Supplementary Information (SI) for Dalton Transactions.
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Cu-exchanged phosphomolybdic acid induced solvent effect to enhance alkene epoxidation with H_2O_2

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Experimental section

Materials

$CuSO_4 \cdot 5H_2O$, phosphomolybdic acid, $Ba(OH)_2$, Benzene, triphenylamine, anhydrous $FeCl_3$, 1, 2-dichloroethane, CH_3OH were purchased from National Medicines Corporation Ltd. of China, all of which were of analytical grade and were used as received. Formaldehyde dimethyl acetal and 30% wt H_2O_2 were obtained from Annaiji. Cyclooctene, 1-hexene, 1-octene, styrene, α-methyl styrene, α-piene were purchased from Aldrich. 1,4-dioxane (chromatographic grade) was purchased from TCI, the peroxides levels were verified by using KI-starch test paper, and no blue coloration developed, indicating the absence of peroxides at detectable levels.

Characteristic techniques

Thermogravimetry (TG) were carried out using the Japan HITACHI STA200 with a N_2 flow and heating rate of 10 ^{o}/min, from room temperature to 800 ^{o}C. XPS measurements were made on a VGESCA LAB MK-II X-ray electron spectrometer using Al Ka radiation. Transmission electron microscopy (TEM), High resolution transmission electron microscopy (HR-TEM) and high angle annular dark field scan transmission electron microscopy (HAADFSTEM) imaging were taken with a H8100-IV electron microscope operating at 200 kV. N_2 adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 110 ^{o}C for 8 h before measurements. Specific surface areas were calculated using BET model. The pore size distributions were calculated from N_2 desorption isotherms by the non-local density functional theory (NLDFT) method. ICP-AES analysis was used to determine the PMA loading by using a Perkin-Elmer plasma 40 emission spectrometer. Solid and liquid FT-IR spectra were recorded on a Nicolet

AVATAR 370 DTGS spectrometer in the range 4000-500 cm^{-1}. DRS solid UV-vis spectra were recorded on a Shimadzu UV-2400PC spectrophotometer using a $BaSO_4$ plate as a reference. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer (40 kV, 30 mA), using Ni filtered Cu Ka radiation. Liquid ^{31}P MAS NMR spectra ($NH_4H_2PO_4$ as the standard) were recorded on a 400 MHz Bruker spectrometer.

Synthesis of composites PMA/POPs and CuPMA/POPs

Triphenylamine (NPh_3) functionalized POPs support was synthesized with a simple one-step Friedel-Crafts reaction using benzene and NPh_3 as the monomer, formaldehyde dimethyl acetal as the external cross-linker according to the related literature [1]. Cu substituted phosphomolybdic acid (CuPMA) was prepared followed with a well-established analogous cation-exchange procedure for cobalt salts, as commonly used for various transition metal salts of heteropoly acids according to the literature [2]. The 30 wt% Cu-PMA or PMA supported POPs catalysts were gained as follows, the as-synthesized POPs support was added into the CH_3OH solution containing a certain of CuPMA or PMA. The mixture was stirred at room temperature for 24 h, then the solid products was recovered through filtration and washed with methanol in a Soxhlet extractor for 24 h. The resultants were dried in vacuum at 60 °C for 8 h, and denoted as PMA/POPs and CuPMA/POPs, respectively. The actual CuPMA loading in the CuPMA/POPs catalyst, as determined by ICP-OES, is 23.8 wt%, which is slightly lower than 30 wt% used during the initial preparation of the supported materials. The difference can likely be attributed to a partial loss of the CuPMA species, such as dissolution or incomplete immobilization, during the synthesis and subsequent washing steps. Besides, the amount of Cu and Mo were calculated according to the ICP-OES results, where the molar ratio of Cu/Mo/H is 1:12:1 (Table S2).

Alkene epoxidation with H_2O_2 as oxidant

The alkene epoxidation reaction was used as the probe reaction to investigated the catalytic properties of composites CuPMA/POPs and PMA/POPs with H_2O_2 as oxidant in different solvents. The oxidation reaction was conducted in temperature-controlled glass vessels at beforehand designed temperature under vigorous stirring. The detail procedure as follows: 10 mg catalyst was added in a 10 ml round bottom flask containing a certain of solvent and alkene, next the whole device was placed in an oil bath with a reflux condenser. The reaction was started via the addition of H_2O_2, the oxidation products were quantified by Fuli GC-9790II gas chromatograph with a HP-5 capillary column.

Reference

[1] B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan, T. Li, *Adv. Mater.,* ***2012****, 24,* 3390–3395.

[2] S. Benadji, S. Benadji, L. Dermeche, N. Salhi, E. Cadot, C. Rabia, *Catal. Lett.*, ***2013***, 143, 749-755.

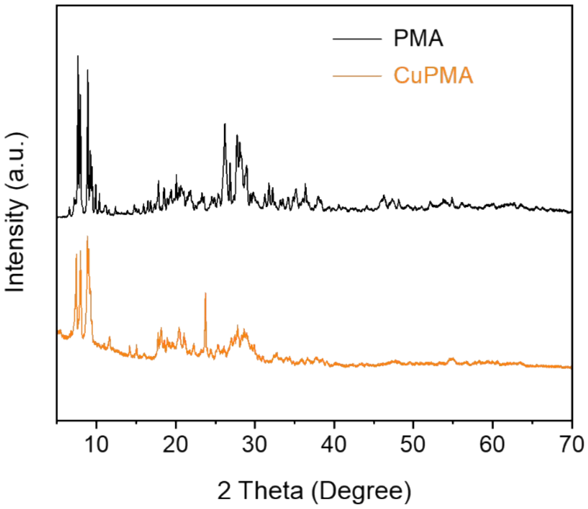

Figure S1. XRD patterns of PMA and CuPMA.

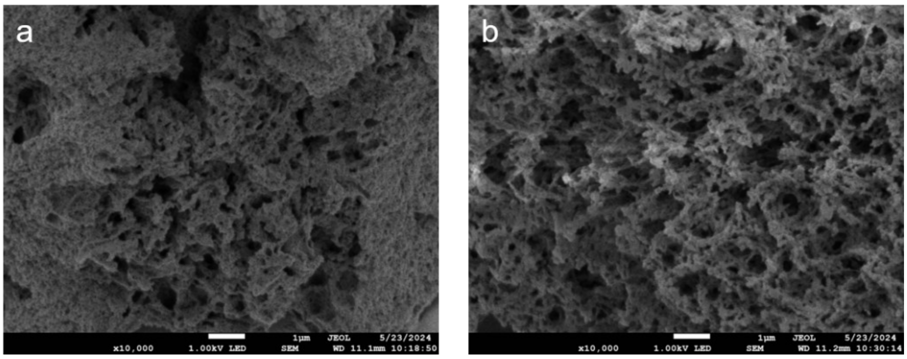

Figure S2. SEM images of (a) CuPMA and (b) CuPMA/POPs.

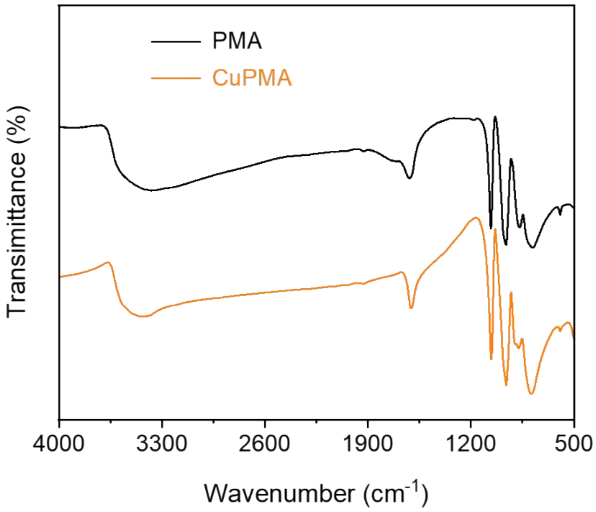

Figure S3. FTIR spectra of PMA and CuPMA.

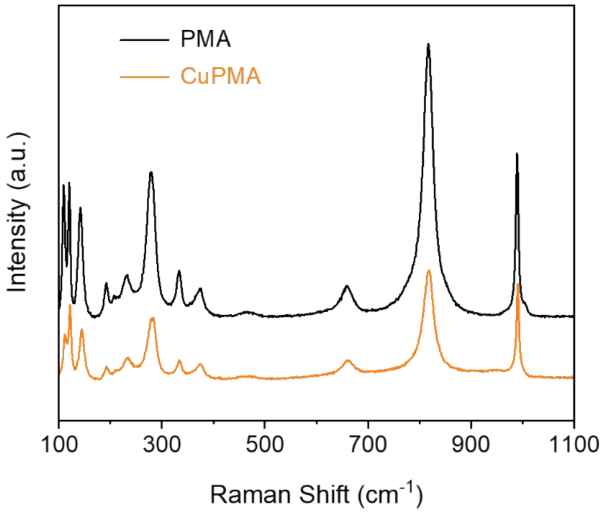

Figure S4. Raman spectra of PMA and CuPMA.

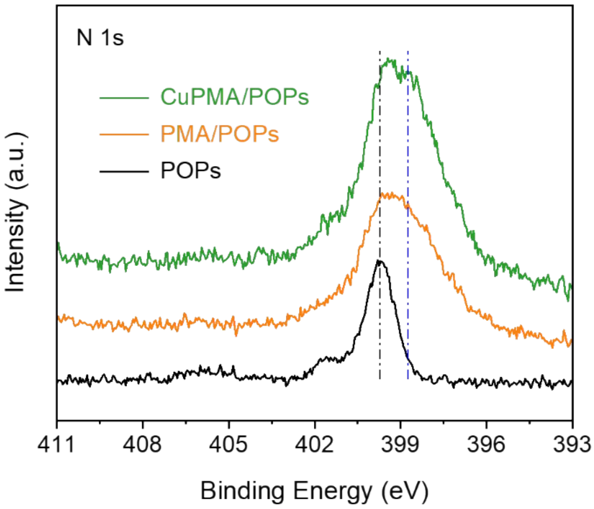

Figure S5. XPS spectra of N 1s for POPs, PMA/POPs and CuPMA/POPs.

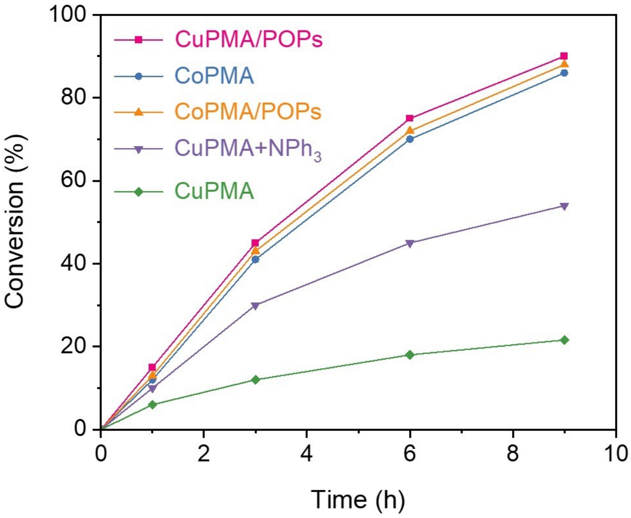

Figure S6. Time-course tests over different catalysts. Reaction conditions: catalyst, 10 mg; solvent, 1, 4-dioxane, 1 mL; H_2O_2 2 mmol; reaction temperature, 80 ^oC.

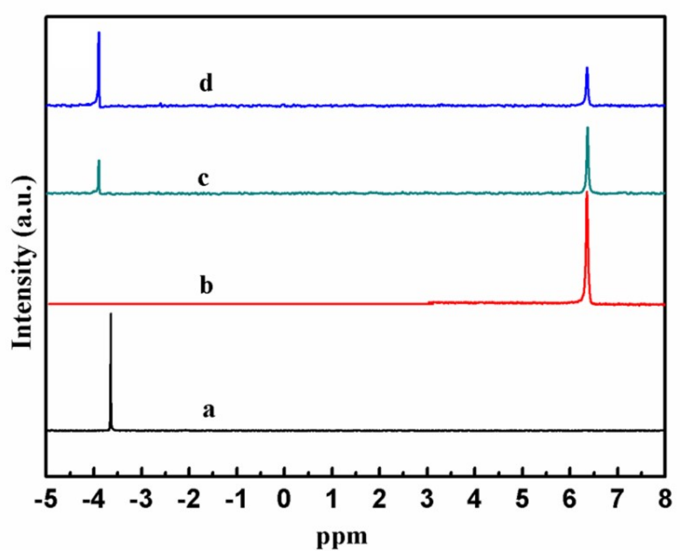

Figure S7. Liquid ^{31}P NMR with CD_3CN as solvent, in which (a) CoPMA, (b) CoPMA+H_2O_2, (c) CoPMA+H_2O_2+cyclooctene 3 h and (d) CoPMA+H_2O_2+cyclootene 5 h.

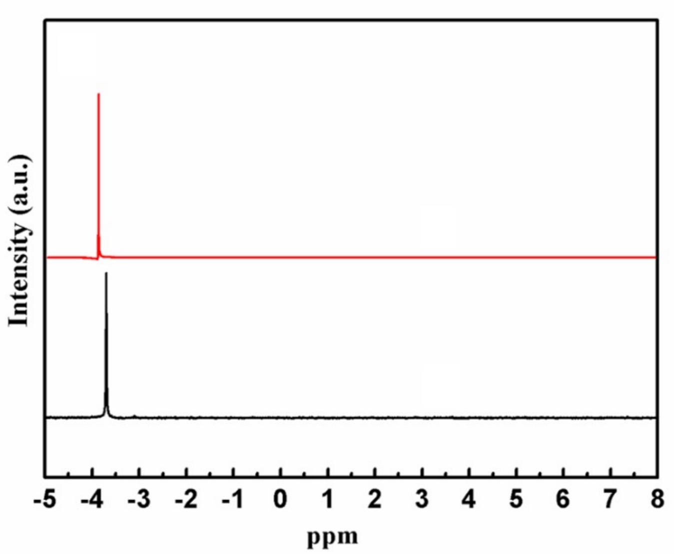

Figure S8. Liquid ^{31}P NMR of CuPMA (Black) and CuPMA+H_2O_2 (Red) in CD_3CN solvent.

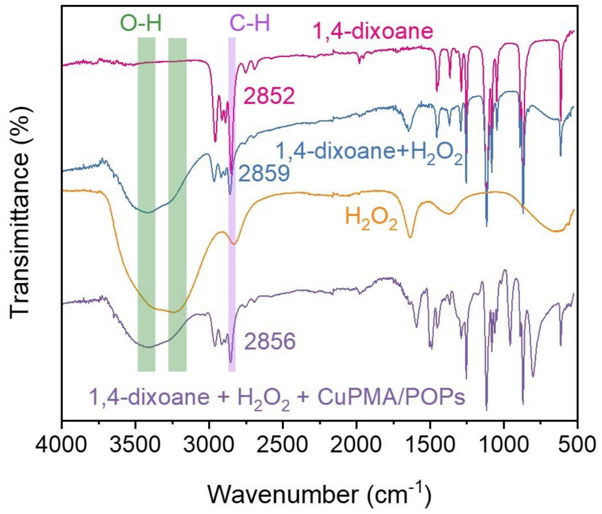

Figure S9. FT-IR spectra of CuPMA/POPs with 1,4-dioxane and H_2O_2.

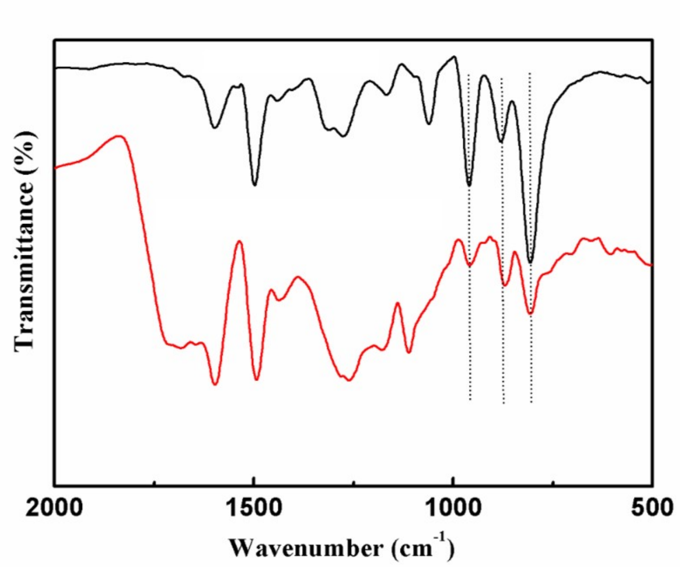

Figure S10. FTIR spectra of CuPMA/POPs before (Black) and after (Red) reaction.

Table S1. The physical and chemical parameters of POPs, PMA/POPs and CuPMA/POPs.

Catalyst	Cu loading (mmol/g)	Mo loading (mmol/g)	S_{BET}[a] (m^2/g)	V_p[b] (m^3/g)	D_p[c] (nm)
POPs	-	-	664.0	0.80	7.5
PMA/POPs	-	1.53	555.0	0.68	7.8
CuPMA/POPs	0.13	1.61	527.4	0.66	8.1

[a] Surface area calculated from nitrogen adsorption isotherms at 77.3 K using BET equation.

[b] Pore volume calculated from nitrogen isotherm at $P/P_0 = 0.995$, 77.3 K.

[c] Average pore size calculated by BarretteJoynereHalenda (BJH) adsorption mode.

Table S2. The elemental analysis of POPs, PMA/POPs and CuPMA/POPs via ICP-OES.

Catalyst	Cu (mmol/g)	Cu (wt%)	Mo (mmol/g)	Mo (wt%)
POPs	-	-	-	-
PMA/POPs	-	-	1.53	14.6
CuPMA/POPs	0.13	8.32	1.61	15.4