

## Supporting Information

### **Immobilizing highly catalytically molybdenum oxide nanoparticles on graphene-analogous BN: stable heterogenous catalysts with enhanced aerobic oxidative desulfurization performance**

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## Experimental

**Materials:** Ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, A.R. grade), boric acid (H<sub>3</sub>BO<sub>3</sub>, A.R. grade), urea (CO (NH<sub>2</sub>)<sub>2</sub>, A.R. grade), decalin (A.R. grade), ethanol (C<sub>2</sub>H<sub>6</sub>O, A.R. grade), *p*-benzoquinone (BQ, 99%), dimethyl sulfoxide (DMSO, A.R. grade), potassium bromide (KBr, A.R. grade), and barium sulfate (BaSO<sub>4</sub>, A.R. grade) were purchased from Shanghai Sinopharm Chemical Reagent Company and used as received without purification. Dibenzothiophene (DBT, 98%), 4-methyl dibenzothiophene (4-MDBT, 97%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 97%), and tetradecane (99%) were obtained from Sigma-Aldrich and used without further purification.

**Synthesis of molybdenum oxide (MoO<sub>x</sub>):** 5.0 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O was dissolved in 40 mL of ultrapure water and heated at 55 °C until the water was boiled away, and a white solid was gained. Then the white solid was transferred to a tube furnace and heated to 700 °C for 2 h at a heating rate of 5 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere, and then allowed to cool to room temperature. A dark brown product was obtained and designated simply as “MoO<sub>x</sub>”.

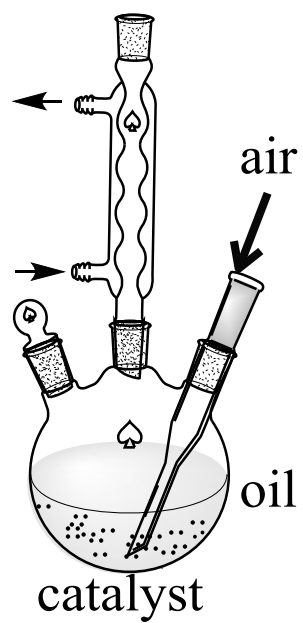
**Preparation of model oil:** Different model oils were prepared by dissolving DBT, 4-MDBT and 4,6-DMDBT in decalin to give solutions with a sulfur content of 500ppm. In addition, tetradecane was added into the model oil as an internal standard.

**Characterization methods:** Fourier transform infrared spectroscopy (FT-IR) spectra of both the reactants and products were obtained on a Nicolet Nexus 470 FT-IR spectrometer by using KBr pellets at room temperature. Ultraviolet-visible diffuse

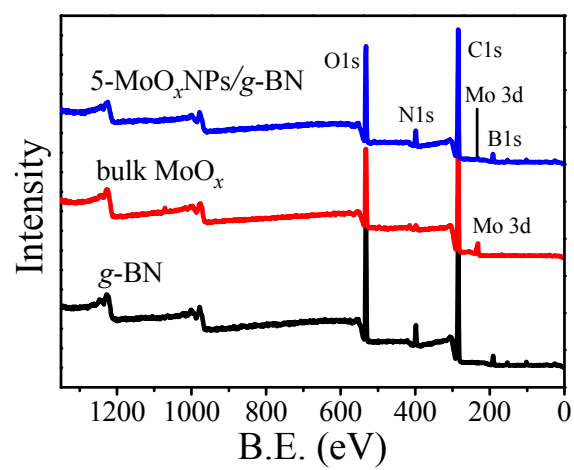
reflectance (UV-Vis DRS) spectra were measured with a UV-2450 UV/Vis spectrophotometer (Shimadzu, Japan) in the range of 200-800 nm. BaSO<sub>4</sub> was used as the reflectance standard. X-ray diffraction (XRD) measurements were obtained on a D8 ADVANCE X-ray diffraction using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  (Å)) with angle range from 10° to 80° (2 $\theta$ ) at a scanning rate of 7° min<sup>-1</sup>). Raman spectra were performed on a Thermo Scientific DXR Smart Raman spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Amicus spectrometer with Mg K $\alpha$  radiation. The morphology of samples was determined by a Hitachi H-700 transmission electron microscope (TEM). High resolution transmission electron microscopy (HR-TEM) analysis was performed using a JEOL EM-2010F instrument operating at accelerating voltage of 200 kV. The sample powder was ultrasonically dispersed in ethanol and the obtained suspensions were deposited on a lacey carbon film on a copper micro-grid. The nitrogen adsorption/desorption isotherms at 77 K were investigated with a TriStar II 3020 surface-area and porosity analyzer (Micromeritics Instrument Corporation, USA). X-band electron spin resonance (ESR) spectra were recorded at ambient temperature on a JES FA200 spectrometer. The O<sub>2</sub> temperature-programmed desorption (O<sub>2</sub>-TPD) was conducted by employing 50 mg sample in each measurement. The samples were firstly pretreated in O<sub>2</sub>/He at 300 °C for 60 min, then cooled down to 25 °C, and followed by turning the Ar flow into the system with a flow rate of 25 ml/min. The samples were heated from 50 °C to 700 °C at a rate of 10 °C/min. The concentration signals of the desorbed O<sub>2</sub> were monitored by a TCD detector. Electron paramagnetic resonance (EPR) spectra were obtained using a Bruker ESR JES-FA200 spectrometer

at 77 K.

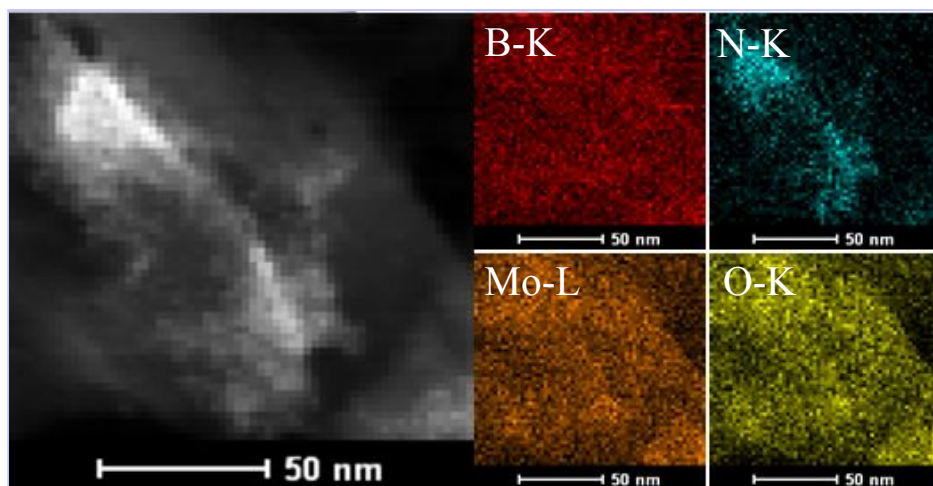
**Supplementary Figures:**



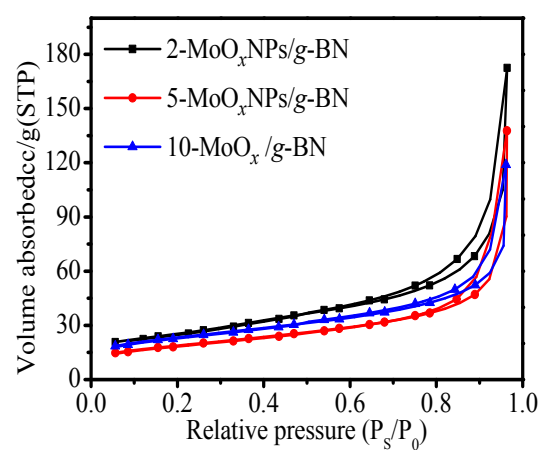
**Figure S1.** Oxidation desulfurization reactor schematic.



**Figure S2.** XPS of *g*-BN, bulk MoO<sub>x</sub> and 5-MoO<sub>x</sub>NPs/*g*-BN.

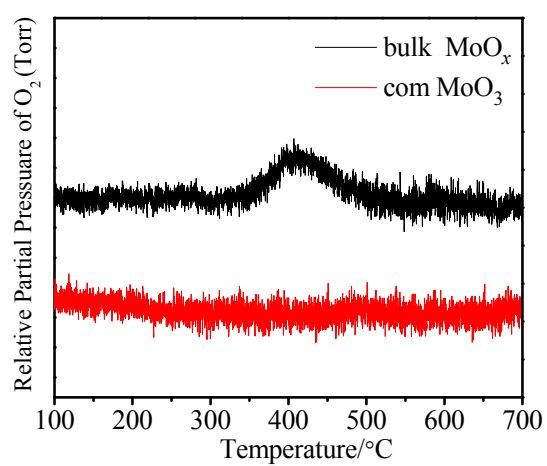


**Figure S3.** The elemental mapping images of 5-MoO<sub>x</sub>NPs/*g*-BN.

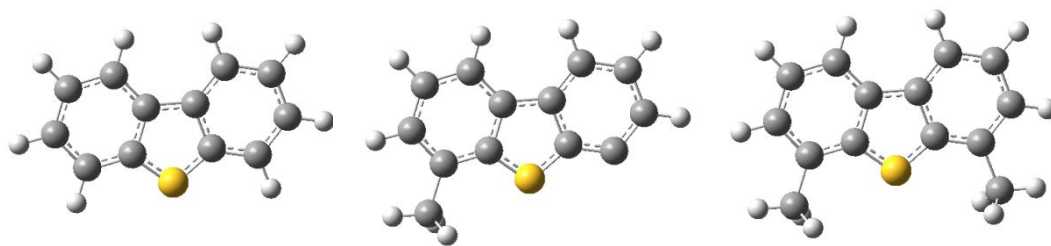


**Figure S4.** Nitrogen adsorption-desorption isotherms of a) 2-MoO<sub>x</sub>NPs/g-BN, b) 5-MoO<sub>x</sub>NPs/g-BN and c) 10-MoO<sub>x</sub>/g-BN.

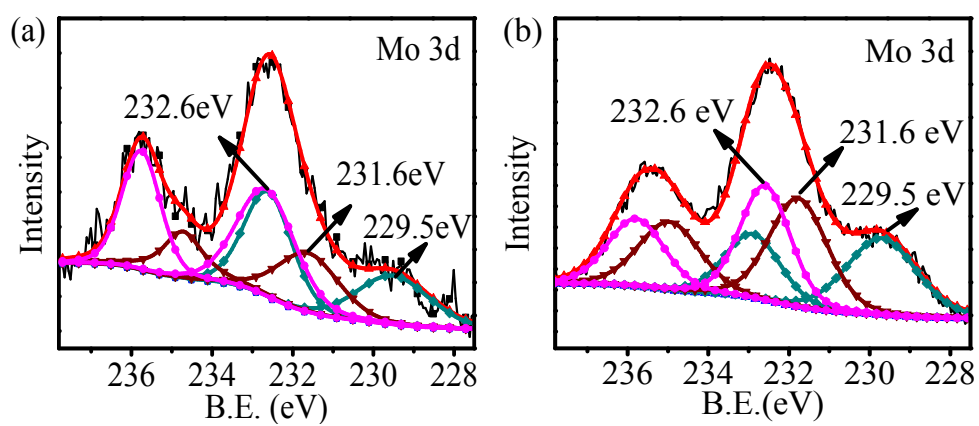




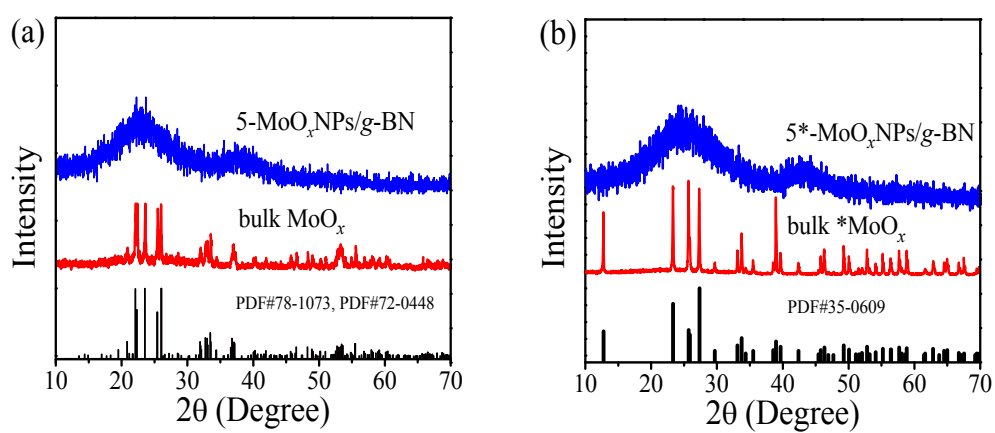
**Figure S5.** Oxygen temperature-programmed desorption (O<sub>2</sub>-TPD) for com MoO<sub>3</sub> and bulk MoO<sub>x</sub> samples.



**Figure S6.** Molecular structures of DBT, 4-MDBT, 4,6-DMDBT (from left to right).



**Figure S7.** XPS Mo 3d spectra of 5-MoO<sub>x</sub>NPs/g-BN catalysts (a) fresh catalyst (b) used catalyst.



**Figure S8.** XRD patterns of (a) catalysts prepared under a nitrogen atmosphere, (b) catalysts of (a) after O<sub>2</sub> treatment.

## Supplementary Tables:

**Table S1.** Catalytic oxidative desulfurization of different supported catalysts in previous reports.

Entry	Catalyst	Oxidant	TOF/h <sup>-1</sup>	Ref
1	MoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	17.74	<sup>1</sup>
2	MoO <sub>3</sub> /SiO <sub>2</sub>	O <sub>2</sub>	1.36	<sup>2</sup>
3	WO <sub>3</sub> /ZrO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	28.48	<sup>3</sup>
4	WO <sub>3</sub> /SBA-15	H <sub>2</sub> O <sub>2</sub>	10.85	<sup>4</sup>
5	MoO <sub>x</sub> NPs/g-BN	O <sub>2</sub>	37.50	this work

**Table S2.** Comparison of catalytic oxidative desulfurization of sulfur compounds by different molybdenum oxide catalysts.

Entry	Catalysts	TOF/h <sup>-1</sup>	Sulfur removal/%
1	com MoO <sub>3</sub>	8.54	8.9
2	bulk MoO <sub>x</sub>	29.14	60.7

**Table S3.** Comparison of catalytic oxidative desulfurization of sulfur compounds by different catalysts.

Entry	Catalysts	Specific surface area (m <sup>2</sup> /g)	TOF/h <sup>-1</sup>	Sulfur removal/%
1	2-MoO <sub>x</sub> NPs/g-BN	200	23.83	33.1
2	5-MoO <sub>x</sub> NPs/g-BN	108	37.50	100
3	10-MoO <sub>x</sub> /g-BN	60	30.12	77.3

**Table S4.** Content of different forms of Mo in the near-surface layers of catalysts.

<b>Catalysts</b>	Content of different forms of Mo (%)		
	Mo <sup>4+</sup>	Mo <sup>5+</sup>	Mo <sup>6+</sup>
fresh catalyst	35	35	30
used catalyst	33	35	32



## References:

- (1) Akbari, A.; Omidkhah, M.; Darian, J. T. Investigation of process variables and intensification effects of ultrasound applied in oxidative desulfurization of model diesel over  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst. *Ultrason. Sonochem.* **2014**, *21*, 692–705.
- (2) Zhang, W.; Xiao, J.; Wang, X.; Miao, G.; Ye, F. Y.; Li, Z. Oxidative Desulfurization Using in-Situ-Generated Peroxides in Diesel by Light Irradiation. *Energy & Fuels* **2014**, *28*, 5339–5344.
- (3) Hasan, Z.; Jeon, J.; Jhung, S. H. Oxidative desulfurization of benzothiophene and thiophene with  $\text{WO}_x/\text{ZrO}_2$  catalysts: effect of calcination temperature of catalysts. *J. Hazard. Mater.* **2012**, *205-206*, 216–221.
- (4) González, J.; Wang, J. A.; Chen, L. F.; Manríquez, M. E.; Dominguez, J. M. Structural Defects, Lewis Acidity, and Catalysis Properties of Mesostructured  $\text{WO}_3/\text{SBA-15}$  Nanocatalysts. *J. Phys. Chem. C* **2017**, *121*, 23988–23999.