

# Supporting Information

## Synergistic Spatial Confining Effect and O Vacancy in WO<sub>3</sub> Hollow Sphere for Enhanced N<sub>2</sub> Reduction

Yuzhou Xia <sup>1,2,3,†</sup>, Xinghe Xia <sup>1,2,†</sup>, Shuying Zhu <sup>1,\*</sup>, Ruowen Liang <sup>2</sup>, Guiyang Yan <sup>2</sup>, Feng Chen <sup>2,\*</sup> and Xuxu Wang <sup>3</sup>

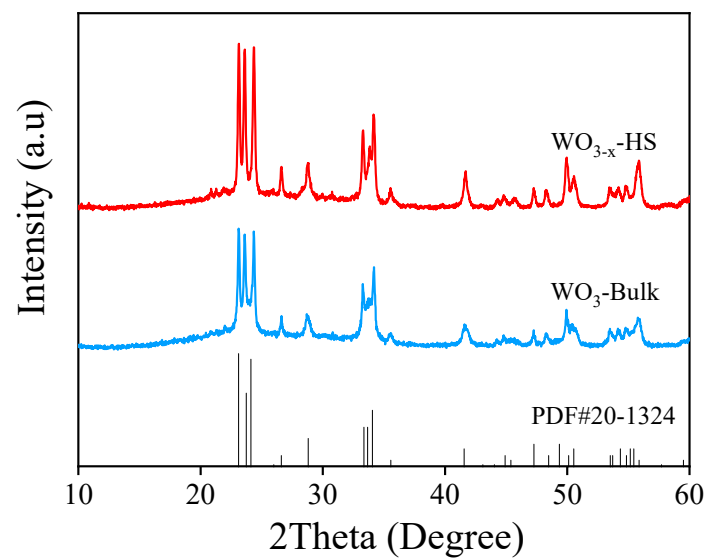
<sup>1</sup> College of Chemistry, Fuzhou University, Fuzhou 350116, China; yzxia@ndnu.edu.cn (Y.X.); 211327039@fzu.edu.cn (X.X.)

<sup>2</sup> Fujian Province University Key Laboratory of Green Energy and Environment Catalysis, Ningde Normal University, Ningde 352100, China; rwliang@ndnu.edu.cn (R.L.); ygyfjnu@163.com (G.Y.)

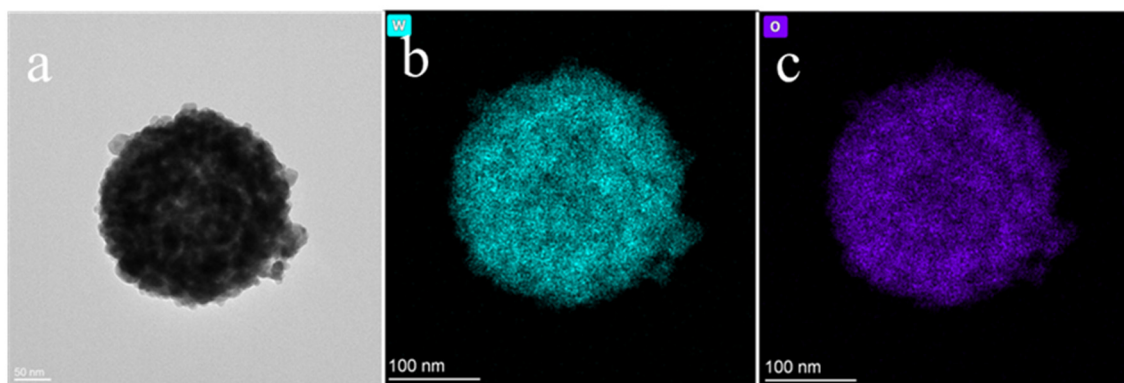
<sup>3</sup> State Key Laboratory of Photocatalysis on Energy and Environment, Research Institute of Photocatalysis, College of Chemistry, Fuzhou University, Fuzhou 350116, China; xwang@fzu.edu.cn

\* Correspondence: syzhu@fzu.edu.cn (S.Z.); t9309@ndnu.edu.cn (F.C.)

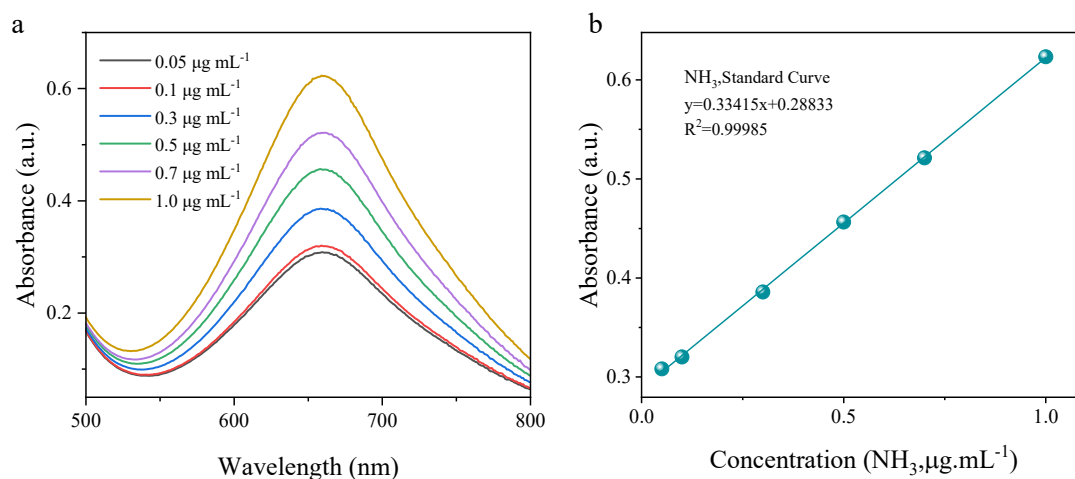
† These authors contributed equally to this work.



**Figure S1.** XRD pattern of  $\text{WO}_{3-x}\text{-HS}$  and  $\text{WO}_3\text{-bulk}$ .



**Figure S2.** HAADF-STEM (a) and corresponding elemental mapping images W (b) and O (c) of  $\text{WO}_{3-x}\text{-HS}$ .



**Figure S3.** The calibration curve of  $\text{NH}_4^+$  reference by UV-vis spectra at room temperature.

**Table S1.** Comparison of photocatalytic N<sub>2</sub> reduction performance among reported catalysts.

Catalyst	Light source	Reaction medium	NH <sub>3</sub> yield rate (μmol g <sup>-1</sup> h <sup>-1</sup> )	Ref.
WO <sub>3-x</sub> -HS	300 W Xe lamp, λ ≥ 420 nm	Water	140.1	This work
WO <sub>3-x</sub>	300 W Xe lamp	Methanol (12.5 vol%) aqueous solution	28.4	1
NP WO <sub>3-x</sub>	LED lamp (4 × 3 W)	Na <sub>2</sub> SO <sub>3</sub> (1 mM) aqueous solution	82.41	2
OVs-BWO	300 W Xe lamp, λ < 420 nm	Water	106.4	3
MoO <sub>3-x</sub> /Fe-W <sub>18</sub> O <sub>49</sub>	300 W Xe lamp	Water	137.5	4
NH <sub>2</sub> -MIL-125 (Ti)	300 W Xe lamp, λ > 400 nm	Water	12.3	5
In <sub>2</sub> O <sub>3</sub> /In <sub>2</sub> S <sub>3</sub>	300 W Xe lamp	Water	40.04	6

FPx	300 W Xe lamp	Water	62.42	7
Cu <sub>2</sub> O/MIL-100(Fe)	300 W Xe lamp, $\lambda > 400$	Water	51.22	8
SMO-10	300 W Xe lamp	Water	3.92	9
Ru-TiO <sub>2</sub> NS	300 W Xe lamp	Ethanol (20 vol%) aqueous solution	3.31	10
NTO-0.5	300 W Xe lamp, $\lambda > 400$	Water	80.09	11
P-Fe/W <sub>18</sub> O <sub>49</sub>	Xenon lamp	Na <sub>2</sub> SO <sub>3</sub> (1 mM) aqueous solution	187.6	12
1 mol% Mo/W <sub>18</sub> O <sub>49</sub>	300 W Xe lamp, $\lambda \geq 400$ nm	Na <sub>2</sub> SO <sub>3</sub> (1 mM) aqueous solution	195.5	13
BCN	250 W Xe lamp, $\lambda \geq 400$ nm	Na <sub>2</sub> SO <sub>3</sub> (1 mM) aqueous solution	313.9	14
BiCN <sub>x</sub> -5	300 W Xe lamp, $\lambda > 420$ nm	Na <sub>2</sub> SO <sub>3</sub> (1 mM) aqueous solution	576.11	15

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