

**Appendix A: Supporting Information (SI):**

**Oxygen vacancies enhance the photocatalytic deep  
oxidation of NO over N-doped KNbO<sub>3</sub> catalyst**

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### SI 1. The figure of the reactor

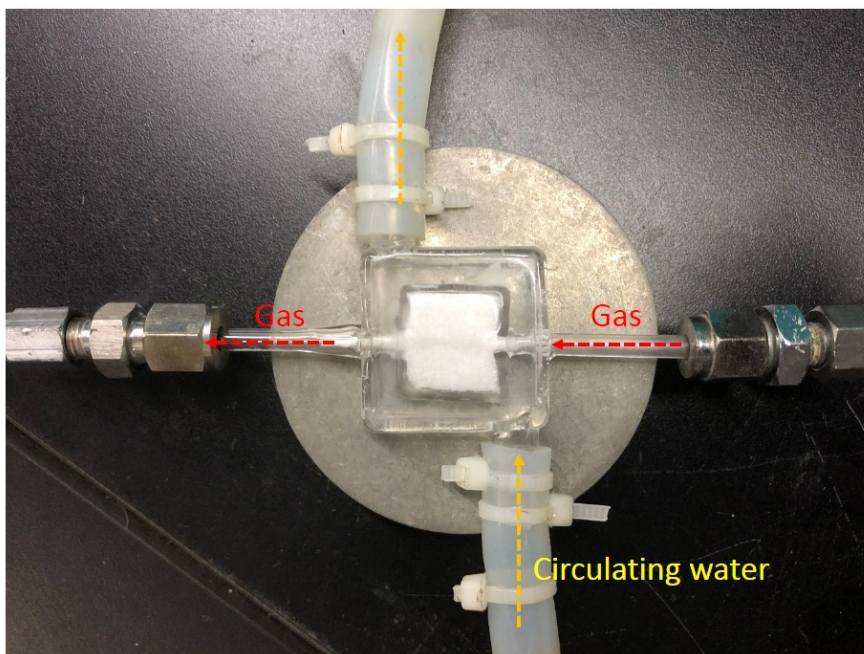


Fig. S1. The reactor with circulating water bath

### SI 2. Reactor schematic and reaction system

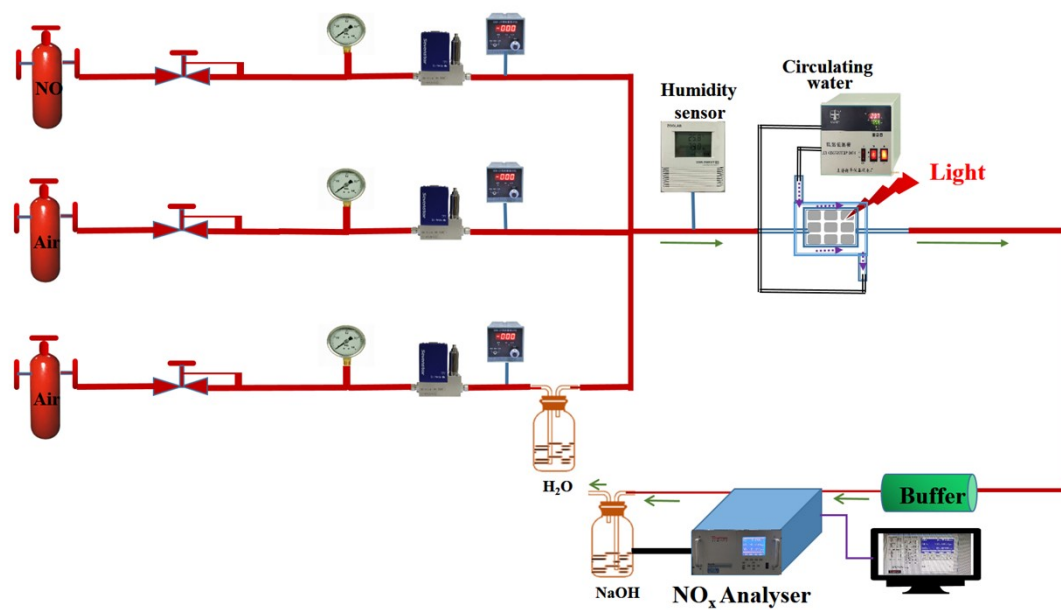
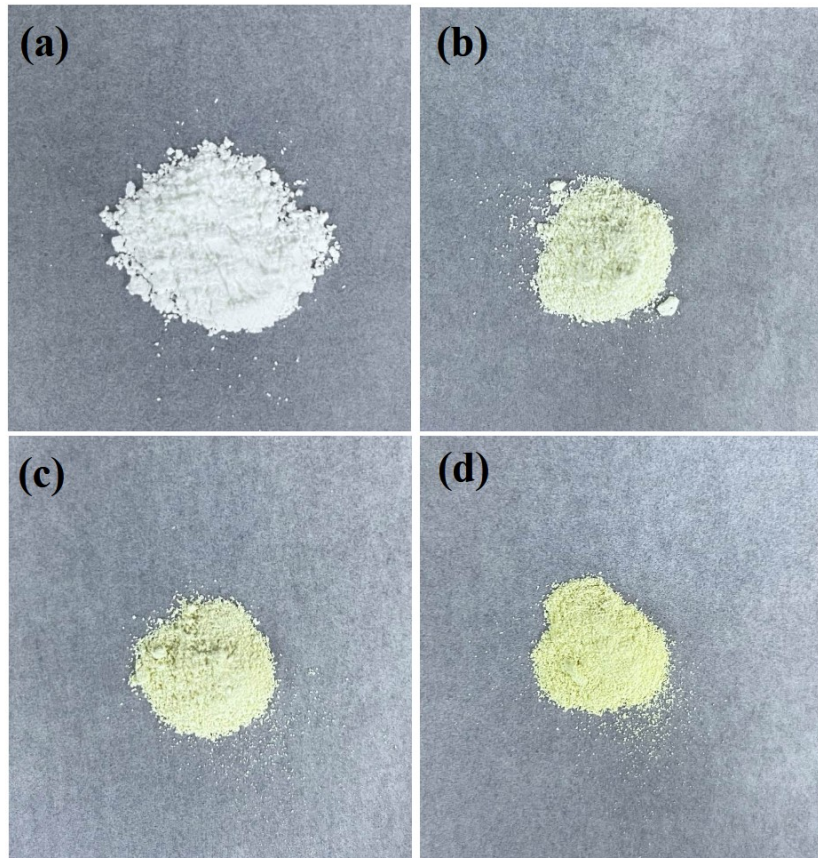


Fig. S2. The reaction system for the catalyst samples evaluation

### SI 3. The digital photo of samples



**Fig. S3.** The digital photo of the  $\text{KNbO}_3$  (a),  $1.0\text{-N-KNbO}_3$  (b),  $1.5\text{-N-KNbO}_3$  (c) and  $2.0\text{-N-KNbO}_3$  (d), respectively

#### SI 4. Lattice parameters

**Table S1.** Lattice parameters of  $\text{KNbO}_3$ ,  $1.0\text{-N-KNbO}_3$ ,  $1.5\text{-N-KNbO}_3$  and  $2.0\text{-N-KNbO}_3$

samples	Lattice parameters ( $\text{\AA}$ )		
	a	b	c
$\text{KNbO}_3$	3.971	5.692	5.719
$1.0\text{-N-KNbO}_3$	3.971	5.697	5.723
$1.5\text{-N-KNbO}_3$	3.971	5.697	5.723
$2.0\text{-N-KNbO}_3$	3.971	5.697	5.723

#### SI 5. Band gaps analyses

The band gaps for as-synthesized samples were calculated using the following empirical equation:

$$(\alpha h\nu)^n = A \cdot (h\nu - E_g)$$

where  $\alpha$  is the absorption coefficient,  $h$  is the Planck constant,  $\nu$  is light frequency,  $A$  is a constant,  $E_g$  is the bandgap energy, respectively. The value of  $n$  is equivalent to 2, which corresponds to direct semiconductors, to 1/2 for the indirect transition. In this case, the direct transition is observed. Thus,  $n$  is 2 in this work.

### SI 6. Textural characteristics (N<sub>2</sub>-physisorption)

The N<sub>2</sub> adsorption-desorption isothermal plots of the as-prepared catalyst were shown in Fig. S4. The isotherms of these samples were classical type IV with a type H3 hysteresis loop according to IUPAC. The specific surface area of KNbO<sub>3</sub> was 3.63 m<sup>2</sup> g<sup>-1</sup> by the BET calculation method. Moreover, the specific surface area, pore volume and pore size did not change significantly after N doping (Table S2).

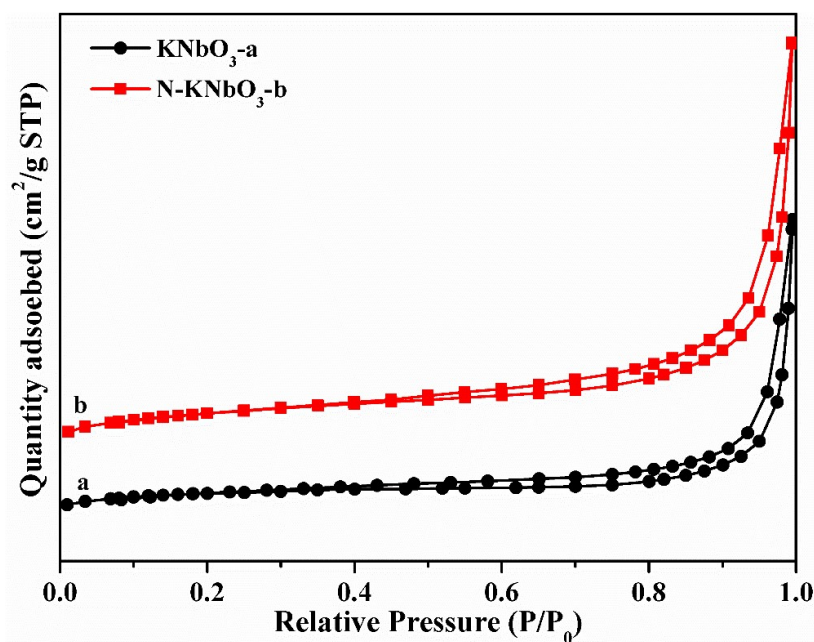
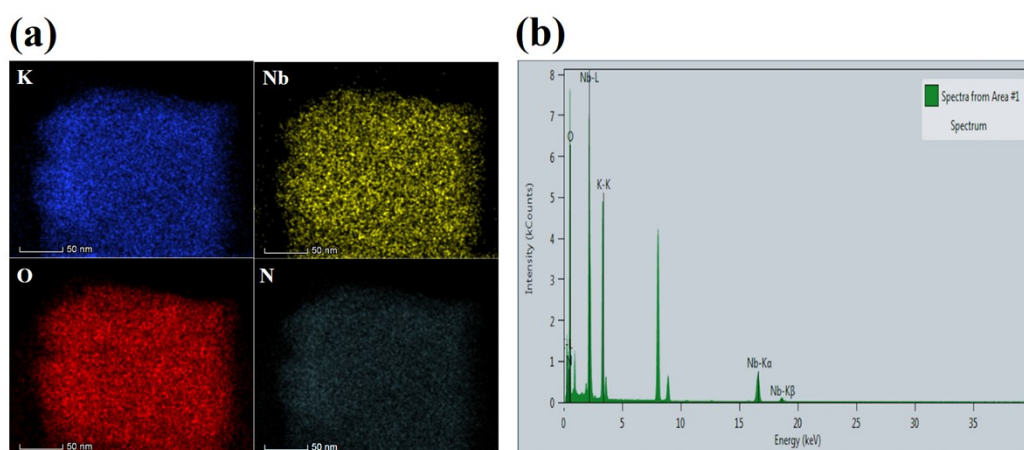


Fig. S4. The N<sub>2</sub> adsorption-desorption isotherms of KNbO<sub>3</sub> and N-KNbO<sub>3</sub>

**Table S2.** Specific surface area and pore structure parameters of KNbO<sub>3</sub> and N-KNbO<sub>3</sub>

sample	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (mL g <sup>-1</sup> ) 1)	Pore diameter (nm)
KNbO <sub>3</sub>	3.63	0.013	14.28
N-KNbO <sub>3</sub>	5.46	0.017	13.35

**SI 7. The mapping and EDX****Fig. S5.** The mapping and EDX spectra of N-KNbO<sub>3</sub> (a, b) of N-KNbO<sub>3</sub>**Table. S3.** Determination of the amount of N doping

Samples	N doping (at.%)	N doping (at.%)
1.5-N-KNbO <sub>3</sub>	7.12 <sup>a</sup>	6.85 <sup>b</sup>

a: Determined by EDX spectra. b: XPS.

According to different test characterizations, the content of incorporated N was approximately 7at.%.

**SI 8. NO<sub>x</sub> species distribution**

The amount of nitrate ( $n_{\text{NO}_3^-}$ ) and nitrite ( $n_{\text{NO}_2^-}$ ) accumulated during the catalytic oxidation of NO was measured by Thermo Fisher Dionex Aquion ion chromatography. The specific method was as follows: fully immerse the catalyst sample after continuous reaction in 100 mL of deionized water, wash and filter to obtain the

supernatant, and then take 5 mL into the ion chromatography tube for sample analysis.

In addition, the total NO removal ( $n_{\text{NO}}$ ) and  $\text{NO}_2$  production ( $n_{\text{NO}_2}$ ) are calculated using the following formula:

$$n_{\text{NO}} = (f/22.4) \int (\Phi_{\text{NO}} - \Phi_{\text{NO}_i}) dt$$

$$n_{\text{NO}_2} = (f/22.4) \int \Phi_{\text{NO}_2} dt$$

**Table S4.** The total amounts of NO removal and different  $\text{NO}_x$  production after five cycle tests at room temperatures over  $\text{KNbO}_3$  and X-N- $\text{KNbO}_3$  samples

Sample	$n_{\text{NO}}/\text{umol}$	$n_{\text{NO}_2}/\text{umol}$	$n_{\text{NO}_2^-}/\text{umol}$	$n_{\text{NO}_3^-}/\text{umol}$	$n_{\text{other}}/\text{umol}$
$\text{KNbO}_3$	1.133	0.283	0.397	0.283	0.170
1.0-N- $\text{KNbO}_3$	4.522	0.565	1.967	0.995	0.995
1.5-N- $\text{KNbO}_3$	5.638	0.676	2.594	1.297	1.071
2.0-N- $\text{KNbO}_3$	4.404	0.616	1.762	1.145	0.881

### SI 9. Band structure analysis

In Fig. S6a and b, the valence band energy of  $\text{KNbO}_3$  and 1.5-N- $\text{KNbO}_3$  is 2.56 and 2.38 eV. According to the formula:  $E_{\text{NHE/V}} = \Phi + \text{VB}_{\text{max}} - 4.44$  ( $\Phi$  is the electronic work function of the instrument, 4.2 eV), the valence band position NHE (PH=7) is 2.32 and 2.14 V. According to the experimental results of DRS in the manuscript, the bandgap of  $\text{KNbO}_3$  and 1.5-N- $\text{KNbO}_3$  are 3.30 and 2.83 eV. Finally, we conclude that the conduction bands of  $\text{KNbO}_3$  and 1.5-N- $\text{KNbO}_3$  are -0.98 and -0.69 V.

The energy band structure of the sample is shown in Fig. S7. The doping of N introduces oxygen vacancies to form defect energy levels, which increases the valence band position of  $\text{KNbO}_3$  and reduces the bandgap. In addition, the positions of the valence band and conduction band can meet the formation requirements of ROS ( $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ ).

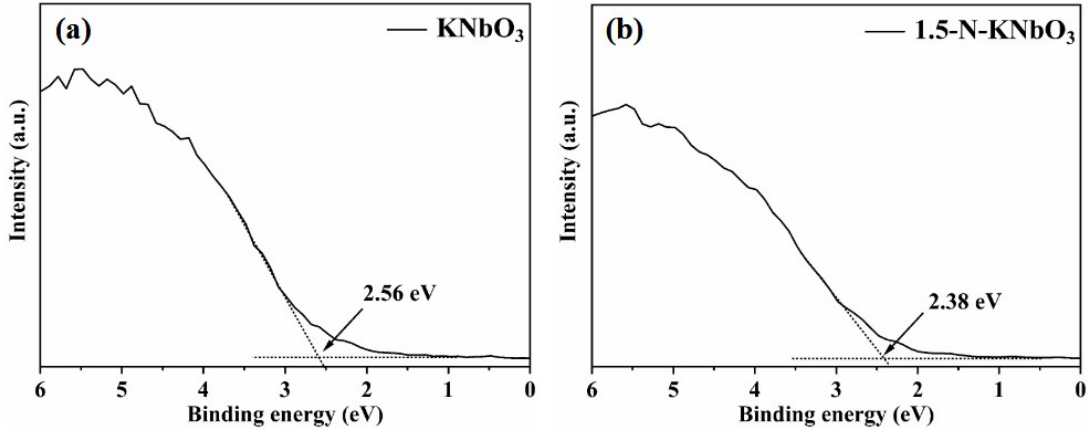


Fig. S6. The value bands of KNbO<sub>3</sub> (a) and 1.5-N- KNbO<sub>3</sub> (b)

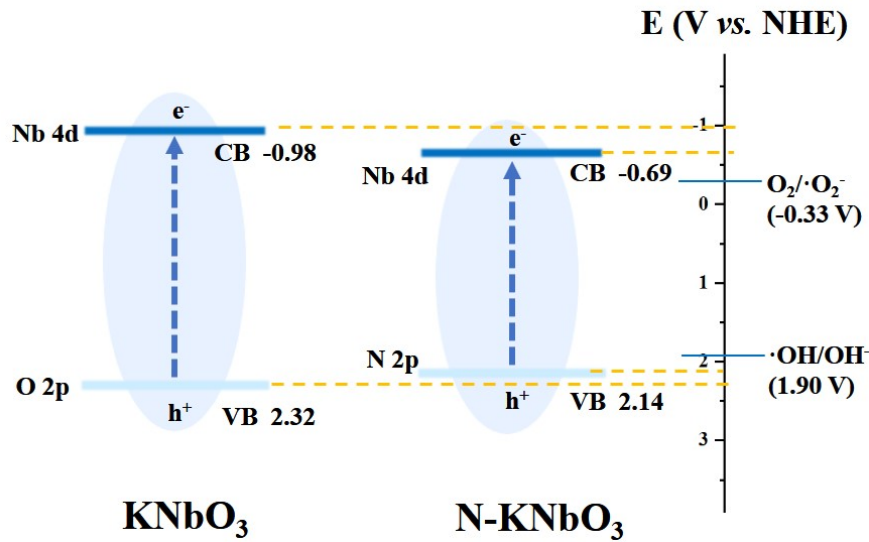
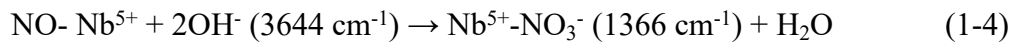
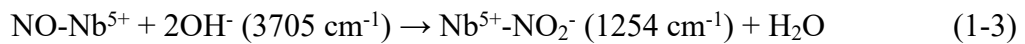
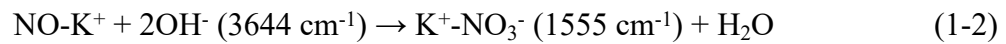
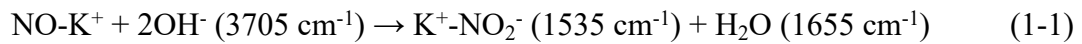


Fig. S7. The band structure of KNbO<sub>3</sub> (a) and 1.5-N- KNbO<sub>3</sub> (b)

## SI 10. Mechanism of NO removal over KNbO<sub>3</sub>

### 1. The adsorption process of NO over KNbO<sub>3</sub> in the dark:

(1) The NO reacted with surface hydroxyl groups:



### 2. The photocatalytic oxidation of NO over KNbO<sub>3</sub>:

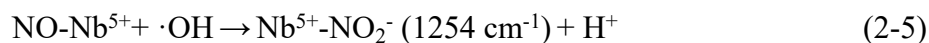
(1) Photogenerated electrons and holes were generated under visible light:



(2) The Photogenerated holes reacted with surface hydroxyl groups and water to generate hydroxyl radicals:



(3) The  $\cdot\text{OH}$  interacted with NO to generate nitrate or nitrite:



## References

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