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Supporting Information

Ternary hybrid CuO-PMA-Ag sub-1 nm nanosheet heterostructures

Junli Liu,[a] Mingxin Wang, [a] Maria C. Dipalo,[a] Jing Zhuang, [a] Wenxiong Shi,[b] and Xun Wang[a]**

Materials

Copper nitrate ($Cu(NO_3)_2 \cdot 6H_2O$), phosphomolybdic acid (PMA), silver nitrate ($AgNO_3$), ethanol, hexane, cyclohexane, chloroform and oleic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Oleylamine was bought from J&K Scientific LTD. Cyclohexene, 1-octene and cis-stilbene were purchased from Alfa Aesar. All chemicals were used as received without further purification.

Characterizations

TEM was tested on a Hitachi H-7700 at 100 KV. High resolution transmission electron microscopy (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were characterized by a Tecnai G2 F20 S-Twin high-resolution transmission electron microscope at 200 KV. XRD measurement was taken with a BrukerD8 Advance using Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectra (XPS) were recorded on a PHI Quantera SXM spectrometer using monochromatic Al KαX-ray sources (1486.6 eV). ICP-OES was measured on iCAP 6300 (ThermoFisher corporation). Small angle X-ray diffraction (SAXRD) characterization was carried on a Bruker D8 X-ray diffractometer using Cu Kα radiation (λ= 1.5418 Å). FT-IR spectra were carried out on a Perkin Elmer Spectrum. Thermogravimetric analysis (TGA) recorded on NETZSCH STA 449F3. GC-MS test was measured on GCMS-QP2010 SE. UV-Vis absorption spectra were obtained with Shimadzu UV-3000 Spectrophotometer.

Experimental Methods

1) **Synthesis of the CuO-PMA sub-1 nm nanosheets (SNSs):** 0.018g PMA dissolved into 2 ml of 0.05 M $Cu(NO_3)_2$ ethanol solution in a 10 ml polytetrafluoroethene autoclave. Then 1.9 ml of oleylamine and 6 ml of hexane were added in the above system with vigorous stirring for 10 min. The autoclave was sealed and put into an oven to heat at 140 ^oC for 4 h. The product were washed by ethanol and centrifugated two times at 10000 rpm for 3 min. Then the CuO-PMA SNSs were dispersed into 36 ml of cyclohexane for use in the synthesis of the ternary hybrid CuO-PMA-Ag THSNHs.
2) **Synthesis of Ag nanoparticles (NPs):** 0.15 g $AgNO_3$ was dispersed into 10 ml oleic acid in the 10 ml polytetrafluoroethene autoclave with vigorous stirring for 10 min. Then the autoclave was sealed and put into an oven to heat at 100 ^oC for 6h. When the reaction finished and temperature decreased to room temperature, the product were washed by ethanol and centrifugated two times at 10000 rpm for 5 min. Then the Ag NPs were dispersed into 20 ml of ethanol for use in the preparation of the CuO-PMA-Ag THSNHs.
3) **Synthesis of the ternary hybrid CuO-PMA-Ag THSNHs:** 9 ml of CuO-PMA THSNHs cyclohexane dispersion was added into a 10 ml glass bottle. Then 30 μl of Ag NPs ethanol dispersion was transferred into the bottle with vigorous stirring for 30 min. Finally, the product were collected and dropped on TEM grid to do the morphology characterization.

4) **General procedure for the epoxidation of alkenes:** 12 mg of CuO-PMA-Ag sub-1 nm nanosheets, 3 μl of olefin and 60 mg of PhIO were added into 1 ml of $CHCl_3$ in a 5 ml glass bottle with continuous magnetic stirring at 50 ^oC for several hours. Finally, the dispersion was centrifuged and the supernatant was tested by the GC-MS. In addition, the corresponding control experiments were operated. The same molar ratio of CuO-PMA THSNHs and Ag NPs were employed and the reaction time was prolonged under same conditions.

Molecular Dynamics (MDs) simulations

Lennard - Jones parameters: The GROMACS 4.67 simulation package[1-3] and GROMOS96 force field[4] were used for MD simulations. The Ag: CuO: PMA ratio was taken from ICP-OES results, which are 36 Ag and 12 CuO for 1 PMA. The CuO-PMA nonosheets were prepared in our former work.[5] The point charge on each atoms of molecule models were obtained from our former work.[5] The Lennard-Jones (LJ) parameters of the polyoxometallate clusters were taken from previous work.[6] The LJ parameters for Cu and Ag were taken from Heinz.[7] For oxygen, carbon, hydrogen atoms, oleylamine, and the protonated oleylamine, the GROMOS96 force fields were used. The snapshots of MD simulation results were prepared by VMD.[1]

Simulations for Ag nanoparticle: One Ag nanoparticle comprised with 36 Ag atoms was placed in a 6×6×6 nm^3 simulation box. 20 oleylamine molecules were randomly inserted into the simulation box. The cutoff distance for short-range non-bonded interactions was chosen to be 12 Å and long-range electrostatic and Berendsen bath coupling scheme[9] were used. The NVT Ensemble was applied, which kept the

temperature (T) and volume (V) as a constant. After simulation running, the oleylamine molecules were absorbed on the surface of Ag nanoparticles.

Simulations for CuO-PMA-Ag THSNHs: To study the formation of CuO-PMA-Ag THSNHs, the SNSs obtained in our former work were amplified 4 times along X and Y directions, and the 16 Ag nanoparticles were placed along the side of SNSs with about 2 nm. The size of total system simulation box was $52\times52\times16$ nm^3. The positions of PMA were frozen. The NVT Ensemble was applied, and other simulation setups were similar to details mentioned above.

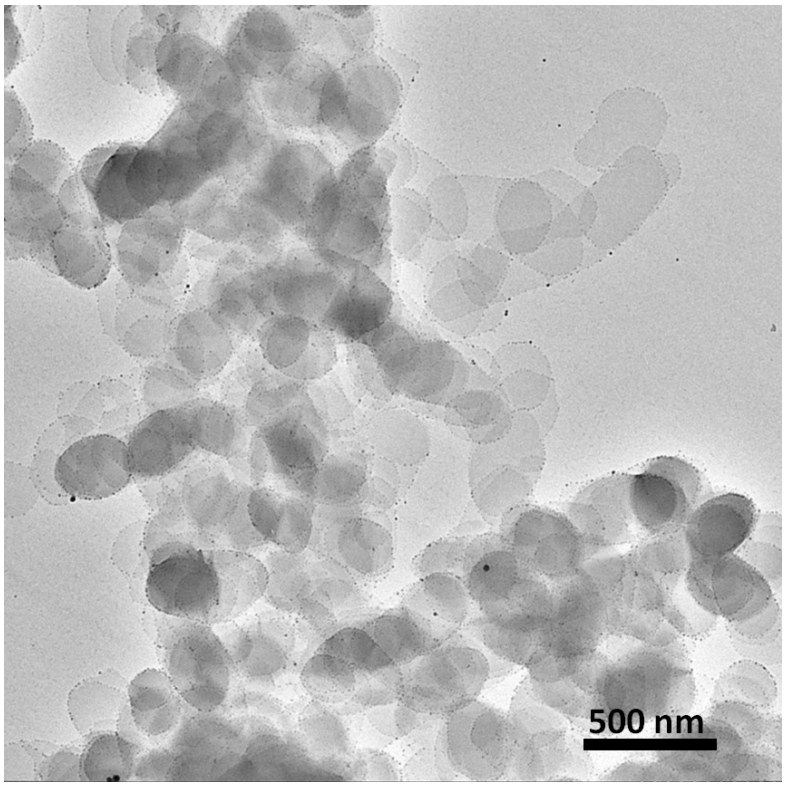


Fig. S1 The TEM image of the CuO-PMA-Ag THSNHs.

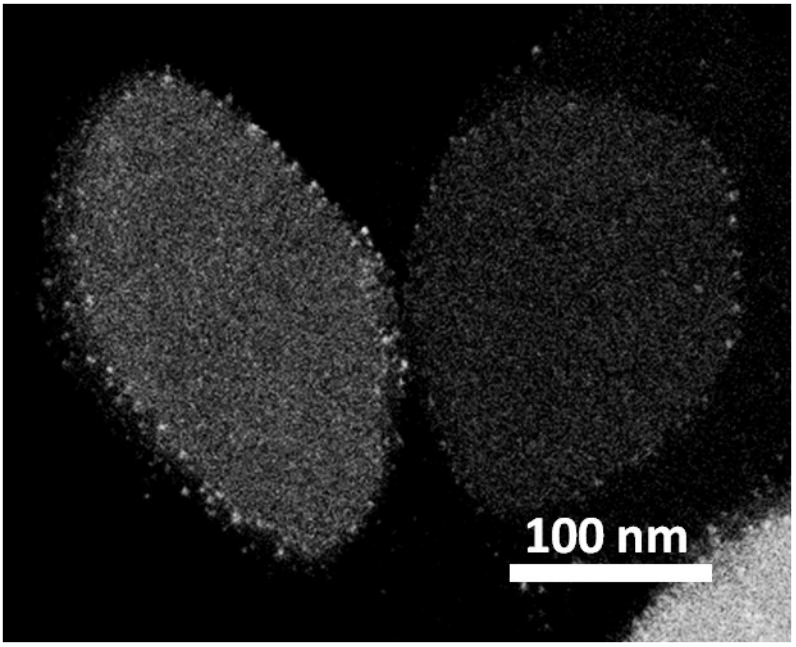


Fig. S2 The HAADF-STEM image of the CuO-PMA-Ag THSNHs.

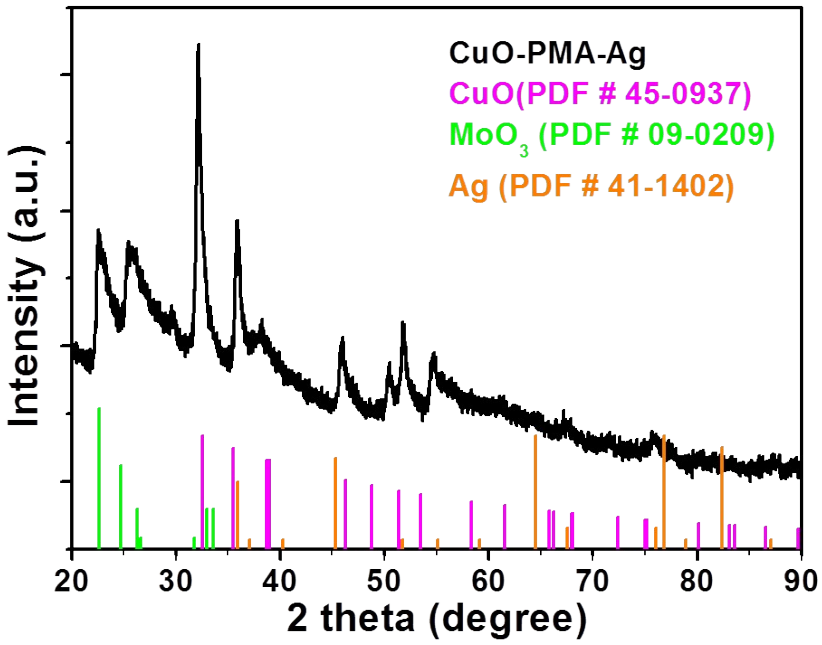


Fig. S3 The XRD pattern of the CuO-PMA-Ag THSNHs.

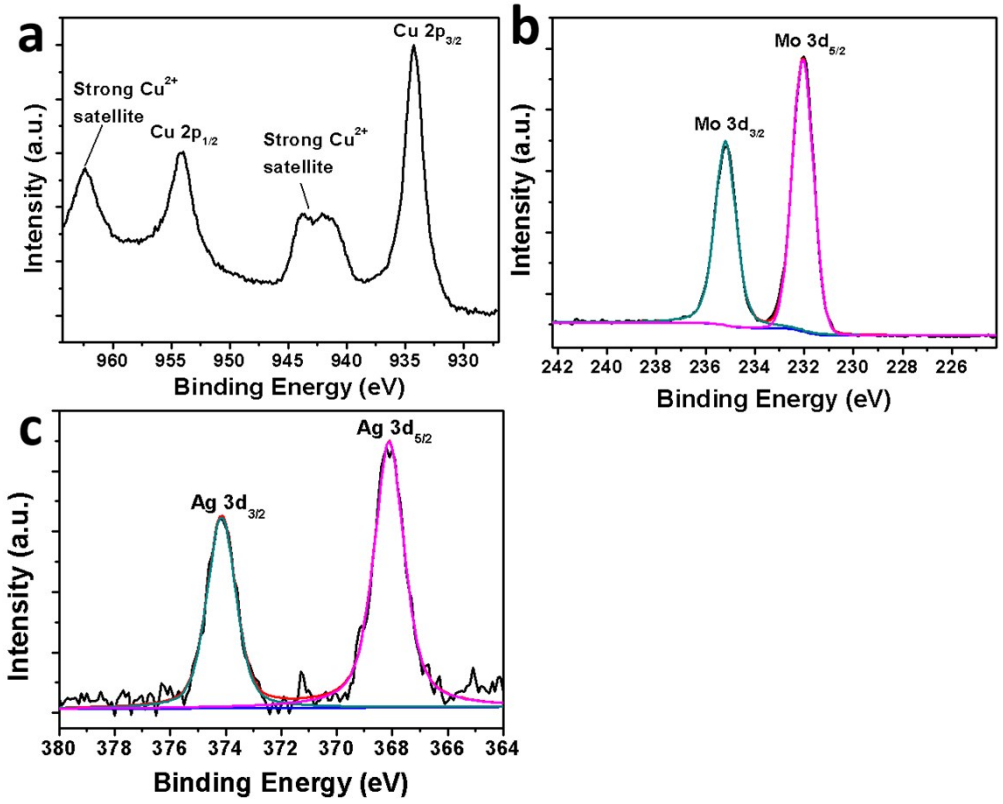


Fig. S4 The XPS spectra of (a) Cu, (b) Mo and (c) Ag in the CuO-PMA-Ag THSNHs.

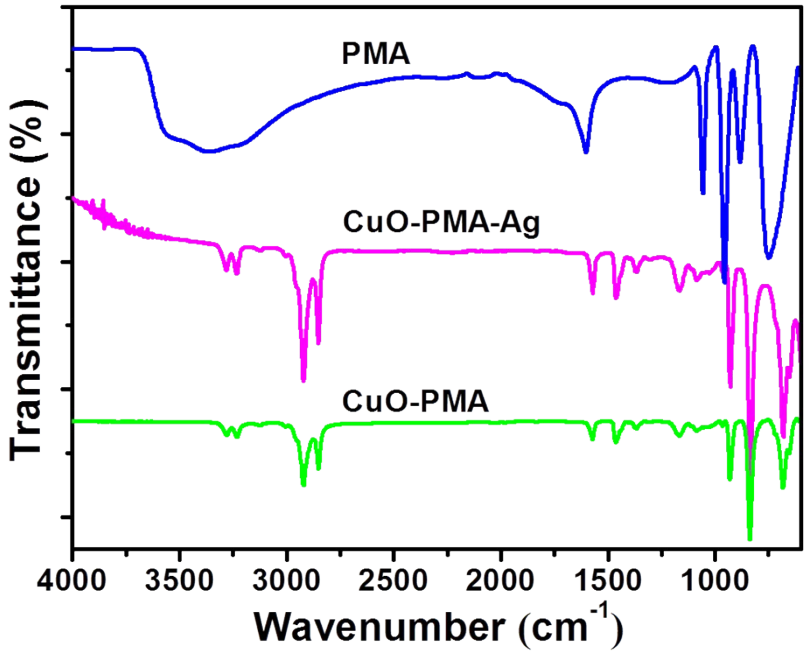


Fig. S5 The FT-IR spectra of PMA, CuO-PMA SNSs and CuO-PMA-Ag THSNHs demonstrated that the PMA clusters really exist in THSNHs. Meanwhile, the peaks appeared between 3000-3500 cm^{-1} can be attributed to v(N-H), which suggested that the oleylamine is present in the final products.

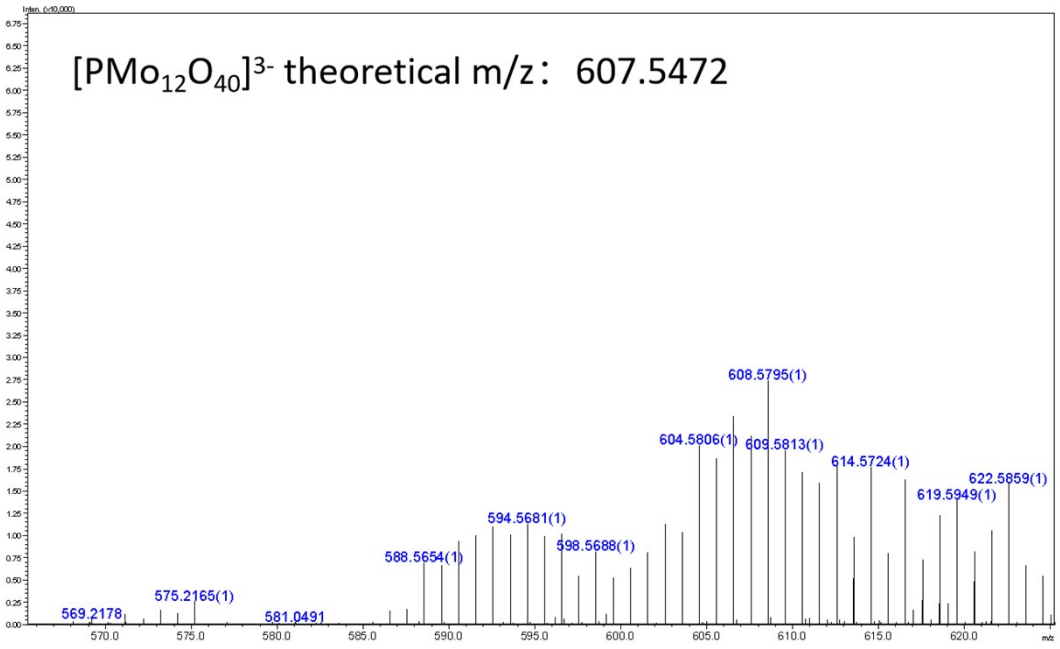


Fig. S6 ESI IT-TOF spectrum of the PMA cluster in the CuO-PMA-Ag THSNHs.

Table S1. ICP-OES data of the CuO-PMA-Ag THSNHs.

	CuO-PMA-Ag THSNHs	
	Weight (%)	Atomic ratio (%)
Cu	15.82	0.2489
Mo	22.22	0.2315
Ag	1.002	0.009290
Chemical formula	$(CuO)_{0.2489}(PMo_{12}O_{40})Ag_{0.009290}$	

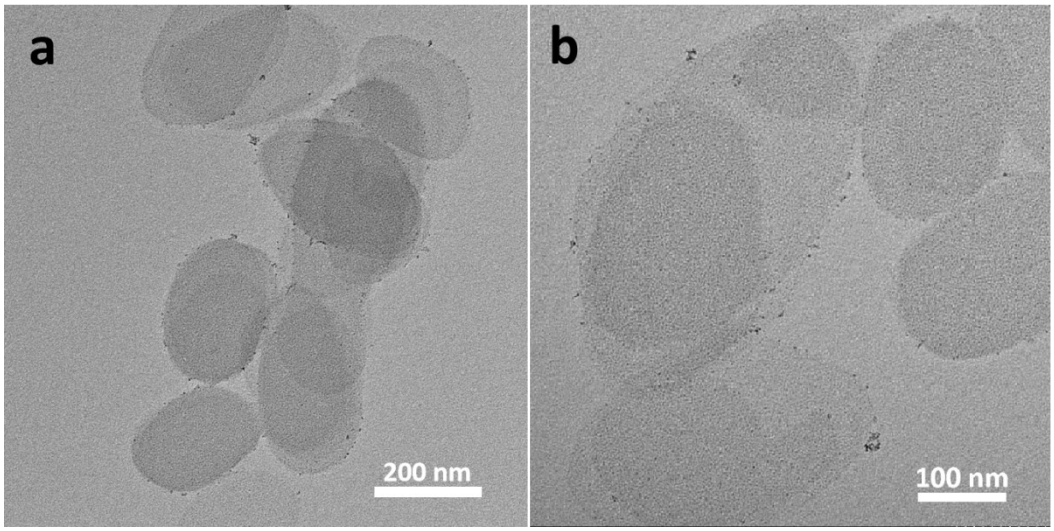
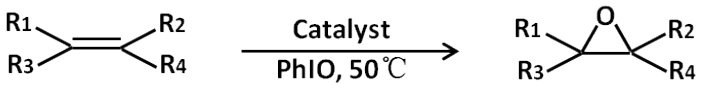


Fig. S7 The TEM images of CuO-PMA-PtP THSNHs.

Table S2. The control experiment results of epoxidation properties of CuO-PMA SNSs and Ag NPs at 50 °C. Conditions: Corresponding molar mass of CuO-PMA SNSs or Ag NPs catalysts were dispersed into 1 ml of $CHCl_3$. 60 mg of PhIO and 3 µl of alkenes were added and stir at 50 °C. GC-MS measurements were used to test the conversion.



Entry	Catalyst	Alkene	Time (h)	Conversion (%)
1	CuO-PMA	1-Octene	6	45.8
2	CuO-PMA	Cyclohexene	6	64.4
3	CuO-PMA	Cis-stilbene	5	53.5
4	Ag NPs	1-Octene	3	6.9
5	Ag NPs	Cyclohexene	2	34.1
6	Ag NPs	Cis-stilbene	5	89.3

Table S3. The catalytic performances of some reported materials.

Catalyst	Substrate	Temperature (°C)	Time (h)	Conversion (%)	Reference
CuO CNCs@meso-SiO_2 nanocomposite	cyclooctene	70	8	66.5	[10]
Polyoxometalate	1-octene	22	4	17.2	[11]
Polyoxometalate	cyclooctene	22	4	67.5	[11]
CuO/Al_2O_3	cyclooctene	100	6	29	[12]

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