# Supporting Information

Enhanced full-spectrum-response photocatalysis and reusability of MoSe<sub>2</sub> via hierarchical N-doped carbon nanofibers as heterostructural supports

Shu Yang, Changlu Shao\*, Ran Tao, Xiaowei Li, Chaohan Han, Haiyang Liu, Xinghua Li\*, Yichun Liu

Center for Advanced Optoelectronic Functional Materials Research, Key Laboratory of UV-Emitting Materials and Technology (Northeast Normal University), Ministry of Education, 5268 Renmin Street, Changchun 130024, People's Republic of China

### **Corresponding Authors**

\*E-mail: clshao@nenu.edu.cn \*E-mail: lixh781@nenu.edu.cn Tel: +86 43185098803

#### (Summary of Content: 23 pages, two tables and 14 figures)

#### **Part I : Experimental section**

#### Characterization

The morphologies of the samples were studied by scanning electron microscopy (SEM; XL-30 ESEM FEG, Micro FEI Philips, USA). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL JEM-2100 instrument (acceleration voltage: 200 kV). X-ray diffraction (XRD) measurements were carried out using a D/max 2500 XRD spectrometer (Rigaku, Tokyo, Japan) with a Cu Ka line of 0.1541 nm. Thermogravimetric analysis (TGA) was performed under an air flow from 0°C to 1000°C at a heating rate of 10°C min<sup>-1</sup>, using a SDT Q600 TG analyzer. The Raman spectra analyses of all samples were performed on a Jobin-Yvon HR800 micro-Raman spectrometer using the 488 nm line of a He-Cd laser as the excitation source at room temperature. X-ray photoelectron spectroscopy (XPS) was performed on a VG-ESCALAB LKII instrument (VG, Waltham, UK) with a Mg K $\alpha$ ADES (h $\upsilon$  = 1253.6 eV) source at a residual gas pressure of below  $10^{-8}$  Pa. The specific surface areas of the samples were measured with a Micromeritics ASAP 2010 instrument (Micromeritics, Norcross, GA, USA) and analyzed by the Brunauer-Emmett-Teller (BET) method. The UV-vis diffuse reflectance spectra (DSR) were measured at room temperature with a UH4150 spectrophotometer (Hitachi, Tokyo, Japan). The total organic carbon (TOC) of the degraded dyes was determined by a TOC analyzer (Vario TOC). The resistance and electron spin resonance (ESR) spectra were performed on a Bruker model ESR JES-FA200 spectrometer by using the spin-trap reagent DMPO (5,5-dimethyl-1-pyrroline N-oxide, Sigma Chemical Co.) under simulated light ( $\lambda > 50$  nm) irradiation. The identification of intermediates in photodegradation was performed by liquid chromatography-mass spectrometer (LC-MS; Agilent 1200HPLC/MicrOTOF II) with an electrospray ionization source. A reversed-phase column (Agilent Eclipse Plus C18) was used with a the eluent comprised 75% methanol and 25% water, and the flow rate was 1.0 mL/min.

#### Photoelectrochemical measurements

Photoelectrochemical measurements were carried out using the conventional three electrode setup connected to an electrochemical workstation (CHI660D, Shanghai Chenhua, China). The as-prepared all samples  $(1 \times 1 \text{ cm}^2)$  in a stainless steel mesh were used as the working electrode, and a Pt wire and an Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode were used as the counter electrode and reference electrode, respectively. The electrolyte was 0.2M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. A 150 W xenon lamp was used as the visible light source. The measurements were carried out at a constant potential of +0.5 V to the working anode.

## **Evaluation of Adsorption**

Adsorption study was done with the H-N-CNF/MoSe<sub>2</sub> heterojunctions under full-spectrum irradiation. In brief, 25 mg catalyst was mixed in 50 mL different pollutants (RhB, MO, and TC, and the concentration varied from 1 to 20 mg L<sup>-1</sup>). The mixtures were stirred in the dark for 30 min to attain adsorption-desorption equilibrium. UV-visible (UV-vis) spectrophotometer was used to find the equilibrium concentration (C<sub>e</sub>) of pollutants, and the adsorption capacity,  $q_e$  (mg g<sup>-1</sup>), is given by the following relation.<sup>1</sup>

$$\mathbf{q}_{\mathrm{e}} = (\mathbf{C}_{0} - \mathbf{C}_{\mathrm{e}}) \,\mathbf{w}/\mathbf{v} \tag{1}$$

Here,  $C_0$  is the initial concentration of pollutants (mg L<sup>-1</sup>), v and w are the volume and weight of the adsorbent, respectively.

## Part II: Supplementary Data

**Table S1.** Row A, B, C corresponds to the full width at half maximum (FWHM) of XRD peaks of (002), (100) and (110) peaks for MoSe<sub>2</sub>, CNF/MoSe<sub>2</sub> and H-N-CNF/MoSe<sub>2</sub> heterojunctions. Row D and E corresponds to the FWHM of  $A_{1g}$  peak and the intensity ratio of  $A_{1g}$  to  $E^{1}_{2g}$  in Raman spectra for MoSe<sub>2</sub>, CNF/MoSe<sub>2</sub> and H-N-CNF/MoSe<sub>2</sub> heterojunctions.

Photocatalyst	А	В	С	D	Е
	(degree)	(degree)	(degree)	(cm <sup>-1</sup> )	$(A_{1g}\!/ E^{1}_{2g})$
MoSe <sub>2</sub>	0.95	0.86	0.92	6.6	2.19
CNFs/MoSe <sub>2</sub>	0.94	0.66	0.82	6.37	2.25
H-N-CNFs/MoSe <sub>2</sub>	0.93	0.66	0.76	5.5	2.42

 Table S2. Summary of adsorption parameters.

Pollutants	Lamgmuir model			Freundlich model		
	$q_{\rm m}$	K <sub>L</sub>	R <sup>2</sup>	$K_{f}$	1/n	R <sup>2</sup>
RhB	5.46	1.09	0.999	1.58	0.456	0.980
МО	3.86	0.508	0.992	0.631	0.496	0.978
TC	6.25	0.115	0.989	1.07	0.730	0.992



**Figure S1.** SEM images of (A) CNFs, (B) H-N-CNFs, and (C) CNFs/PANI at low magnification and high magnification (insets); (D) pure MoSe<sub>2</sub>.



Figure S2. TGA curves of CNF/MoSe<sub>2</sub> and H-N-CNF/MoSe<sub>2</sub> heterojunctions.



**Figure S3.** XRD diffraction patterns of the CNFs, H-N-CNFs, CNF/MoSe<sub>2</sub> heterojunctions, H-N-CNF/MoSe<sub>2</sub> heterojunctions, and MoSe<sub>2</sub>.



**Figure S4.** Raman spectra of (A) CNFs, H-N-CNFs, CNF/MoSe<sub>2</sub> heterojunctions and H-N-CNF/MoSe<sub>2</sub> heterojunctions, and (B) pure MoSe<sub>2</sub>, CNF/MoSe<sub>2</sub> heterojunctions and H-N-CNF/MoSe<sub>2</sub> heterojunctions in the range 200–300 cm<sup>-1</sup>.



Figure S5. HRTEM image of H-N-CNF/MoSe $_2$  heterojuntions at different regions.



**Figure S6.** Degradation curves of RhB in the presence of different photocatalysts in the dark (top) and with visible light irradiation in the absence of photocatalysts (bottom)



**Figure S7.** Adsorption isotherm of (A) RhB, (D) MO, and (G) TC for the H-N-CNF/MoSe<sub>2</sub> heterojunctions. Langmuir adsorption isotherms of (B) RhB, (E) MO, and (H) TC on H-N-CNF/MoSe<sub>2</sub> heterojunctions. Freundlich adsorption isotherms of (C) RhB, (F) MO, and (I) TC on H-N-CNF/MoSe<sub>2</sub> heterojunctions.

The adsorption activity of the H-N-CNF/MoSe<sub>2</sub> heterojunctions is revealed by adsorbing different concentrations of pollutants (RhB, MO, and TC). The equilibrium adsorption capacity (q<sub>e</sub>) increases with an increase in the pollutants concentration, as shown in Figure S7A, D and G. This enhanced adsorption can be attributed to the high adsorption capacity of CNFs/H-N-CNFs and the ultrathin MoSe<sub>2</sub> nanosheets. More pollutants molecules get adsorbed on the surface of the adsorbent to overcome all mass transfer resistances with an increase in pollutants concentration.<sup>1</sup> For interpretating the S13

equilibrium adsorption of pollutants for the H-N-CNF/MoSe<sub>2</sub> heterojunctions, the equilibrium adsorption data were fitted using the Langmuir and Freundlich adsorption isotherm. The corresponding Langmuir and Freundlich isotherms are shown in Figure S7. Various adsorption parameters for both the models are given in Table S2.



**Figure S8.** Kinetic linear simulation curves for degradation of (B) RhB, (E) MO, and (H) TC over different photocatalysts under full-spectrum irradiation ( $300 < \lambda < 2500$  nm).

The apparent first-order rate constant of the photocatalytic reaction is usually used to evaluate the degradation rate of photocatalyst as shown in Equation (2):<sup>3</sup>

$$\ln C/C_0 = kKt = k_{app}t$$
(2)

Here,  $k_{app}$  is the apparent first-order rate constant (min<sup>-1</sup>), and C<sub>0</sub> is the initial concentration (mg/L) of RhB. Terms C (mg/L) and t (min) are the concentration of RhB and the corresponding visible light irradiation time, respectively. Figure S8A shows good linearity between ln(C<sub>0</sub>/C) and time (t) for all the photocatalysts. The obtained  $k_{app}$  ( $k_{RhB}$ ) values are summarized in Table 1.



**Figure S9.** Transient photocurrent response of MoSe<sub>2</sub>, CNF/MoSe<sub>2</sub>, and H-N-CNF/MoSe<sub>2</sub> heterojunction with and without ammonium oxalate under visible light irradiation.



**Figure S10**. Degradation of RhB over H-N-CNF/MoSe<sub>2</sub> heterojunctions in presence of different scavengers under full-spectrum irradiation.



**Figure S11.** UV-vis spectra of (A) RhB, (B) MO, and (C) TC vs photoreaction time for the H-N-CNF/MoSe<sub>2</sub> heterojunctions.



**Figure S12.** The time-of-flight (TOF) mass spectra of (A) RhB before degradation, and (B, C, D, E) degradation products of RhB after full-spectrum irradiation.

R is the structural formula of RhB

 $R(443) - C_2H_4 = 415$ 

 $R(443) - C_6H_5COOH(122) + H + Na = 344$ 

 $R(443) - C_6H_5COOH(122) + 2H = 323$ 

 $323 + C_2H_5(29) = 352$ 

323 + 2H = 325

**Figure S13.** Photocatalytic degradation pathway of RhB by H-N-CNF/MoSe<sub>2</sub> heterojunctions under visible light irradiation.

The photocatalytic degradation pathway and intermediate products of RhB were further analyzed by LC-MS. The time-of-flight (TOF) mass spectra are shown in Figure S12. The main intermediates corresponding to the m/z values. The peak at m/z = 443.2 is attributed to RhB. The other major peaks located at m/z = 415.2, 344.1, 352.1, and 325.2, forming four different products. The rest may be derived from other complex intermediate products. The RhB molecule lost ethyl groups to transform to product [1] (415). The RhB molecule can lose a benzoic acid, add a hydrogen, and add a sodium to form product [2] (344). The RhB molecule can also lose benzoic acid and add two hydrogens to form product [3] (323). Product [4] (352) can be obtained by adding an ethyl on the basis of product [3]. Product [3] add two hydrogens to form product [5] (325). This degradation pathway is different from other literature reports.<sup>4</sup> The reasons might be attribute that the different catalysis possess various adsorption states and interactions with pollutants, and different catalysis product unlike active species during the photocatalytic process. In our system, based on the mass spectral analysis, the entire degradation mechanism of RhB include the process of the N-de-ethylated, and de-benzoic acid along with adding hydrogens. The reaction with added hydrogens might be due to the interaction between  $e^-$  (as mainly active species) and RhB during the photocatalytic process. The added hydrogens might be along with the de-benzoic acid. Thus, this might be lead to the break of RhB molecule in different degrees.



Figure S14. Proposed mechanism for the degradation of different pollutants with

H-N-CNF/MoSe<sub>2</sub> heterojunctions under full-spectrum irradiation.

#### Reference

(1) Lan, S.; Liu, L.; Li, R. Q.; Leng, Z. H.; Gan, S. C. Hierarchical hollow structure ZnO: synthesis, characterization, and highly efficient adsorption/photocatalysis toward congo red. *Ind. Eng. Chem. Res.* **2014**, *53 (8)*, 3131-3139, 10.1021/ie404053m.

(2) Kumar, A.; Reddy, K. L.; Kumar, S.; Kumar, A.; Sharma, V.; Krishnan, V. Rational design and development of Lanthanide-doped NaYF<sub>4</sub>@CdS-Au-RGO as quaternary plasmonic photocatalysts for harnessing visible-near-infrared broadband spectrum. *ACS Appl. Mater. Interfaces* **2018**, *10 (18)*, 15565-15581, DOI: 10.1021/acsami.7b17822.

(3) Lee, M. S.; Park, S. S.; Lee, G. D.; Ju, C. S.; Hong, S. S. Synthesis of TiO<sub>2</sub> particles by reverse microemulsion method using nonionic surfactants with different hydrophilic and hydrophobic group and their photocatalytic activity. *Catal. Today* **2005**, *101* (3-4), 283-290, 10.1016/j.cattod.2005.03.018.

(4) Kumar, S.; Kumar, A.; Kumar, A.; Balaji, R.; Krishnan, V. Highly efficient visible light active 2D-2D nanocomposites of N-ZnO-g-C<sub>3</sub>N<sub>4</sub> for photocatalytic degradation of diverse industrial pollutants. *Chemistry Select* **2018**, *3* (*6*), 1919-1932, DOI: 10.1002/slct.201703156.