Supporting Information

Piezoelectric Activation of Peroxymonosulfate by MoS₂ Nanoflowers for Enhanced Degradation of Aqueous Organic Pollutants

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Supporting information

Synthesis of MoS₂ NFs (Text S1); Theoretical methodology (Text S2); Dipole moment calculation (Text S3); The atomic charges of each Mo and S atom under various strains (Table S1); Some specific parameters of MoS_2 under compressive and tensile strains (Table S2); The spin determination of all the structures in PMS activation (Table S3); First-order kinetic fitting of phenol degradation in different systems: US/PMS, US/MoS₂ NFs and MoS₂ NFs/PMS, US/MoS₂ NFs/PMS (Fig. S1); Phenol degradation in ms/MoS₂ NFs/PMS system at different stirring rate (Fig. S2); Degradation efficiency of non-piezoelectric material CNT for phenol (Fig. S3); Degradation efficiency of tap water prepared phenol solution by different systems (Fig. S4); The favorable structure of MoS₂ (Fig. S5); The dipole moment of MoS₂ under compressive and tensile strains along the "Zigzag" (black), "Armchair" (red) and biaxial (blue) directions (Fig. S6); Structural mechanism of in-plane polarization and the schematic of external current by strains (Fig. S7); The band structures of MoS₂ under various strains along uniaxial and biaxial directions (Fig. S8); The schematic diagram of cutting MoS₂ (Fig. S9); Phenol degradation by US/MoS₂ NFs/PMS system in cycling tests and X-ray diffraction pattern of MoS₂ NFs before and after reaction (Fig. S10);

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Text S1. Synthesis of MoS2 NFs

A hydrothermal method as reported in the literature was employed to synthesize $MoS_2 NFs^{-1}$. Briefly, 0.9 g $Na_2MoO_4 \cdot 2H_2O$ and 1.2 g thiourea were dissolved in 90 mL ultrapure water to form a homogeneous solution. Concentrated HCl was added dropwise into the solution to adjust the pH to 1. After stirring for 30 min, the solution was transferred into a Teflon-lined autoclave and heated at 180 °C for 24 h. Finally, the black precipitates produced in the autoclave were filtrated and washed several times with ultrapure water and ethanol, and then dried by a freeze dryer to obtain clean $MoS_2 NFs$ for further use.

Text S2. Theoretical methodology

The theoretical calculations of geometrical optimization, adsorption structure and transition properties were performed based on DFT by DMol³ code ². Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) method was used as the exchange-correlation function ³. Spin-polarization was included in all calculations. The Tkatchenko-Scheffler (TS) method for DFT-D correction was used in order to take van der Waals forces for adsorption into account ⁴. All calculations were carried out using the DFT semi-core Pseudopots. To take relativity effects into account, all electrons were included in the calculations to obtain more accurate results. Double numerical plus polarization (DNP) functions were adopted as the basis set ⁵. A 4.9 Å global orbital cutoff for the plane-wave basis set was used in all calculations. For geometric optimization, adsorption structure and transition properties, the Brillouin zone integration was performed with $5 \times 5 \times 1$, $3 \times 3 \times 1$ and $2 \times 2 \times 1$ k-point sampling, respectively.

The positions of all the atoms in the supercell were not constrained and could be fully relaxed until the residual forces on individual atoms were smaller than 10⁻⁵ Ha (1 Ha = 27.2114 eV) ⁴, ⁶. The maximum force was set to 0.002 Ha/Å. In order to better simulate the experimental environment, the water solvation model (COSMO) with a dielectric constant of 78.54 was used during all the calculations to mimic the aqueous condition. In addition, the calculations on systems including PMS were given charge -1|e| to consider the charge state of HSO₅⁻. For simplicity, a single layer $4 \times 4 \times 1$ supercell of MoS₂ with a vacuum width of 20 Å is constructed in this work to ensure the interaction between the repeated slabs along the normal of surface as weak as possible ⁷, ⁸

Text S3. Dipole moment calculation

A larger dipole moment would appear subjecting to stronger piezoelectricity for piezoelectric materials ⁹. Hence, the specific dipole moments of MoS₂ under applications of different uniaxial strains were calculated. The direction of the dipole moment is specified from the positive electric center to the negative electric center. As illustrated in Fig. S5b, the dipole moment increases with the uniaxial tensile or compressive strains, indicating that the strains strengthen the polarization effect. However, the biaxial strains (tensile or compressive) barely affect the dipole moment (Fig. S6). In addition, the direction of the dipole moment maintains along Y-axis regardless of the uniaxial strains along the "Armchair" or "Zigzag" direction. This phenomenon indicates that MoS₂ becomes polarized only in Y-axis. Fig. S6 shows that the dipole moment is positive under compressive strains along the "Zigzag" direction, while it becomes negative under tensile strains. This is opposing to the cases of that strains along "Armchair" direction that the diploe moment is negative under compressive strains, while it becomes positive under tensile strains. Hence, the dipole in MoS₂ has a different directivity under tensile and compressive strains. Meanwhile, the dipole moments under compressive strains along "Zigzag" or "Armchair" directions are higher than those under the uniaxial tensile strains with the same strength. This suggested that compressive strains are more favorable to the piezoelectricity in MoS₂. Additionally, larger dipole moment is induced by the "Armchair" compressive strain than the "Zigzag" compressive strains as shown in Fig. S5b, which is in consistent with previous reports ^{9, 10}. Therefore, only strains along "Zigzag" direction is considered in the following DFT calculations for piezocatalytic activation of PMS due to a similar effect of strains along "Zigzag" or "Armchair" directions.

TABLES.

Table S1. The atomic charges of each Mo and S atom under various strains for the periodic MoS_2 layer as shown in Fig. S5a.

	Atom	-10%	-5%	0	+5%	+10%
Zigzag strain	Мо	0.209	0.224	0.236	0.247	0.255
	S	-0.105	-0.112	-0.118	-0.123	-0.128
Armchair strain	Mo	0.209	0.224	0.236	0.247	0.256
	S	-0.105	-0.112	-0.118	-0.123	-0.128
Biaxial strain	Mo	0.182	0.212	0.236	0.257	0.274
	S	-0.091	-0.106	-0.118	-0.128	-0.137

		E_{Fermi}/eV	E_g/eV	VB edge/eV	CB edge/eV
Pristine MoS ₂	0	-5.266	1.739	-6.078	-4.339
Zigzag	-5	-5.187	2.042	-6.138	-4.096
	-10	-5.070	1.479	-5.671	-4.193
	+5	-5.375	1.271	-5.904	-4.633
	+10	-5.495	0.831	-5.777	-4.946
Armchair	-5	-5.179	2.023	-6.118	-4.094
	-10	-5.100	1.806	-5.941	-4.135
	+5	-5.382	1.167	-5.913	-4.746
	+10	-5.475	0.713	-5.777	-5.065
Biaxial	-5	-5.152	1.915	-6.051	-4.136
	-10	-5.115	1.513	-5.836	-4.323
	+5	-5.474	0.749	-5.763	-5.014
	+10	-5.654	0.041	/	/

Table S2. Some specific parameters of MoS_2 under compressive and tensile strains.

Influence factors	Activating PMS	А	В
e-	-OH	\checkmark	\checkmark
	$-SO_4$	×	×
h^+	-H	×	×
	-SO ₅	\checkmark	\checkmark

Table S3. The spin density of moieties in PMS activation.

"A": manually provided the spin moieties in PMS activation;

"B": automatically provided the spin by software in PMS activation;

"">E": the atoms are covered with spin density after PMS activation;

" \square ": the atoms are not covered with spin density after PMS activation.

FIGURES



Fig. S1. First-order kinetic fitting of phenol degradation in different systems: US/PMS, US/MoS₂ NFs and MoS₂ NFs/PMS, US/MoS₂ NFs/PMS. Conditions: [PMS] = 3.25 mM, $[Phenol]_0 = 10 \text{ ppm}$, $[MoS_2 \text{ NFs}]_0 = 0.3 \text{ g L}^{-1}$, US power =300 W, temperature = 25 °C.



Fig. S2. Phenol degradation in ms/MoS₂ NFs/PMS system at different stirring rates. Conditions: [PMS]= 3.25 mM, [Phenol]₀ = 10 ppm, [MoS₂ NFs]₀ = 0.3 g L^{-1} , temperature = 25 °C.



Fig. S3. Degradation efficiency of non-piezoelectric material CNTs for phenol under US and stirring conditions. Experimental conditions: [PMS] = 3.25 mM, $[Phenol]_0 = 10 \text{ ppm}$, $[CNTs]_0 = 0.3 \text{ g L}^{-1}$, US power=300 W, temperature = 25 °C.



Fig. S4. Phenol removal rate of tap water prepared phenol solution by different systems: US/MoS₂ NFs/PMS, US/PMS, US/MoS₂ NFs; Conditions: [PMS] = 3.25 mM, $[Phenol]_0 = 10 \text{ ppm}$, $[MoS_2 \text{ NFs}]_0 = 0.3 \text{ g L}^{-1}$, US power = 300 W, temperature = 25 °C.



Fig. S5. (a) The favorable optimized configuration of MoS_2 from top and side views; (b) The dipole moment of MoS_2 along the Y-axis under different uniaxial strains. The yellow and cyan balls are S and Mo atoms, respectively, in this and following figures. The arrows indicate the different uniaxial strains along the "Armchair" (Mo and S parallel) and "Zigzag" (Mo and S in the same line) directions.



Fig. S6. The dipole moment of MoS₂ under compressive and tensile strains along the "Zigzag" (black), "Armchair" (red) and Biaxial (blue) directions.



Fig. S7. (a) Structural mechanism of in-plane polarization by strains; (b) The schematic of external current by Armchair tensile and Zigzag compressive strains; (c) The schematic of external current by Armchair compressive and Zigzag tensile strains.



Fig. S8. The band structures of MoS₂ under various strains along different directions (a) Zigzag;

(b)	Armchair	and	(c)	Biax
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Fig. S9. The schematic diagram of cutting MoS_2 . The red dotted line represents the cutting line.



Fig. S10. (a) Phenol degradation by US/MoS₂ NFs/PMS system in cycling tests; (b) X-ray diffraction patterns of MoS_2 NFs before and after reaction.

REFERENCES

- 1. Z. Hu, L. Wang, K. Zhang, J. Wang, F. Cheng, Z. Tao and J. Chen, MoS2 nanoflowers with expanded interlayers as high-performance anodes for sodium-ion batteries, *Angew. Chem. Int. Ed. Engl.*, 2014, **53**, 12794-12798.
- 2. Z. M. Ao, J. Yang, S. Li and Q. Jiang, Enhancement of CO detection in Al doped graphene, *Chem. Phys. Lett.*, 2008, **461**, 276-279.
- 3. T. Liao, C. Sun, A. Du, Z. Sun, D. Hulicova-Jurcakova and S. Smith, Charge carrier exchange at chemically modified graphene edges: a density functional theory study, *J. Mater. Chem.*, 2012, **22**, 8321-8326.
- 4. Y. Su, W. Li, G. Li, Z. Ao and T. An, Density functional theory investigation of the enhanced adsorption mechanism and potential catalytic activity for formaldehyde degradation on Al-decorated C2N monolayer, *Chinese J. Catal.*, 2019, **40**, 664-672.
- 5. Y. Su, Z. Ao, Y. Ji, G. Li and T. An, Adsorption mechanisms of different volatile organic compounds onto pristine C2N and Al-doped C2N monolayer: A DFT investigation, *Appl. Surf. Sci.*, 2018, **450**, 484-491.
- 6. X. Hu, Q. Zhang and S. Yu, Theoretical insight into the hydrogen adsorption on MoS₂ (MoSe₂) monolayer as a function of biaxial strain/external electric fiel, *Appl. Surf. Sci.*, 2019, **478**, 857-865.
- 7. Z. M. Ao, S. Li and Q. Jiang, Thermal stability of interaction between the CO molecules and the Al doped graphene, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1683-1687.
- 8. B. Liu, W. Zhao, Q. Jiang, Z. Ao and T. An, Enhanced adsorption mechanism of carbonyl-containing volatile organic compounds on Al-decorated porous graphene monolayer: A density functional theory calculation study, *Sustainable Mater. Technol.*, 2019, **21**, e00103.
- M. Dai, W. Zheng, X. Zhang, S. Wang, H. Lin, K. Li, Y. Hu, E. Sun, J. Zhang, Y. Qiu, Y. Fu, W. Cao and P. Hu, Enhanced piezoelectric effect derived from grain boundary in MoS₂ monolayers, *Nano letter*, 2020, 20, 201-207.
- S. K. Kim, R. Bhatia, T.-H. Kim, D. Seol, J. H. Kim, H. Kim, W. Seung, Y. Kim, Y. H. Lee and S.-W. Kim, Directional dependent piezoelectric effect in CVD grown monolayer MoS₂ for flexible piezoelectric nanogenerators, *Nano Energy*, 2016, 22, 483-489.