

Supporting Information

Fe₃O₄ nanostructure films as solar-thermal conversion materials for ammonia synthesis

Rong Fu,^{*a,b} Di Lei,^a Zhenlu Li,^b Hangjian Zhang,^b Xiaofei Zhao,^c Shuo Tao^a

^a School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng 252059, P. R. China

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China

^c School of Physics and Electronics, Shandong Normal University
Jinan 250014, P. R. China

*Correspondence to: furong1225@163.com

Experimental details

1. Chemicals

316L stainless steel sheets (2.5 cm × 5.5 cm × 0.35 mm) were produced by Japan Iron and Steel. NaOH were obtained from Alfa Aesar. Anhydrous ethanol (AR grade) and acetone were purchased from Sinopharm Chemical Reagent Co, Ltd. All chemicals were used without further purification. The nitrogen and hydrogen feed gas were purified by utilizing H₂SO₄ and H₂O as adsorbent throughout the whole process to eliminate the interference from nitrogen-containing impurity.

2. Preparation of HFO

316L stainless steel sheets were respectively wipes three times with ethanol, acetone and distilled water. Typically, the cleaned sheet was put into the Teflon-lined stainless steel autoclave with 100 mL of NaOH aqueous solution (12 M), followed by heating at 393 K for 8 h under the autogenous pressure. Deep black coatings were washed with anhydrous ethanol and distilled water for several times and dried in the air. The as-prepared Fe₃O₄ was tiled on the surface of a quartz boat and then the quartz boat was placed in a tube furnace and heated at a ramp of 2 °C/min and kept at 200 °C for 2h in a 5% H₂/Ar, obtained HFO.

3. Preparation of OFO

The as-prepared Fe₃O₄ was tiled on the surface of a quartz boat and then the quartz boat was placed in a muffle and heated at a ramp of 2 °C/min and kept at 450 °C for 4 h, obtained OFO.

4. Photo-driven ammonia synthesis

The as-prepared catalyst (Fe₃O₄ film) was placed in the bottom of a quartz reactor in a vacuum ($P < 0.1$ Pa), followed by the activation at 453 K. After cooling to room temperature, a mixture of nitrogen (150 μmol, 0.05 atm) and hydrogen gases (450 μmol, 0.15 atm) was introduced into the quartz reactor. The whole photocatalytic tests were conducted by using a 300 W Xenon lamp with the different cutoff filters. The nitrogen, hydrogen and oxygen were identified by gas chromatography. NH₃ product was

detected by using a colorimetric method or ion chromatography (IC, ICS-5000+, CS17, Dionex). After the reaction, the deionized water (2 mL) was injected into the quartz reactor to adequately dissolve the formed ammonia (gas phase) after the reaction and held for 30 minutes until the ammonia is completely dissolved. Then, 80 μ L of an aqueous solution of EDTA tetrasodium salt hydrate (1.3 M) was added to 1.5 mL of deionized water dissolving the ammonia, 160 μ L of the mixture of sodium salicylate (1.46 M) and pyrazole (0.24 M) and 520 μ L of the mixture of sodium hydroxide (1.25 M) and sodium hypochlorite (0.25 M) were added into the above aqueous, respectively. At some time, the solution is finally green with absorption at 650 nm measured by UV/vis spectrometer. 0.5 mL of the deionized water dissolved ammonia was injected the ion chromatography with the absorbance peak of 3.8 min.

5. Characterization methods

The power X-ray diffraction (XRD) spectrums of the material were executed on a Rigaku D/Max 2500/PV X-ray diffractometer with monochromator Cu $K\alpha$ radiation ($\lambda=0.15418\text{nm}$) from 25° to 70° with the scanning rate of $6^\circ/\text{min}$. The morphologies and EDX of the obtained samples were identified by using field emission scanning electron microscopy (SEM) on a Tecnai F20 electron microscope. Transmission electron microscope (TEM) was performed by using a Tecnai G2S-Twin F20 with 200 kV accelerating voltage of electron beam. X-ray photoelectron spectroscopy (XPS) and XPS valence band were recorded with a Thermo ESCALAB 250 analyzer operating at the constant analyze energy mode and using monochromatic Al $K\alpha$ radiation. The properties of the solar selective absorber films in the wavelength range of $0.2\ \mu\text{m}$ - $2.0\ \mu\text{m}$ were performed by a Lambda 950 UV/vis/NIR double beam spectrophotometer equipped with an integrating sphere from Perkin-Elmer company. The solar absorptance (α) and the normal thermal emittance (ϵ) are calculated by the following formula:

$$\alpha = \frac{\int_{0.3}^{2.5} S(\lambda)(1 - R(\lambda))d(\lambda)}{\int_{0.3}^{2.5} S(\lambda)d\lambda} \quad (1)$$

(2)

$$\varepsilon = \frac{\int_{2.5}^{20} r(\lambda, T)(1 - R(\lambda))d(\lambda)}{\int_{2.5}^{20} r(\lambda, T)d\lambda}$$

Supporting Figures

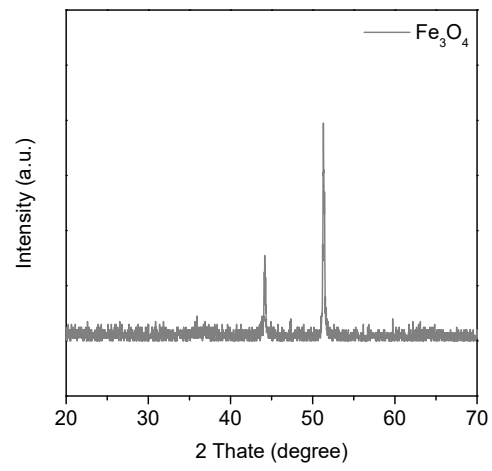


Figure S1 The XRD pattern of FO.

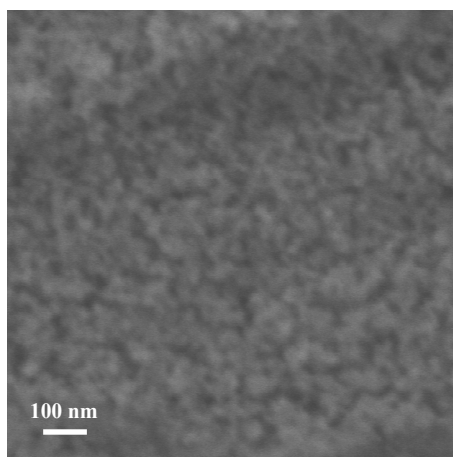


Figure S2 SEM image of FO.

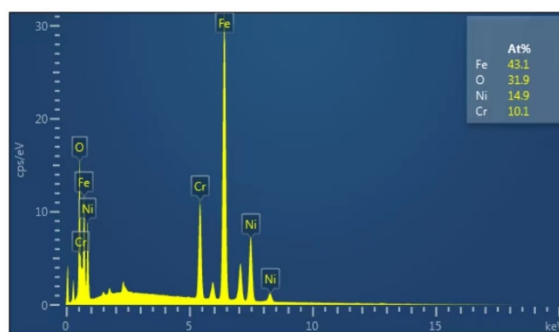


Figure S3 Energy-dispersive X-ray spectroscopy of HFO.

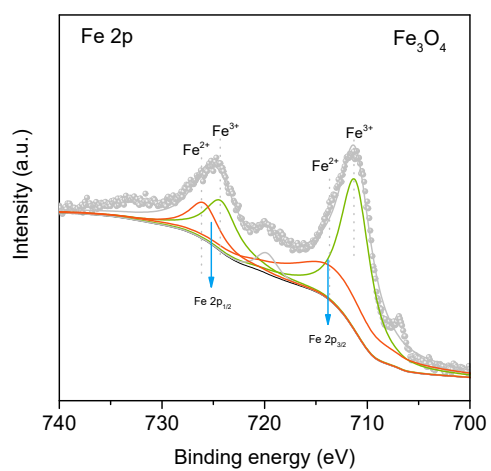


Figure S4 XPS spectra of Fe 2p peaks for FO.

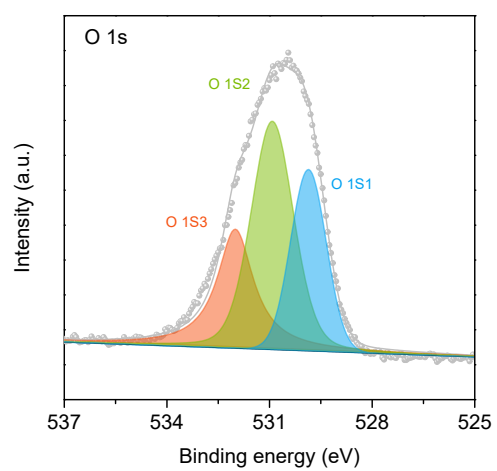


Figure S5 XPS spectra of O 1s peaks for FO.

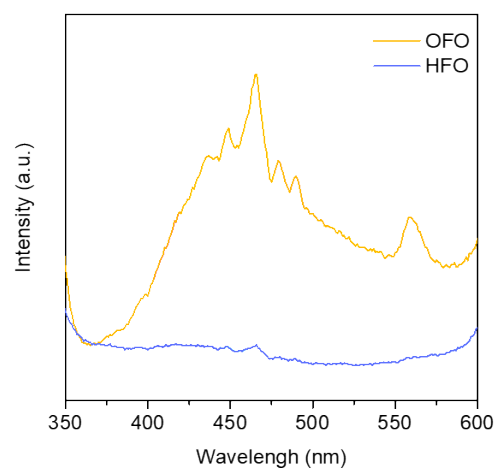


Figure S6 PL of OFO and HFO.

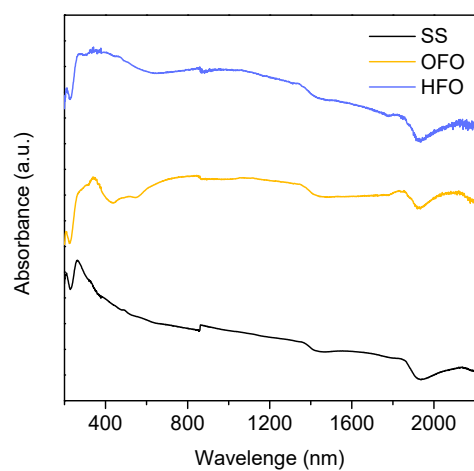


Figure S7 UV-VIS absorbance spectra of SS, OFO and HFO.

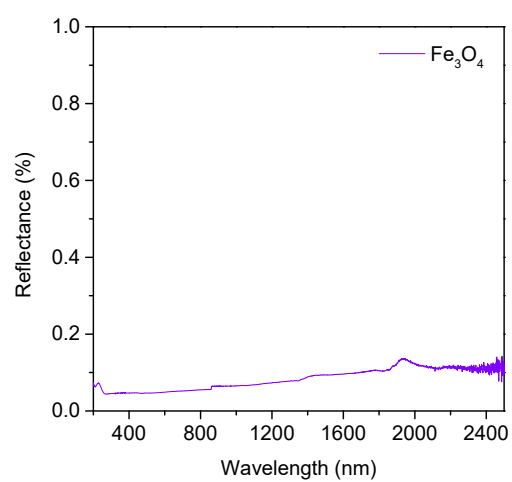


Figure S8 UV-vis reflectance spectra of FO.

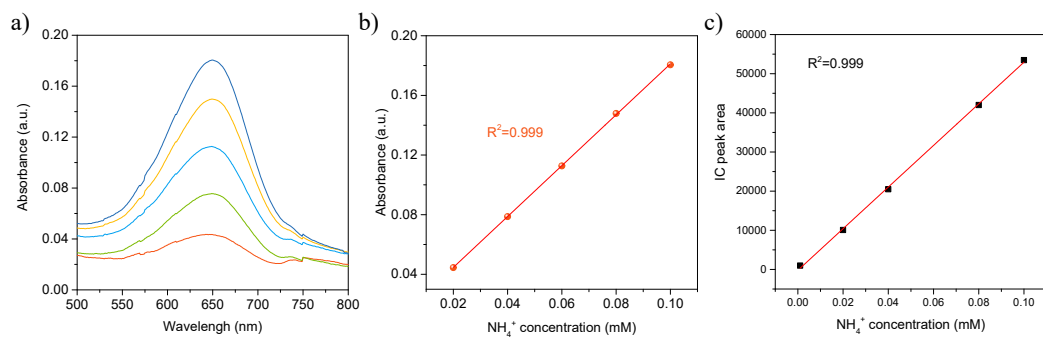


Figure S9 a) UV-vis spectroscopy data for the quantitative determination of NH_3 at maximum absorbance peak of 650 nm; b) Standard ammonia curve by colorimetric method; c) Standard ammonia curve by ion chromatography.

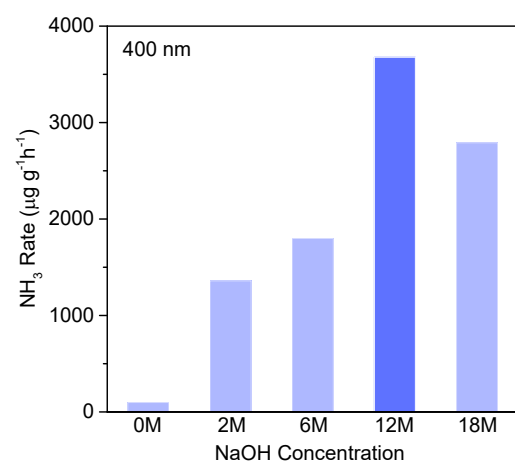


Figure S10 NH_3 rate of HFO with various NaOH concentration.

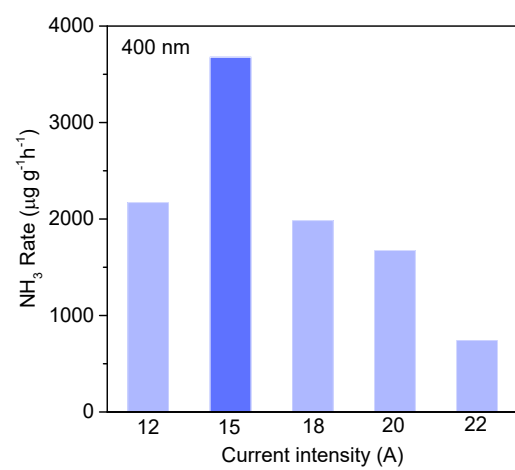


Figure S11 NH_3 rate of HFO with various current intensity.

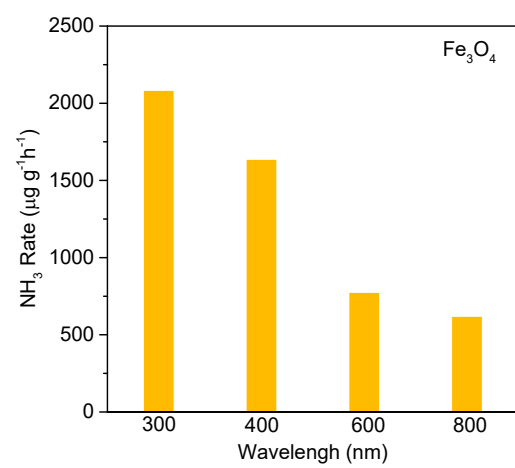


Figure S12 Wavelength dependence of the ammonia synthesis rate for FO.

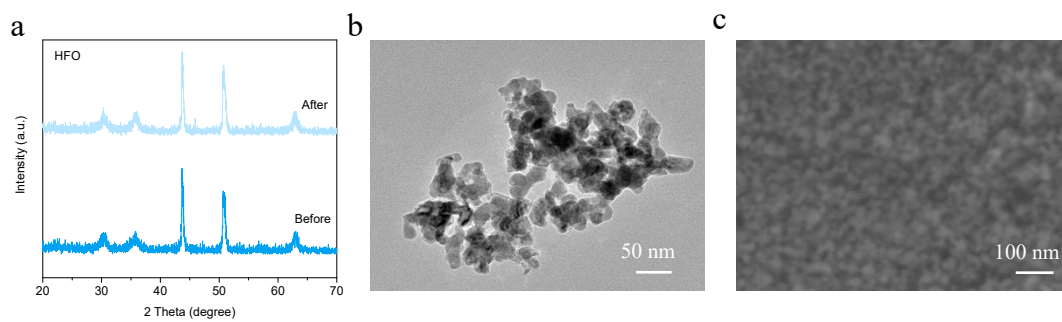


Figure S13 Sample characterizations of HFO film after six cyclic tests for photocatalytic N₂ fixation: (a) XRD pattern; (b) TEM image; (c) SEM image.

In the associative mechanism of photocatalytic N₂ reduction, a continuous N₂ photoreductive protonation process is indispensable. Specifically:

- (1) $3\text{H}_2^* + 6h^+ \rightarrow 6\text{H}^+$
- (2) $\text{N}_2^* + e^- + \text{H}^+ \rightarrow \text{N}_2\text{H}^*$
- (3) $\text{N}_2\text{H}^* + e^- + \text{H}^+ \rightarrow \text{NNH}_2^*$
- (4) $\text{NNH}_2^* + e^- + \text{H}^+ \rightarrow \text{N}^* + \text{NH}_3$
- (5) $\text{N}^* + e^- + \text{H}^+ \rightarrow \text{NH}^*$
- (6) $\text{NH}^* + e^- + \text{H}^+ \rightarrow \text{NH}_2^*$
- (7) $\text{NH}_2^* + e^- + \text{H}^+ \rightarrow \text{NH}_3$

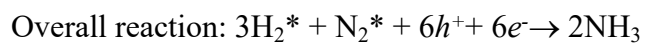


Figure S14 Schematic diagram of the photocatalytic mechanism.

Table S1. The peaks parameters of O 1s for FO, OFO and HFO.

Sample	Name	BE (eV)	Area	O_V/O_L+O_V
FO	O-Lattice	530.3	64598	44.7%
	O-Vacancy	531.9	63236	
	O Surface adsorbed	532.8	12095	
OFO	O-Lattice	530.3	63014	39.1%
	O-Vacancy	531.9	53994	
	O Surface adsorbed	532.8	20065	
HFO	O-Lattice	530.3	33854	49.9%
	O-Vacancy	531.9	55965	
	O Surface adsorbed	532.8	34081	
	O Surface adsorbed			

Table S2. Representative works on photocatalytic nitrogen fixation.

Catalysts	Conditions	Temperature (K)	NH ₃ rate ($\mu\text{g g}^{-1} \text{h}^{-1}$)	Ref.
Defect-TiO ₂	$\lambda \geq 280 \text{ nm}$	313	12.41	S1
7Fe@AC	UV light ($\lambda < 400 \text{ nm}$)	473	408	S2
Fe-Al@graphene	UV light ($\lambda < 400 \text{ nm}$)	473	430.1	S3
K/Ru/TiO _{2-x} H _x	300 W Xe lamp	633	1914	S4
Ru@K ₂ Ta ₂ O _{6-x}	Visible light (400-800 nm)	453	1735	S5
Ni/TiO ₂	Visible light	673	55.7	S6
TiO _{2-x} H _y /Fe hybrid	Visible light	768	7.74	S7
OFO	Visible light (400-800 nm)	≥ 623	460	<i>This work</i>
HFO	Visible light (400-800 nm)	≥ 623	3677	<i>This work</i>

References

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