

Supplementary information

Coverage of surfactants on polyoxometalate tunes the selectivity of alkenes epoxidation

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1. Experimental Procedures

1.1. Materials

Sodium tungstate dihydrate ($\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), potassium chloride (KCl), sodium perchlorate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$), hydrogen peroxide (H_2O_2), and acetone ($\text{C}_3\text{H}_6\text{O}$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Dodecyltrimethylammonium bromide (DTB), sodium carbonate (Na_2CO_3), decamethonium bromide ($\text{C}_{16}\text{H}_{38}\text{Br}_2\text{N}_2$), acetonitrile (MeCN), cyclohexene (C_6H_{10}), cyclopentene (C_5H_8), 1-hexene (C_6H_{12}), and 3-methyl-1-cyclohexene (C_7H_{12}) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Cyclooctene (C_8H_{14}), 1-octene (C_8H_{16}), and ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. 1-methyl-1-cyclohexene (C_7H_{12}) was obtained from Anhui Senrise Technologies Co., Ltd.

1.2. Characterizations

The morphologies of the samples were characterized by the scanning electron microscopy (SEM, Hitachi S4800). Fourier transform infrared spectroscopy (FTIR) spectra were carried out on a NICOLET 6700 Spectrum. Thermogravimetric analysis (TGA) was tested by TG209F1 under a N_2 atmosphere. Raman spectra were recorded on a Renishaw in Via Reflex spectrometer (laser with excitation wavelength 532 nm). Electron paramagnetic resonance (EPR) spectra signals of radicals were detected on Bruker ESRA-300. Small angle x-ray scattering of the samples were measured with Xeuss 3.0 UHR. X-ray diffraction (XRD) patterns of samples were run on a Bruker D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) was measured by Scientific K-Alpha using $\text{Al K}\alpha$ ($h\nu = 1486.6 \text{ eV}$) radiation source. The binding energy was calibrated with the measured C1s peak at 284.6 eV.

1.3. Synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]$ (Donated as P_2W_{18})

P_2W_{18} was synthesized following the procedure described in the literature.¹ Briefly, 30 g of $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 35 mL of deionized water. To this solution, 25 mL of 4 M HCl was added dropwise with vigorous stirring. Once the solution became clear, 25 mL of 4 M H_3PO_4 was slowly introduced. The mixture was then heated at 120 °C for 12 hours, resulting in a bright yellow solution. The solution was transferred

to a beaker and allowed to cool. Subsequently, 15 g of KCl was added, causing the formation of a yellow precipitate. After stirring for an additional 10 minutes, the precipitate was filtered out. The solid was then redissolved in 65 mL of deionized water, and the resulting yellow solution was covered with a piece of plexiglass and heated at 80 °C for 48 hours. After 48 hours, the plexiglass cover was removed to accelerate evaporation. Upon the appearance of yellow crystals, the solution was taken out of the oven and cooled to room temperature. The yellow crystals were filtered, dried in an oven at 60 °C, and set aside.

1.3. Synthesis of Na₁₂[α -P₂W₁₅O₅₆] (Donated as P₂W₁₅)

P₂W₁₅ was synthesized following the procedure outlined in the literature.² Briefly, 7.7 g of P₂W₁₈ was dissolved in 25 mL of deionized water. To this solution, 7 g of NaClO₄·H₂O was added, and the mixture was stirred for 20 minutes. The resulting solution was then refrigerated at 4 °C for 3 hours. The precipitate formed was filtered, and the filtrate was mixed with 20 mL of 1 M Na₂CO₃ solution while stirring. A white precipitate gradually formed over 30 minutes, which was then filtered and dried at 60 °C.

1.4. Synthesis of POMs-based nanosheets (PD1, PD2, PD3)

0.2 g of P₂W₁₅ and 0.125 g of DTB were dissolved in 20 mL of deionized water. The solution gradually became clear during stirring. After stirring for 2 hours, 20 mL of acetone was slowly added to the clear solution. The solution became turbid over time and, after 6 hours, the product PD3 was obtained by centrifugation. The preparation of PD1 and PD2 followed the same procedure as for PD3, with the only difference being the reduced amounts of DTB, which were 0.031 g and 0.063 g, respectively.

1.5. Epoxidation of cyclooctene

The substrate, catalyst, and H₂O₂ were added to a 5 mL tube containing acetonitrile as the solvent. The tube was then placed in an oil bath. Upon completion of the reaction, a small portion of the reaction mixture was taken and extracted with ethyl acetate. The extracted solution was quantitatively analyzed using a G3540-60005 chromatograph equipped with an HP-5 capillary column.

After the reaction, the mixture in the tube was transferred to a centrifuge tube and slowly evaporated until a viscous solid remained. The solid was washed with a small

amount of ethyl acetate and then dried in an oven at 60 °C for 12 hours. The dried catalyst was reused for recycling reactions.

1.6. GC and GC-MS

The quantitative measurements of conversion of substrate and selectivity of products were made on a gas chromatography (Agilent 8860A) equipped with a flame ionization detector (FID) and Agilent Technology 19091J-413 capillary column (30 m × 0.32 mm × 0.25 µm) using high pure N₂ as the carrier gas. Standard analysis conditions: injector temperature 300 °C, detector temperature 300 °C, column temperature program: 40 °C (hold 2 min) raised up to 200 °C (hold 0 min) at a rate of 10 °C/min. Gas chromatography–mass spectrometry analysis was performed on an Agilent 7890B-5977A GC-MS using an HP-5 capillary column (30 m × 0.25 mm × 0.25 µm) with high pure He as the carrier gas.

1.7. In-situ EPR

The in situ EPR spectra were obtained using a Bruker A300 spectrometer equipped with a 100 kHz field modulation and a modulation amplitude of 150 G. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was chosen as a spin trap. For trapping OH radicals, a mixture containing 10 mg of catalyst and 2 µL of DMPO was dispersed in 1 mL of deionized water. The reaction was initiated by introducing 500 µL of H₂O₂ aqueous solution (30%) at 70 °C. After 10 minutes of reaction, a small aliquot of the mixture was collected, followed by catalyst removal via centrifugation at 10,000 rpm for 3 minutes. The resulting supernatant was transferred to a quartz capillary, and the EPR spectra were recorded at room temperature. For the detection of OOH radicals, methanol was used as the solvent instead of deionized water.

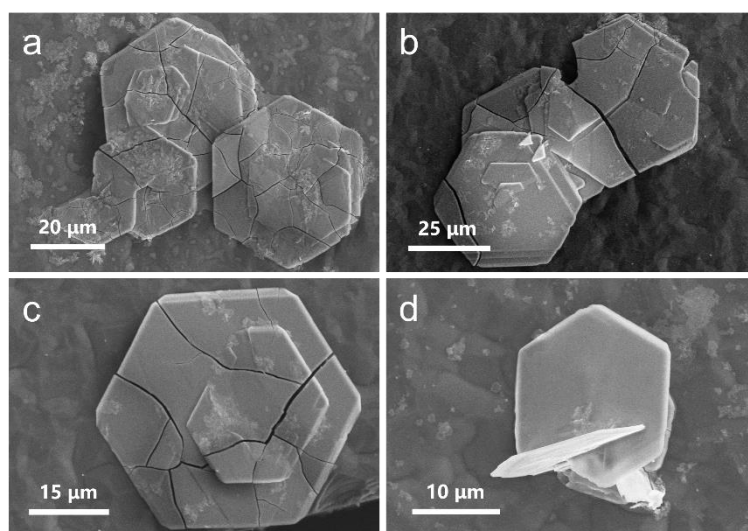


Fig. S1. SEM images of PD1.

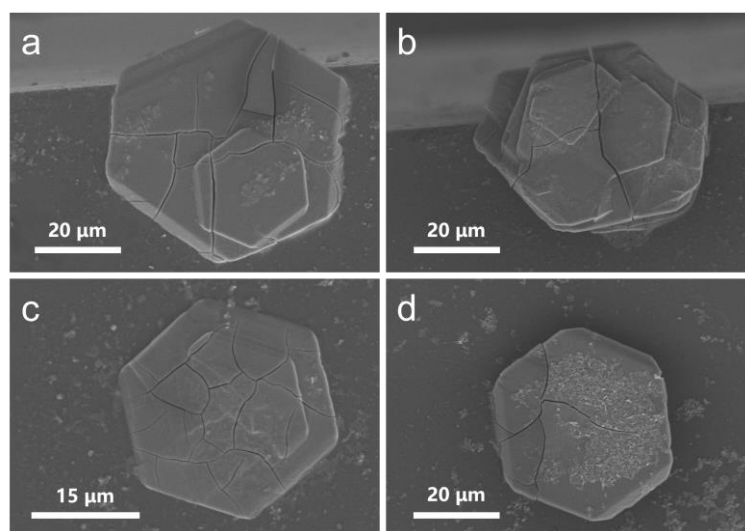


Fig. S2. SEM images of PD2.

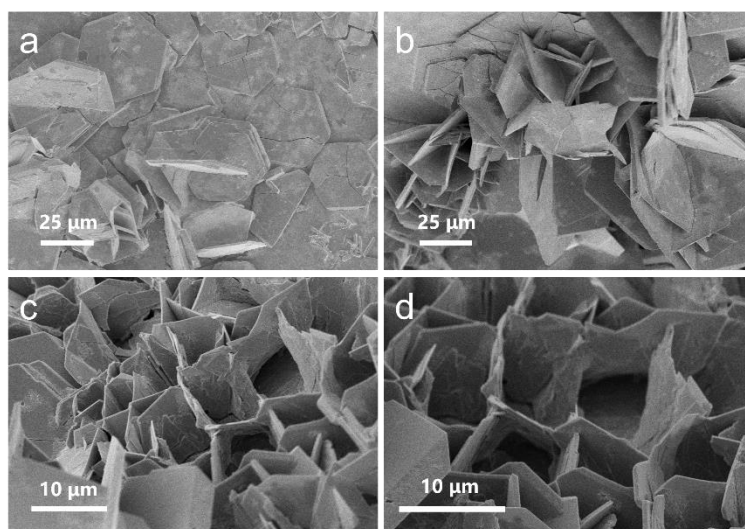


Fig. S3. SEM images of PD3.

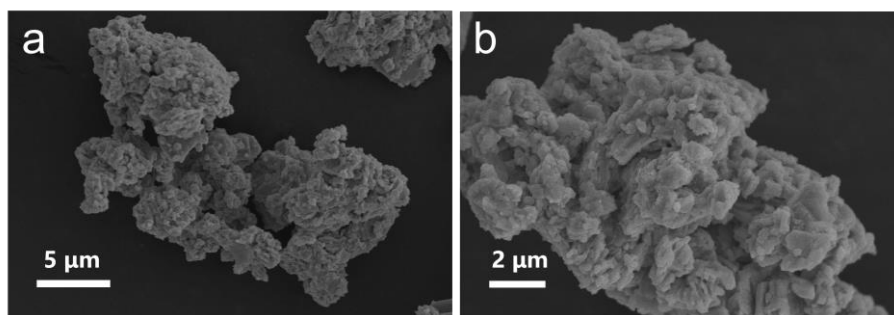


Fig. S4. SEM images of P_2W_{15} .

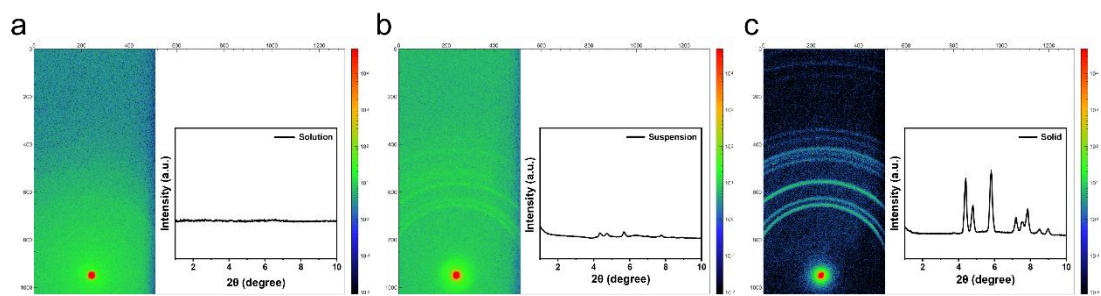


Fig. S5. SAXS data of different states during formation of PD3, (a) solution, (b) suspension, and (c) solid.

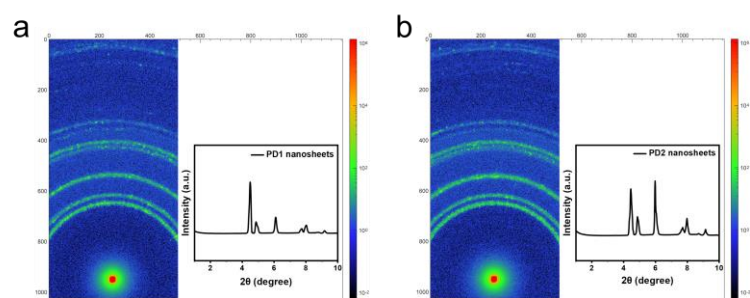


Fig. S6. SAXS data of (a) PD1 nanosheets and (b) PD2 nanosheets.

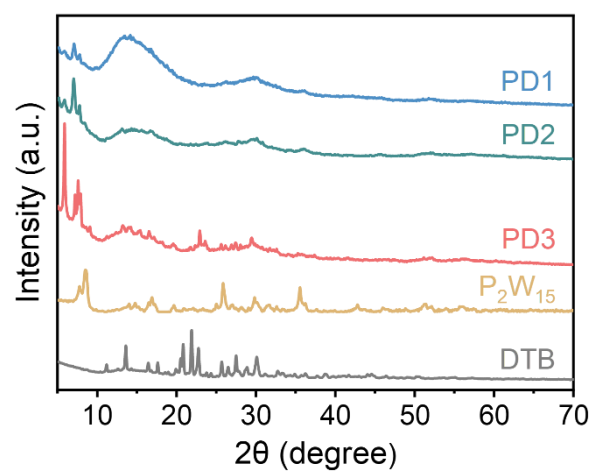


Fig. S7. XRD patterns of PD1, PD2, PD3, P₂W₁₅, and DTB.

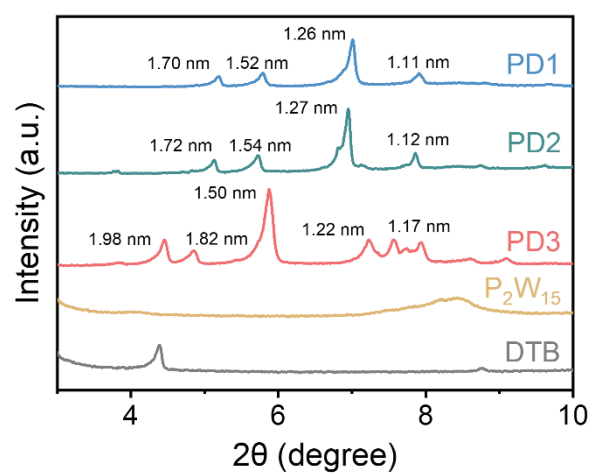


Fig. S8. SAXRD patterns of PD1, PD2, PD3, P₂W₁₅, and DTB.

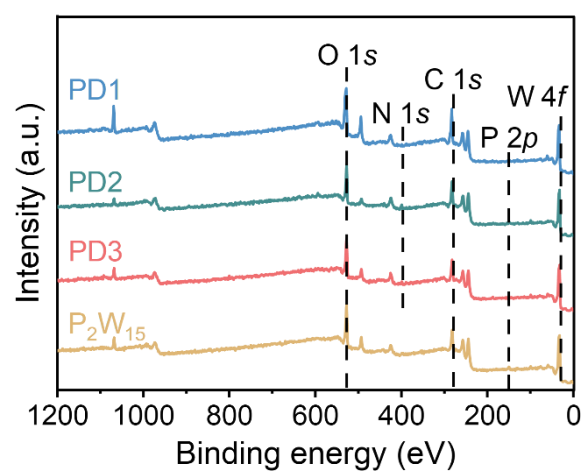


Fig. S9. XPS survey spectra of PD1, PD2, PD3, and P_2W_{15} .

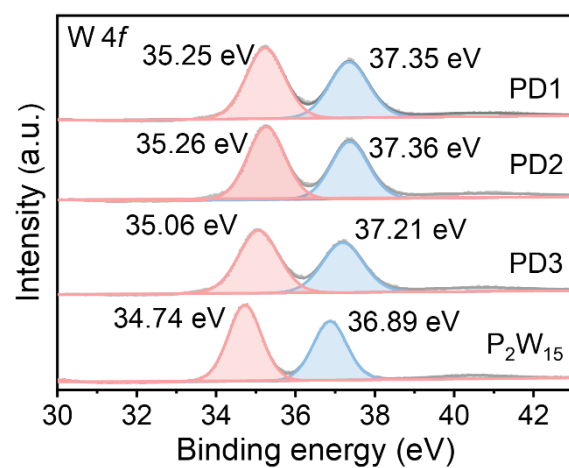


Fig. S10. High-resolution XPS spectra of W 4f in PD1, PD2, PD3, and P₂W₁₅.

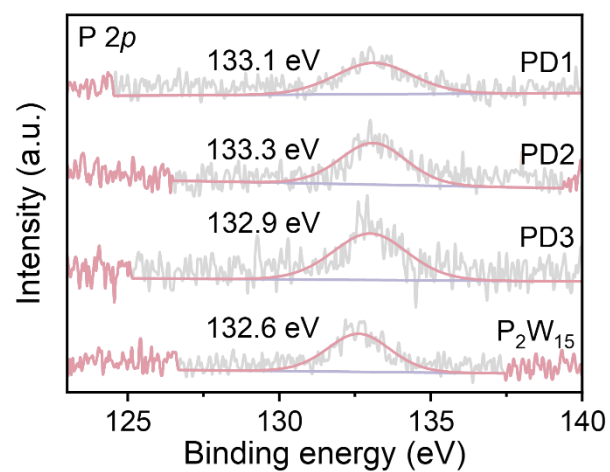


Fig. S11. High-resolution XPS spectra of P 2*p* in PD1, PD2, PD3, and P₂W₁₅.

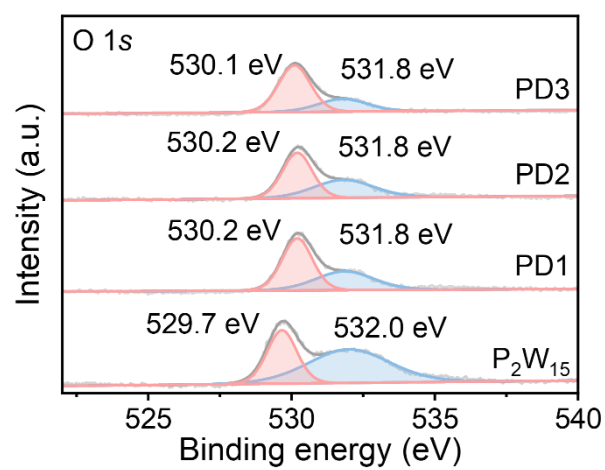


Fig. S12. High-resolution XPS spectra of O 1s of PD1, PD2, PD3, and P₂W₁₅.

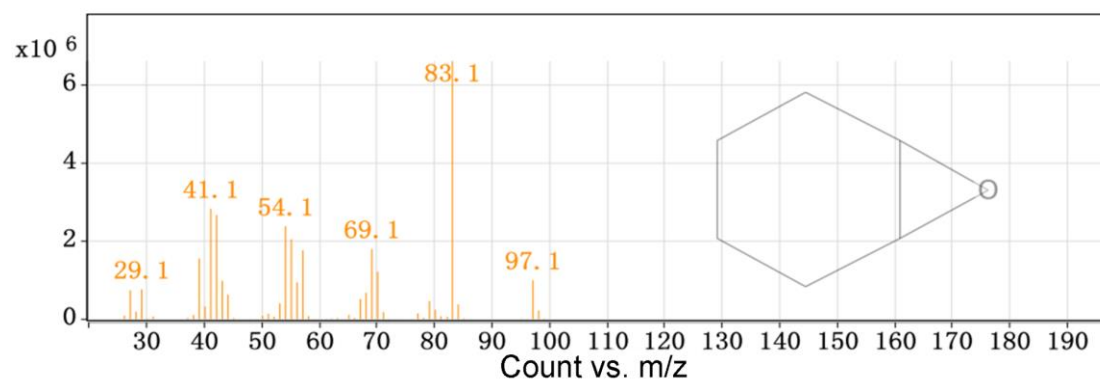


Fig. S13. The mass spectra of target product generated by epoxidation of cyclohexene.

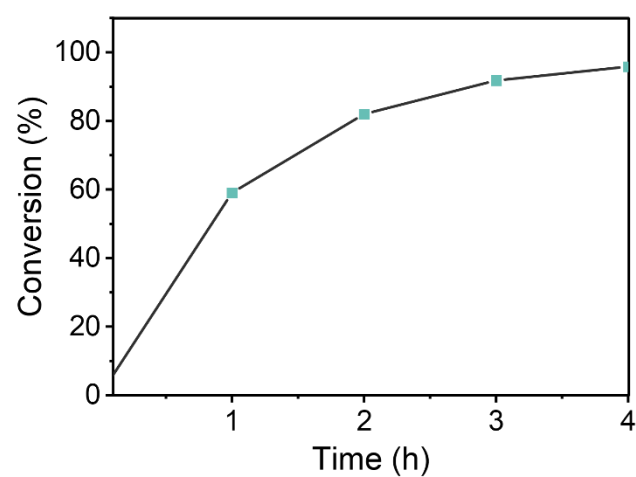


Fig. S14. Catalytic performance of PD3 with different times (1 mmol cyclohexene, 30 mg PD3, 3.5 mmol H₂O₂, 2 mL acetonitrile, 70 °C).

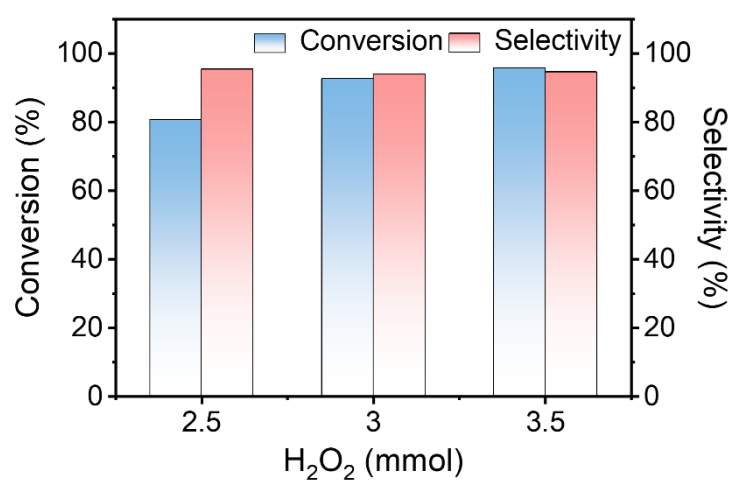


Fig. S15. Effect of different amounts of H₂O₂, including 2.5 mmol (283 μ L), 3 mmol (340 μ L), and 3.5 mmol (397 μ L) H₂O₂, on the epoxidation of cyclohexene (1 mmol cyclohexene, 30 mg PD3, 2 mL acetonitrile, 70 $^{\circ}$ C, 4 h).

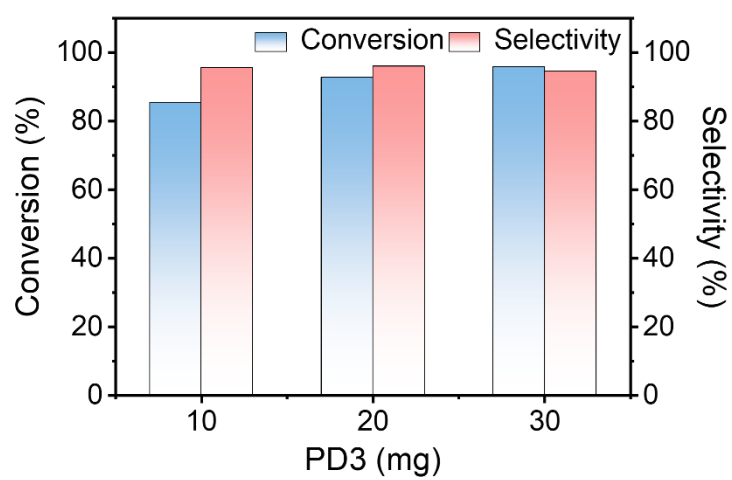


Fig. S16. Effect of different catalyst amounts on cyclohexene epoxidation (1 mmol cyclohexene, 3.5 mmol H_2O_2 , 2 mL acetonitrile, 70 °C, 4 h).

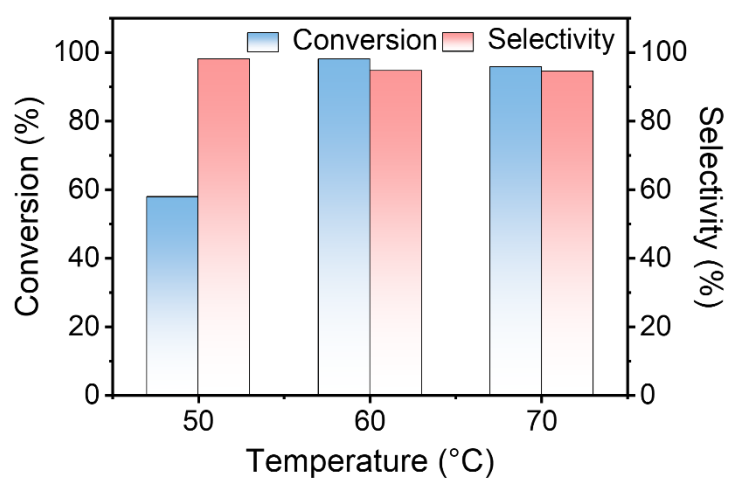


Fig. S17. Effect of temperature on cyclohexene epoxidation (1 mmol cyclohexene, 30 mg PD3, 3.5 mmol H₂O₂, 2 mL acetonitrile, 4 h).

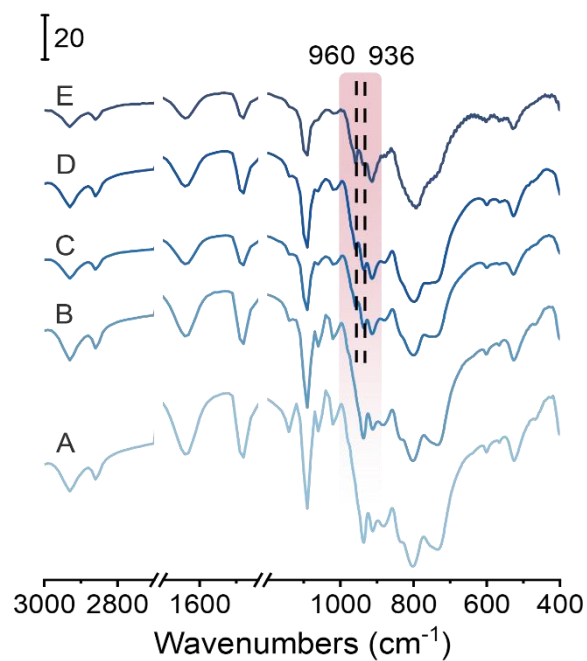


Fig. S18. The FTIR spectra of **A** (PD3), **B** (PD3/acetonitrile), **C** (PD3/acetonitrile/H₂O₂), **D** (PD3/acetonitrile/H₂O₂/cyclohexene, 0.5 h), and **E** (PD3/acetonitrile/H₂O₂/cyclohexene, 4 h) at 70 °C.

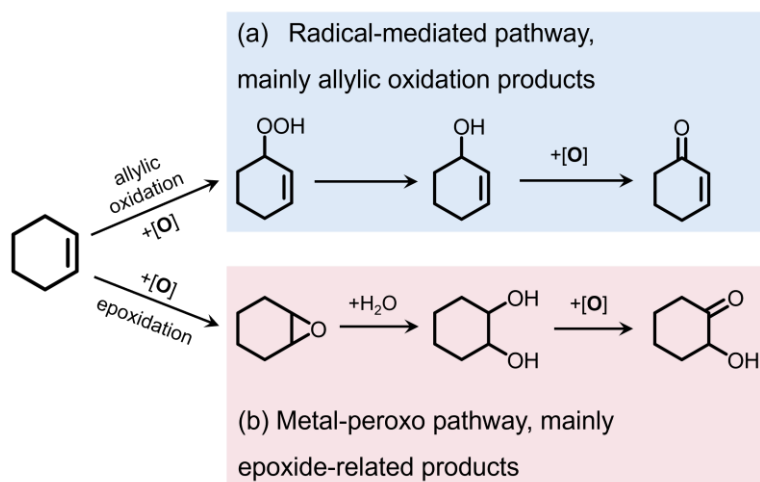


Fig. S19. Cyclohexene oxidation with H₂O₂ via (a) radical-mediated pathway, mainly allylic oxidation products, and (b) metal-peroxo pathway, mainly epoxide-related products.

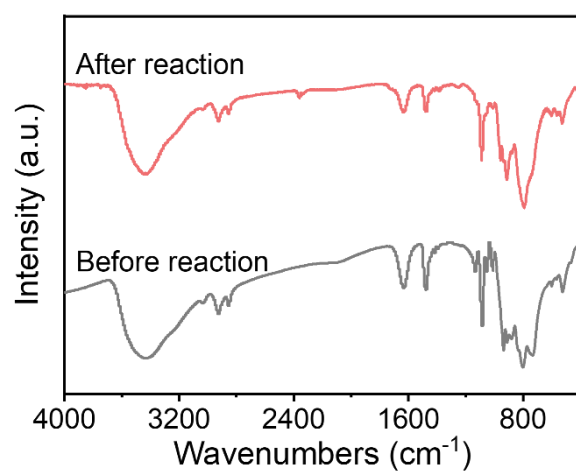


Fig. S20. FTIR spectra of PD3 before and after catalytic reaction.

Table. S1 Comparison of the epoxidation of cyclohexene performance of PD3 nanosheets with recently reported catalysts.

| Entry | Catalysts | Oxidant | T (°C) | t (h) | C% (S%) | Ref. |
|-------|---|-------------------------------|--------|-------|-------------|-----------|
| 1 | PD3 | H ₂ O ₂ | 70 | 4 | 95.8 (94.6) | This work |
| 2 | [Ni(4,4'-bpy) ₂] ₂ [V ^{IV} ₇ V ^V ₉ O ₃₈ Cl]·(4,4'-bpy)·6H ₂ O | O ₂ | 35 | 2 | 95 (86) | 3 |
| 3 | PMo ₁₁ Co@UiO-66 | TBHP | 60 | 12 | 55 (69) | 4 |
| 4 | K ₆ Na ₄ [H ₃₂ {Nd ₄ (WO ₄)(H ₂ O) ₁₆ [W ₇ O ₂₂ (O ₂) ₂] ₄ } ₃]·105H ₂ O | H ₂ O ₂ | 75 | 6 | 78.9 (53.2) | 5 |
| 5 | H ₂ O-WO _x @C-18.7 | H ₂ O ₂ | 75 | 24 | 71.1 (66.3) | 6 |
| 6 | PW ₁₂ /MIL-101 | H ₂ O ₂ | 50 | 3 | 72 (76) | 7 |
| 7 | s-HNb ₃ O ₈ | H ₂ O ₂ | 60 | 1 | 78 (41) | 8 |

Table. S2 Controlled experiment of epoxidation of cyclohexene.^[a]

| <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">A</div> <div style="text-align: center;">B</div> <div style="text-align: center;">C</div> <div style="text-align: center;">D</div> </div> | | | | | | | |
|---|--------------------------------|----------------|-----------------|----------|----------|----------|-------|
| Entry | Catalyst | Conversion (%) | Selectivity (%) | | | | |
| | | | A | B | C | D | Other |
| 1 ^[b] | PD3 | 0.44 | 3 | 0 | 0 | 0 | 97 |
| 2 | P ₂ W ₁₅ | 1.57 | 49 | 6 | 0 | 0 | 45 |
| 3 | P ₂ W ₁₈ | 0.41 | 1 | 0 | 0 | 0 | 99 |

[a] Reaction conditions: cyclohexene (1 mmol), catalyst (30 mg), H₂O₂ (2.5 mmol), MeCN (2 mL), 70 °C, 5 h.

[b] Without H₂O₂.

Table. S3 The acidity content of PD1, PD2, and PD3.

| Catalysts | Quality (mg) | Temperature (°C) | BA ($\mu\text{mol/g}$) | BA ($\mu\text{mol/g}$) | Total acid ($\mu\text{mol/g}$) |
|-----------|-----------------|---------------------|-----------------------------|-----------------------------|-------------------------------------|
| PD1 | 100 | 19.2 | 3.17 | 37.22 | 40.40 |
| PD2 | 100 | 19.2 | 3.23 | 43.60 | 46.83 |
| PD3 | 100 | 19.2 | 4.93 | 55.64 | 60.58 |

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