the products.

Table S1. The ICP-OES result of Fe-EDTA-CNNS.

Sample	Test element	Sampling quality (g)	Constant volume (mL)	Dilution factor	Instrument display (mg/L)	Content (wt.%)
Fe-EDTA -CNNS	Fe	0.0953	50	10	4.60289	7.23
	Na	0.0953	50	1	0.176247	0.03

Table S2. The absorptions in the FTIR spectrum of the pure EDTA-2Na.

Bond	Vibration types	Wavenumber（cm^{-1}）
O-H	δ	~3400
	V	~1300
		950-900
$-CH_2-$	δ	~3000
	V	1010-650
C=O (from carboxyl)	δ	~1690
C-O	δ	1440-1390
C-N	δ	1230-1030
C-C	δ	1250-960
	V	1490-1350
Na-O	δ	~590

Table S3. The apparent quantum efficiency of state-of-the-art samples.

Photocatalyst	AQE (%)	Wavelength (nm)	Ref.
Fe-EDTA-CNNS	0.86	420	This work
A-SmOCl	0.32	420	1
Au/P25	0.62	550	2
Au/TiO_2-OV	0.82	550	3
Mo-doped $W_{18}O_{49}$	0.33	400	4
m-PCN-V	0.10	500	5
BiOBr-(001)	0.23	440	6

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