# NiFeB hydroxides assisted adsorption and activation of nitrogen to improve the photooxidation activity of zinc porphyrin

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## Experimental

## Reagents and materials

Zinc chloride(Macklin), nickel chloride hexahydrate(Macklin), ferric chloride hexahydrate(Sinopharm), tetrakis(4-carboxyphenyl)-porphyrin (TCPP) (Macklin), sodium borohydride(Sinopharm), potassium hydroxide (Sinopharm), polyvinylpyrrolidone(PVP) (Sinopharm), N, N-dimethylformamide (DMF) (Sinopharm), absolute ethyl alcohol(Sinopharm). All chemicals are of analytical grade and used without further purification. Distilled water was used in all experiments.

# Synthesis of material

#### Synthesis of NiFeB hydroxide nanosheets

NiFeB hydroxide nanosheets were synthesized according to the literature method. <sup>1</sup> In a typical synthesis, 727  $\mu$ L of 0.14 M NiCl<sub>2</sub> • 6H<sub>2</sub>O and 673  $\mu$ L of 0.05 M FeCl<sub>3</sub> • 6H<sub>2</sub>O were dissolved in 10 mL of ethanol. After ultrasonic treatment for 5 min, 1mL of 0.5 M NaBH<sub>4</sub> was added dropwise to the above solution—ultrasonic treatment of mixed solution for 45 min. The solid product (NiFeB alloy nanoparticles) is obtained by centrifugal washing with ethanol and drying. Then, the solid product was added to 50 mL KOH (1 M in H<sub>2</sub>O) for ultrasonic treatment and centrifugal drying to collect NiFeB hydroxide nanosheets. In addition to this, NiFe hydroxide was prepared without the addition of NaBH<sub>4</sub>.

# Synthesis of ZnTCPP

Zinc nitrate (45 mg, 0.15 mmol), pyrazine (8 mg, 0.1 mmol), and PVP (600 mg) in 60 mL of the mixture of DMF and ethanol (V: V=3:1). Then TCPP (40 mg, 0.05 mmol) in 20 mL of the mixture of DMF and ethanol (V: V=3:1) were added drop wise under stirring.<sup>2</sup> Later, the solution was sonicated for 10 min. The vial was heated to 80 °C and kept the reaction for 16 h. After cooling to room temperature, the resulting purple nanosheets were washed five times with ethanol and collected by centrifuging at 9,000 r.p.m. for 10 min. Finally, the ZnTCPP nanosheets dried at 60°C.

## Synthesis of ZT-NFB composites

Zinc nitrate (45 mg, 0.15 mmol), pyrazine (8 mg, 0.1 mmol), and PVP (600 mg) in 60 mL of the mixture of DMF and ethanol (V: V=3:1). Then TCPP (40 mg, 0.05 mmol) in 20 mL of the

mixture of DMF and ethanol (V: V=3:1) were add drop wisely under stirring. Different volumes of 0.002 g/mL of NiFeB-hydroxide solution were added separately. After that, the solution was sonicated for 10 min. The vial was heated to 80°C and kept the reaction for 16 h. After cooling to room temperature, the resulting purple nanosheets were washed five times with ethanol and collected by centrifuging at 9,000 r.p.m. for 10 min. Finally, the samples dried at 60°C. The volumes of NiFeB-hydroxide solution measured in the composites were 100  $\mu$ L, 200  $\mu$ L, and 400  $\mu$ L, and the corresponding samples were labeled as ZT-NFB-0.5%, ZT-NFB-1%, and ZT-NFB-2%, respectively.

#### Photocatalytic N<sub>2</sub> Fixation Measurement

The gas-liquid reaction system was used to carry out a photocatalytic nitrogen fixation experiment. First, 10 mg of catalyst was ultrasonically dispersed in 60 mL ultrapure water in a 100 mL Shi Ying three-necked flask. Then, simulated air ( $N_2:O_2=3:1$ ) was introduced into the three-neck flask and purged for 30 min to remove air. Using a 300W Xe arc lamp as a light source, the experiment of photocatalytic nitrogen oxidation was carried out for 3 h. Finally, 10 mL solution was extracted from the reactor, filtered with 0.2 µm water-based ultrafiltration membrane, and introduced into ion chromatography (Thermo Fisher Scientific DIONEX AQUION ICS-600) to detect the concentration of  $NO_3$ <sup>-</sup>.

#### **Characterization**

The morphology of the samples was characterized by field emission scanning electron microscopy (FESEM) on a JSM-7500 electron microscope (JEOL, Japan) operating at an accelerating voltage of 15 kV. Morphological observation was further visualized by transmission electron microscopy (TEM) on a Tecnai G<sup>2</sup> F20 S-TWIN microscope with a field emission gun at a 200 kV accelerating voltage. The crystalline phases of the obtained samples were recorded on X-ray diffraction (XRD) by an X-ray diffractometer (Rigaku, Japan) using Cu K<sub>a</sub> radiation ( $\lambda = 0.15418$  nm) at a scan rate (20) of 0.05° s<sup>-1</sup>. The samples' Fourier transform infrared (FT-IR) spectra were recorded using a Tensor27 (Bruker) spectrometer. To measure the IR spectra, the samples were mixed with KBr and pressed into tablets for analysis. X-ray photoelectron spectroscopy (XPS) measurements were operated by an ultrahigh-vacuum VG channel detector. The spectra were excited using Al Ka (1486.7 eV) radiation (operated at 300 W) of a twin anode in the constant a

analyzer energy mode with an energy of 30 eV. The Brunauer-Emmett-Teller (BET) surface area was carried by Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All the samples were degassed at 150°C before nitrogen adsorption measurements. The BET-specific surface area was tested by a multipoint BET method using the adsorption data in the relative pressure (P/P<sub>0</sub>) range of 0.05-0.25. The pore size distributions were measured utilizing desorption data by the Barrett-Joyner-Halenda (BJH) method. The pore volume and average pore size were determined by the nitrogen adsorption volume at the relative pressure (P/P<sub>0</sub>) of 0.972. UV-vis diffuse reflectance spectra (DRS) were investigated by a UV-vis spectrophotometer (UV-2600, Shimadzu, Japan) using BaSO<sub>4</sub> powder as a reference standard. XPS was performed on a Thermo ESCALAB 250Xi instrument with Al K $\alpha$  X-ray radiation. The spectra were excited using Al K $\alpha$  (1486.7 eV) radiation (operated at 300 W) of a twin anode in the constant analyzer energy mode with an energy of 30 eV.

#### Theoretical simulation: Computational details:

DFT calculations were conducted through the Vienna ab initio Simulation Package (VASP) with the projector-augmented wave method.<sup>3,4</sup> Generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) functional was used as the exchange-correlation functional.<sup>5</sup> The cutoff energy was set as 500 eV, and structure relaxation was performed until the convergence criteria of energy and force reached  $1 \times 10^{-4}$  eV and 0.03 eV Å<sup>-1</sup>, respectively. A vacuum layer of 15 Å was constructed to eliminate interactions between periodic structures of surface models. The van der Waals (vdW) interaction was amended by the zero damping DFT-D3 method of Grimme.<sup>6</sup>

The adsorption energy ( $\Delta E_{ads}$ ) of N<sub>2</sub> adsorption on the surface is defined as

$$\Delta E_{ads} = E(*N_2) - E(*) - E(N_2)$$

where  $E(*N_2)$  and E(\*) are the total energy of surface systems with and without  $N_2$  molecule, respectively,  $E(N_2)$  is the energy of an isolated  $N_2$  molecule. According to this definition, negative adsorption energy suggests that the adsorption process is exothermic and the adsorption system is thermodynamically stable. Contrarily, a positive value corresponds to an endothermic and unstable adsorption.

Converte	BET surface	BJH average pore	
Sample	area $(m^2 \cdot g^{-1})$	Pore volume(cm <sup>2</sup> ·g <sup>2</sup> )	diameter(nm)
ZnTCPP	77	0.08	44.9
NiFeB hydroxide	432	0.24	17.8
ZT-NFB-1%	320	0.43	10.1
Samuela	BET surface		BJH average pore
Sample	$area(m^2 \cdot g^{-1})$	Pore volume(cm <sup>2</sup> ·g <sup>-1</sup> )	diameter(nm)
ZnTCPP	77	0.08	44.9
ZT-NFB-1%	320	0.43	10.1

Table S1. The corresponding pore data of the prepared sample.

Table S2. Recent studies on  $N_2$  photo-oxidation to  $NO_3^-$  over different photocatalysts.

Photocatalyst	NO <sub>3</sub> <sup>-</sup> yield activity	Light source	Apparent quantum efficiency	Ref.
Pd/H-TiO <sub>2</sub>	$4.58 \ \mu mol \ g^{-1}$	Thermal-assisted	0.99% (350 nm)	7
	$h^{-1}$	photocatalysis (200 °C)	× ,	
Pothole-rich WO <sub>3</sub> nanosheets	1.92 mg g <sup>-1</sup> h <sup>-1</sup>	300 W Xe lamp	0.11% (380 nm)	8
BiVO <sub>4</sub> /ZnTCPP	$4.72 \text{ mg g}^{-1} \text{ h}^{-1}$	300 W Xe lamp, >420 nm	0.80% (420 nm)	9
WO <sub>3</sub> /CdS	14.2 $\mu$ mol L <sup>-1</sup> h <sup>-1</sup> g <sup>-1</sup>	300 W xenon lamp	_	10
BiVO <sub>4</sub> /rGO	1.45 mg h <sup>-1</sup> g <sup>-1</sup>	300 W Xe lamp, >420 nm	0.64% (420 nm)	11
Mo <sub>72</sub> Fe <sub>30</sub> @UiO-66	702.4 $\mu g g^{-1} h^{-1}$	300 W xenon lamp	0.072% (380 nm)	12
ZnTCPP/NiFeB	689.4 μmol∙g⁻	200 W		This
hydroxide	<sup>1</sup> ·h <sup>-1</sup>	300 w xenon lamp	_	work



Fig. S1. EDX mappings of the ZT-NFB-1% sample.



Fig. S2. TEM images of the prepared ZT-NFB-1% samples.

As shown in Fig. 2 and S2, both NiFeB hydroxides and ZnTCPP exhibit clearly sheet-like structures, and the composite sample NiFeB/ZnTCPP exhibits an obvious 2D lamellar stacking arrangement, and such close contact between ZnTCPP and NiFeB nanosheets could efficiently promote the inter-interface charge transfer.



Fig. S3 XRD pattern of the prepared NiFeB hydroxides.



Fig. S4. FTIR spectra (a) and Raman spectroscopy of NiFeB hydroxide.

The FTIR profile of NiFeB hydroxide (Fig. S4a) reveals the absorption peaks of BO<sub>3</sub><sup>-</sup> at 1280 cm<sup>-1</sup> and 975 cm<sup>-1</sup>. Additionally, the characteristic peaks of Ni-OH and Fe-OH were also detected, which confirms the successful synthesis of NiFeB hydroxide. This observation should be corroborated by the results of Raman spectroscopy (Fig. S4b).<sup>13</sup>



**Fig. S5.** XPS profiles of Zn 2p (a), N 1s (b), Ni 2p (c), and Fe 2p (d) of different samples.

X-ray photoelectron spectroscopy (XPS) analyses were conducted to investigate the elemental composition and chemical states of the materials. The XPS spectra of Zn 2p, N 1s, Ni 2p, and O 1s for the different samples are presented in Fig. S5. The Zn 2p peaks are observed at approximately 1022.2 eV and 1045 eV, corresponding to Zn  $2p_{3/2}$  and Zn  $2p_{1/2}$  of Zn<sup>2+</sup>, respectively. Notably, the peak positions of Zn 2p for both ZnTCPP and ZT-NFB-1% remain unchanged, indicating that the chemical state of Zn remains essentially unaltered. Regarding Ni 2p, the characteristic peaks at around 855.6 eV and 873.4 eV correspond to Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$ , respectively, with no significant peak shifts, suggesting that Ni is in a stable oxidation state. In terms of N 1s, the strong peaks at approximately 398.2 eV and 400.0 eV correspond to pyridine nitrogen (CN-C) and diaspora tertiary nitrogen (N-C<sub>3</sub>), respectively.



Fig. S6. XPS survey spectra of different samples.



Fig. S7. N<sub>2</sub> adsorption-desorption isotherm (a) and pore size distribution (b) of samples.

According to the IUPAC classification of nitrogen adsorption-desorption isotherms, the nitrogen adsorption-desorption curves of ZnTCPP and ZT-NFB-1% samples belong to type IV isotherms.<sup>14</sup> When  $P/P_0$  is close to 1, an adsorption hysteresis loop appears, indicating the coexistence of mesoporous and macroporous structures of samples. (Fig. S7a.). It can be seen from the pore size distribution diagram in Fig. S7b. that the pore size distribution of the samples is in the range of 2-50 nm, which further proves the existence of mesoporous structure. Compared with

ZnTCPP (77 m<sup>2</sup>·g<sup>-1</sup>), the BET surface area of ZT-NFB-1% of the composite sample increased to  $320 \text{ m}^2 \cdot \text{g}^{-1}$  after NiFeB-hydroxide was introduced, and the large specific surface area provided more reactive sites, which was beneficial to the adsorption and activation of N<sub>2</sub> (Table. S1).



Fig. S8 The control experiments that nitrate formation under different conditions on ZT-NFB-1%

(a), performance comparison between ZnTCPP/NiFeB and ZnTCPP/NiFe samples (b).



Fig. S9 XRD patterns (a) and SEM image (b) of ZT-NFB-1% sample before and after the photocatalytic reaction.

Figure S9a shows the XRD spectra of the ZT-NFB-1% sample before and after the photocatalytic cycling experiments, and no obvious change can be observed. In addition, the SEM image of the post-illumination sample (Fig. S9b) revealed that the 2D/2D structure of the composite retained after the photocatalytic reaction, confirming the good stability of the ZT-NFB-1% sample.



Fig. S10 UV-vis DRS absorption spectra of different samples.

The UV-Vis diffuse reflectance results (Fig. S10) reveal a redshift in the light absorption edge of ZT-NFB-1% (704 nm) compared to ZnTCPP (681 nm). The addition of NiFeB hydroxide expands the light absorption range of the semiconductor material, increasing the sunlight utilization efficiency.



Fig. S11 Band gap (a) and conduct band position (b) of ZnTCPP.

According to the converted Kubelka-Munk function (Fig. S8b)<sup>15</sup>, the intrinsic band gap of ZnTCPP is calculated as 1.64 eV. As shown in Fig. S8a, the Mott-Schottky diagram shows that ZnTCPP is an n-type semiconductor material, and the flat potential  $V_{\rm fb}$  is -1.31 V (vs Ag/AgCl, PH=7). Generally, for n-type semiconductors, the flat potential  $V_{\rm fb}$  is 0.1-0.3 V higher than the 11

bottom of the conduction band (CB) of the semiconductor itself, <sup>16</sup> so the CB position of ZnTCPP is estimated to be -1.013 V (vs NHE, PH=7), and the VB position of ZnTCPP can be calculated to be 0.627 V (vs NHE, PH=7).



Fig. S12 The  $N_2$ -TPD spectra of ZnTCPP and ZT-NFB-1% samples.

## References

1 Y. Bai, Y. Wu, X. Zhou, Y. Ye, K. Nie, J. Wang, M. Xie, Z. Zhang, Z. Liu, T. Cheng and C. Gao, *Nat Commun*, 2022, **13**, 6094.

Z. Jin, J. Zhang, J. Qiu, Y. Hu, T. Di and T. Wang, *Journal of Colloid and Interface Science*,
2023, 652, 122–131.

3 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.

4 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.

5 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.

6 S. Grimme, S. Ehrlich and L. Goerigk, *J Comput Chem*, 2011, **32**, 1456–1465.

7 X. Zhang, R. Shi, Z. Li, J. Zhao, H. Huang, C. Zhou and T. Zhang, *Advanced Energy Materials*, 2022, **12**, 2103740.

8 Y. Liu, M. Cheng, Z. He, B. Gu, C. Xiao, T. Zhou, Z. Guo, J. Liu, H. He, B. Ye, B. Pan and Y. Xie, *Angew Chem Int Ed*, 2019, **58**, 731–735.

9 D. Zhou, S. Shao, X. Zhang, T. Di, J. Zhang, T. Wang and C. Wang, *J. Mater. Chem. A*, 2023, 11, 401–407.

10 P. Xia, X. Pan, S. Jiang, J. Yu, B. He, P. M. Ismail, W. Bai, J. Yang, L. Yang, H. Zhang, M. Cheng, H. Li, Q. Zhang, C. Xiao and Y. Xie, *Advanced Materials*, 2022, **34**, 2200563.

S. Shao, J. Zhang, L. Li, Y. Qin, Z.-Q. Liu and T. Wang, *Chem. Commun.*, 2022, 58, 2184–2187.

12 X. Li, L. Yang, Q. Liu, W. Bai, H. Li, M. Wang, Q. Qian, Q. Yang, C. Xiao and Y. Xie, *Advanced Materials*, 2023, 2304532.

13 B. Tekin and H. Güler, *Materials Chemistry and Physics*, 2008, **108**, 88–91.

14 G. Anandhababu, Y. Huang, D. D. Babu, M. Wu and Y. Wang, *Adv Funct Materials*, 2018, 28, 1706120.

15 R. Wang, X. Wang, Y. Xiong, Y. Hou, Y. Wang, J. Ding and Q. Zhong, *ACS Appl. Mater. Interfaces*, 2022, **14**, 35654–35662.

W. Yin, L. Bai, Y. Zhu, S. Zhong, L. Zhao, Z. Li and S. Bai, ACS Appl. Mater. Interfaces,
2016, 8, 23133–23142.