

Single-cluster dispersed high-nuclearity Cu-W-oxo polyoxometalate for efficient epoxidation

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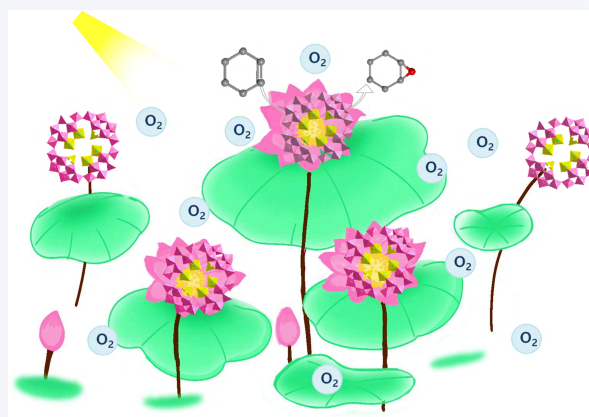
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ABSTRACT: Atomic-level structural precision and dynamic control of metal clusters during catalytic processes remain great challenges. Herein, Cu-W₄₈/CNNS single cluster catalyst was fabricated by dispersing wheel-shaped [(Cu(H₂O))₂[Cu₄(OH)₄(H₂O)₈]P₆W₄₈O₁₈₄]²⁸⁻ (Cu-W₄₈) polyoxometalate (POM) onto carbon nitride nanosheets (CNNS). The tetranuclear copper cluster [Cu₄(OH)₄(H₂O)₈] (Cu₄) consists of two binuclear copper units [Cu₂(OH)₂(H₂O)₄] (Cu₂). Encapsulated within the POM cavity, the Cu₄ cluster demonstrates exceptional catalytic performance toward molecular oxygen activation, achieving highly selective monooxygenation of cyclohexene to epoxycyclohexane with unprecedented efficiency (96.5% yield and 97.6% selectivity). Notably, the single-cluster catalyst exhibits remarkable performance across diverse monooxygenation reactions, including epoxidation, aromatic hydrocarbon oxidation and thiooxidation. This work provides new insights into the rational design of atomic-precision multinuclear metal cluster catalysts by precisely integrating transition-metal-oxo clusters into the cavities of monodispersed POMs.

KEYWORDS: polyoxometalate, single dispersed catalyst, high-nuclear cluster, binuclear copper, epoxidation



1 Introduction

Multinuclear metal clusters have garnered significant attention due to their unique advantages in multielectron-transfer catalysis [1]. Compared to single-nuclear sites, multinuclear structures can store multiple redox equivalents through synergistic interactions between metal centers, thereby avoiding the formation of undesirable high-valent/low-valent metal ions [2–6]. Simultaneously, they provide multiple active sites to facilitate multi-molecule cooperative reactions [7, 8]. These characteristics render them ideal catalysts for small-molecule activation. Cu₂S₂Cl₂ clusters with binuclear copper sites that emulate CuA have been reported to enable consecutive

photoactivation of O₂ molecules and C(sp³)-H bonds [9]. Inspired by multicopper oxidases, MOF-818 with a trinuclear copper unit similar to natural catechol oxidase showed high catechol oxidase activity [10]. The trinuclear copper catalyst [(app²⁻)Cu^{II}₃(μ-OH)] showed a turnover frequency (TOF) of 20,000 s⁻¹ in sodium bicarbonate solution for water oxidation, which is about 150 times higher than that of mononuclear copper catalyst [11]. Lin et al. have loaded binuclear copper sites and binuclear iron sites within metal-organic frameworks (MOFs), exhibiting high activity towards monooxygenation processes [12, 13]. The enhancement in catalytic performance stems not only from the multinuclear structure itself, but also hinges upon the synergistic interaction between the active center and its coordination environment. In the epoxidation of olefins, multinuclear metal clusters likewise exhibit considerable potential: Through the synergistic activation of oxygen to generate highly reactive metal-oxygen species, they can efficiently convert olefins into high-value-added epoxides, a process of great importance for the synthesis of fine chemicals [14]. Despite the significant progress achieved through the aforementioned strategies,

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the structural stability of multinuclear metal clusters in catalytic reactions and the atomic-level precise regulation of active sites remain significant challenges.

Polyoxometalates (POMs) as a class of metal-oxygen clusters have been widely used as electron sponge for multiple electron transfer to drive various challenging reactions [15–19]. Importantly, POMs with well-defined structure, compositional diversity and nano-scale size can act as ideal support to construct heterometallic cluster catalysts [20–22]. In the POM family, high-nuclearity wheel-shaped POMs have high stability and nanoscale cavities, which can provide confined reaction space for restricted growth of active clusters [23, 24]. As a typical wheel-shaped POM composed of four $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ (W_{12}) units [25], $[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]^{33-}$ (W_{48}) with 1 nm cavity can accommodate multiple of metal cations to form diverse structures as suitable platforms for active site design and cluster stabilization [26]. In the past decades, single metal center and transition-metal clusters from 2 to 30 atoms have been encapsulated within the cavity of W_{48} , such as $[\text{Cu}_4\text{P}_8\text{W}_{48}\text{O}_{176}(\text{OCH}_3)_8]^{24-}$, $[\text{Cu}_8\text{P}_8\text{W}_{48}\text{O}_{176}(\text{OCH}_3)_8]^{16-}$, $[\text{Cu}_{16}\text{P}_8\text{W}_{48}\text{O}_{184}]^{24-}$, $[\text{Cu}_{20}\text{Cl}(\text{OH})_{24}\text{P}_8\text{W}_{48}\text{O}_{184}]^{25-}$, $[\text{Cu}_{12}\text{P}_8\text{W}_{48}\text{O}_{184}]^{16-}$, $[\text{Ga}_{16}(\text{OH})_{32}\text{P}_8\text{W}_{48}\text{O}_{184}]^{24-}$, and $[\text{Ag}_{30}\text{P}_8\text{W}_{48}\text{O}_{184}]^{18-}$ [27–34]. The close spatial proximity between the active sites and W_{48} shell is beneficial for promoting synergistic catalytic interactions.

In this work, the highly symmetric Cu_4 unit consisting of two structurally well-defined $[\text{Cu}_2(\text{OH})_2(\text{H}_2\text{O})_4]$ (Cu_2) subunits confined within the cavity of W_{48} . This unique architecture not only ensures atomic-level precision of the active centers but also effectively suppresses migration and aggregation of copper species through the confinement effect of the POM cavity. Furthermore, through an efficient electrostatic self-assembly strategy, the Cu-W_{48} clusters with precisely organized Cu centers were uniformly immobilized on carbon nitride nanosheets (CNNS) to form the $\text{Cu-W}_{48}/\text{CNNS}$ hybrid catalyst. Notably, the monodisperse distribution and intimate interaction of Cu-W_{48} on CNNS facilitate efficient electron transfer from CNNS during catalytic processes. The $\text{Cu-W}_{48}/\text{CNNS}$ -4 composite exhibited excellent catalytic performance both high activation selectivity and an impressive epoxycyclohexane yield of 96.5%. Mechanistic studies reveal that the Cu_2 in Cu_4 units play a pivotal role in oxygen activation, highlighting the functional relevance of this well-defined structural architecture.

2 Experimental

2.1 Synthesis of carbon nitride nanosheets

Urea (20.0 g) was heated to 520 °C in air at a heating rate of 5 °C/min for 240 min. The obtained bulk $\text{g-C}_3\text{N}_4$ were ground for further experiments. CNNS were fabricated by thermal oxidative etching. The obtained bulk $\text{g-C}_3\text{N}_4$ was heated to 500 °C at a rate of 5 °C/min and heated for 120 min. The obtained yellowish powder was ground in a quartz mortar and used for the next experiments.

2.2 Synthesis of Cu-W_{48}

Cu-W_{48} was synthesized by improving on the previous synthesis [35]. $\text{K}_{28}\text{Li}_{15}[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]\cdot 92\text{H}_2\text{O}$ (W_{48}) (0.37 g, 0.025 mmol) and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.10 g, 0.60 mmol) were added to a LiCH_3COO buffer solution (20 mL, pH = 5). Then, the solution was heated to 80 °C for 1 h, cooled to room temperature and filtered. The filtrate was evaporated at room temperature in an open beaker. After 3–4 days, blue crystals were obtained. Continue evaporation until the beaker

walls were covered with blue crystals, then collected by filtration and air dried.

2.3 Synthesis of POM/CNNS

The $\text{Cu-W}_{48}/\text{CNNS-X}$ ($X = 1, 2, 3, 4, 5$, and 6) were constructed by a simple self-assembly strategy. CNNS (1 g) were dispersed in HCl solution (40 mL, pH = 4) and sonicated for 10 min with the addition of Cu-W_{48} (10, 100, 150, 200, 250, and 300 mg) or control POMs. Then the mixture was stirred vigorously for 12 h. The solid was obtained by centrifugation at 10,000 rpm for 5 min and washed with deionized water until neutral. $\text{Cu-W}_{48}/\text{CNNS-4}$ was obtained by freeze-drying for 24 h. Other POM/CNNS composite were constructed similarly except for variations in POMs loading.

2.4 Catalytic activity measurement

The catalyst (4 mg), isobutyraldehyde (1.0 mmol), cyclohexene (0.50 mmol), and 6.0 mL 1,2-dichloroethane (DCE) were added to a 25 mL round-bottom flask at room temperature, and the reaction flask was capped and equipped with an O_2 -filled balloon. The reaction was carried out under LED irradiation for 8 h. The supernatant was analyzed by gas chromatography-mass spectrometry (GC-MS) to determine the yield of cyclohexene oxide.

3 Results and discussion

3.1 Preparation and characterization of catalyst

Cu-W_{48} was synthesized following a reported literature procedure [35], in which copper ions were immobilized on the building block of W_{12} . The resulting copper centers within Cu-W_{48} comprise two monomeric $[\text{Cu}(\text{H}_2\text{O})]$ units (Cu_1) and two Cu_4 clusters, with each Cu_4 cluster consisting of two Cu_2 units. As depicted in Fig. 1, bulk $\text{g-C}_3\text{N}_4$ was synthesized by calcining urea at 520 °C, and then exfoliated into ultrathin CNNS through ultrasonic treatment and thermal oxidative etching by reheating $\text{g-C}_3\text{N}_4$ at a temperature of 500 °C, leading to the conversion of bulk $\text{g-C}_3\text{N}_4$ to two-dimensional (2D) materials.

The $\text{Cu-W}_{48}/\text{CNNS}$ composites were synthesized through electrostatic assembly in an HCl aqueous solution (pH 3), followed by a freeze-drying process. To systematically investigate the effect of Cu-W_{48} loading on CNNS, a series of $\text{Cu-W}_{48}/\text{CNNS}$ composites were prepared by varying the amount of Cu-W_{48} (10, 100, 150, 200, 250, and 300 mg) while maintaining a constant amount of CNNS (1 g). The resulting materials were designated as $\text{Cu-W}_{48}/\text{CNNS-X}$, where $X = 1-6$ corresponds to the increasing Cu-W_{48} mass. The negatively charged Cu-W_{48} clusters were uniformly dispersed on the CNNS support with positive charges through electrostatic interactions (Fig. S1 in the Electronic Supplementary Material (ESM)). For comparison, control samples were prepared by immobilizing structurally distinct POMs on CNNS, including W_{12} , $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (W_{18}), $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ (W_{30}), and isolated W_{48} (Fig. S2 in the ESM).

Transmission electron microscopy (TEM) images revealed the curved and sheet-like morphology of CNNS (Fig. S3 in the ESM). As shown in Fig. 2(a), $\text{Cu-W}_{48}/\text{CNNS-4}$ exhibits 2D layered morphology with highly dispersed clusters, and no obvious aggregated nanoparticles were observed. Bright spots corresponding to Cu-W_{48} anions were observed in the aberration-corrected high-angle annular dark-field TEM (AC-HAADF-TEM) image (Fig. 2(b)). The sizes of these bright spots ranged from 1.7 to

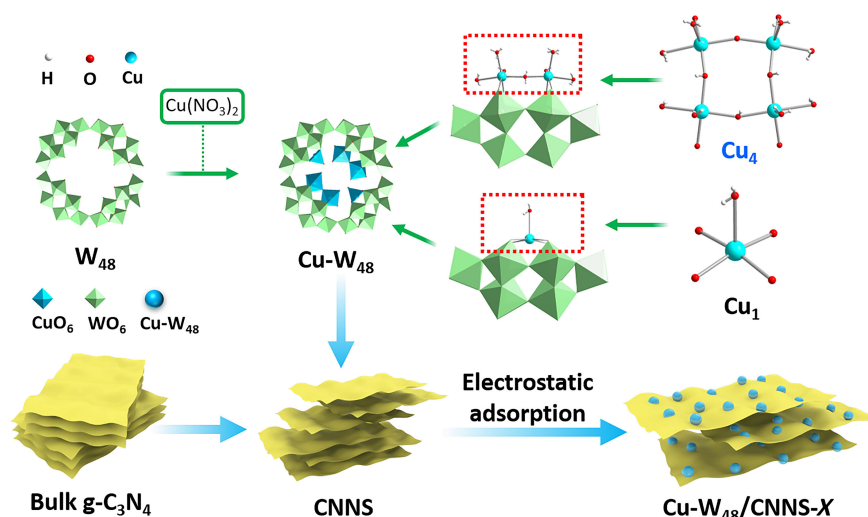


Figure 1 Schematic fabrication of Cu-W₄₈ and Cu-W₄₈/CNNS-*X* samples (Cu₁: [Cu(H₂O)], Cu₄: [Cu₄(OH)₄(H₂O)₈]; blue octahedron: CuO₆, green octahedron: WO₆, blue sphere: Cu-W₄₈).

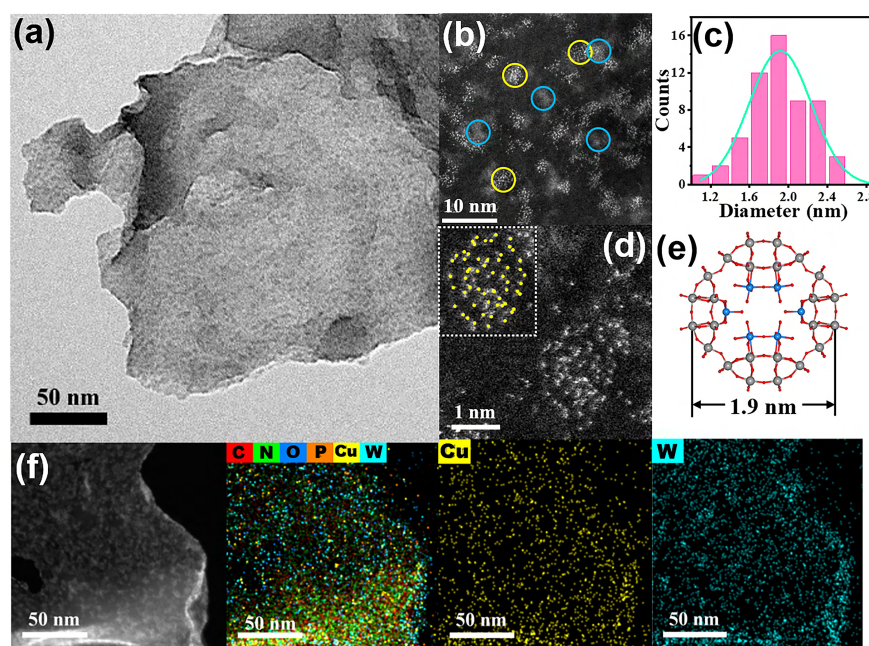


Figure 2 (a) HRTEM image of Cu-W₄₈/CNNS-4. (b) AC-HAADF-STEM image of Cu-W₄₈/CNNS-4. (c) The size distribution histogram of Cu-W₄₈. (d) AC-HAADF-STEM image of Cu-W₄₈/CNNS-4 (inset: highlighted heavy atoms of Cu-W₄₈). (e) Ball-and-stick representation of the structure of Cu-W₄₈ (W gray, O red, Cu blue). (f) HRTEM image and EDS elemental mapping images of Cu-W₄₈/CNNS-4.

2.4 nm, which agrees well with the cluster size of Cu-W₄₈, thereby confirming the monodispersed distribution of Cu-W₄₈ on CNNS (Fig. 2(c)). AC-HAADF-TEM image was performed to further disclose their structure at the atomic scale (Fig. 2(d)). The corresponding cluster with 2 nm size matches the individual Cu-W₄₈ cluster with the 1.9 nm size, confirming monodispersed Cu-W₄₈ on CNNS. Moreover, elemental mapping analysis revealed the uniform distribution of Cu, W, P, C, and N elements on the CNNS (Fig. 2(f) and Fig. S4 in the ESM). Subsequently, other Cu-W₄₈/CNNS-*X* (*X* = 1, 2, 3, 5, 6) samples with different loading amount of Cu-W₄₈ were further characterized by TEM (Figs. S5–S9 in the ESM), where the monodispersed Cu-W₄₈ clusters were consistently observed on the CNNS support. It can be observed that the density of dark spots (POMs) on CNNS becomes more and more dense with increasing the loading amount of Cu-W₄₈.

Powder X-ray diffraction (PXRD) and Fourier-transform infrared spectroscopy (FT-IR) were employed to characterize the structural features of Cu-W₄₈/CNNS-*X* composites. As shown in Fig. S10(a) in the ESM, CNNS exhibited diffraction peaks at 27.6° and 13.2°, corresponding to the (002) interlayer and (100) in-plane structural periodicity of g-C₃N₄ [36]. In the PXRD patterns of Cu-W₄₈/CNNS-4, no characteristic diffraction peaks of Cu-W₄₈ were observed, indicating the high dispersion of Cu-W₄₈ on CNNS. Significantly, all characteristic peaks of CNNS remain intact after Cu-W₄₈ incorporation, indicating preservation of the structure of CNNS. The diffraction peak of Cu-W₄₈/CNNS-6 (highest loading) shifts slightly to 27.4° compared to pristine CNNS (27.6°), indicating an expanded interlayer spacing due to Cu-W₄₈ intercalation (Fig. S10(b) in the ESM). Combined with the different brightness of clusters observed in the AC-HAADF-STEM images

(within yellow and blue circle in Fig. 2(b)), Cu-W₄₈ is not only absorbed on the surface but also distributed between the layers of CNNS. The introduction of Cu-W₄₈ increased the interlayer spacing between of CNNS, which help to suppress the recombination of photogenerated carriers [37]. Additionally, PXRD of CNNS loaded with various POMs (W₁₂, W₁₈, W₃₀ and W₄₈) showed no observable peaks corresponding to POMs (Fig. S11(a) in the ESM), which reveal the high dispersion of these POMs on the CNNS support. The peaks of Cu-W₄₈ at 1072, 935, 789, and 606 cm⁻¹ are attributed to $\nu(\text{P}-\text{O}_a)$, $\nu(\text{W}-\text{O}_d)$, $\nu(\text{W}-\text{O}_b-\text{W})$, and $\nu(\text{W}-\text{O}_c-\text{W})$ in the FT-IR, respectively (Fig. S11(b) in the ESM). The peaks in the range of 1200–1600 cm⁻¹ in the CNNS sample are attributed to stretching vibrations of C=N and C-N. Cu-W₄₈/CNNS-4 exhibited characteristic vibrational modes of CNNS and distinctive peaks of Cu-W₄₈, confirming successful hybrid formation. As shown in Fig. S12 in the ESM, the peaks of CNNS and POMs were detected in POM/CNNS composites with different loading amounts of Cu-W₄₈ or different POMs, confirming the universality of the synthesis method.

The surface chemical composition, elemental valence states, and interactions between Cu-W₄₈ and CNNS in the composites and CNNS of the composites were investigated by X-ray photoelectron spectroscopy (XPS). The elements C, N, O, P, W, and Cu were observed in the survey spectra, which confirmed the presence of Cu-W₄₈ in these composites (Fig. S13 in the ESM). From the fitted C 1s XPS spectrum (Fig. 3(a)), three peaks at 284.5, 285.6, and 288.0 eV in CNNS were identified, corresponding to graphitic carbon (C-C/C=C), C-NH_x, and N-C=N, respectively [38]. The introduction of Cu-W₄₈ increased the binding energies of all three chemical states of C, indicating a reduction in the charge density of C elements in the sample. In the high-resolution N 1s spectra, three peaks located at 398.5, 399.3, and 400.9 eV (Fig. 3(b)) in Cu-W₄₈/CNNS-4 (dark) were ascribed to C=N-C, N-(C)₃, and -NH_x, respectively. The N 1s spectra of Cu-W₄₈/CNNS-4 (dark) exhibited

three peaks with higher binding energies compared to CNNS (398.3, 399.1, and 400.7 eV), which suggests a transfer of electrons from CNNS to Cu-W₄₈ [39]. The peaks with binding energies of 935.0 eV (Cu 2p_{3/2}) and 955.0 eV (Cu 2p_{1/2}) confirmed the +2 state of Cu (Fig. 3(c)). A slight negative shift was observed of the Cu 2p binding energy in the Cu-W₄₈/CNNS-4 sample compared to that of Cu-W₄₈. The Cu 2p XPS spectrum of Cu-W₄₈/CNNS-4 exhibited two characteristic peaks at 933.1 and 952.7 eV, assigned to Cu⁺ species [40]. Upon light irradiation, two additional peaks emerged at 932.0 and 953.3 eV, which were assigned to Cu⁺ species. This observation indicates that photoexcited electrons from CNNS facilitated the reduction of Cu²⁺ to Cu⁺, while the photogenerated holes remained localized within the CNNS.

The W 4f XPS spectrum of Cu-W₄₈ exhibited two characteristic peaks at 37.8 eV (W 4f_{5/2}) and 35.7 eV (W 4f_{7/2}), confirming the presence of W⁶⁺ (Fig. 3(d)). Notably, the W 4f binding energies in Cu-W₄₈/CNNS-4 (dark condition) shows a positive shift compared to pristine Cu-W₄₈. Under light irradiation, two additional peaks emerged at 36.6 and 34.5 eV, corresponding to W⁵⁺ species. These observations demonstrate that Cu-W₄₈ exhibits exceptional electron-storing capability under illumination, resulting in the partial reduction of W⁶⁺ to W⁵⁺. This electron accumulation process effectively suppressed photogenerated carrier recombination (Fig. 3(d)) [41]. UV-vis diffuse reflectance spectroscopy (UV-vis DRS) revealed strong absorption in the ultraviolet region for all synthesized samples (Fig. S14(a) in the ESM). The optical characteristics of Cu-W₄₈/CNNS composites closely resembled those of pristine CNNS, with Cu-W₄₈ exhibiting an additional characteristic absorption peak at 800 nm attributable to Cu²⁺ d-d transitions [42]. Band gap energies (E_g) were determined using Tauc plots (Fig. S14(b) in the ESM), yielding values of 3.01 eV for Cu-W₄₈ and 2.89 eV for CNNS. Mott-Schottky analysis provided the flat-band potentials (Figs S14(c) and S14(d) in the ESM), with conduction band (E_{CB}) positions at -0.84 V (Cu-W₄₈) and -1.09 V

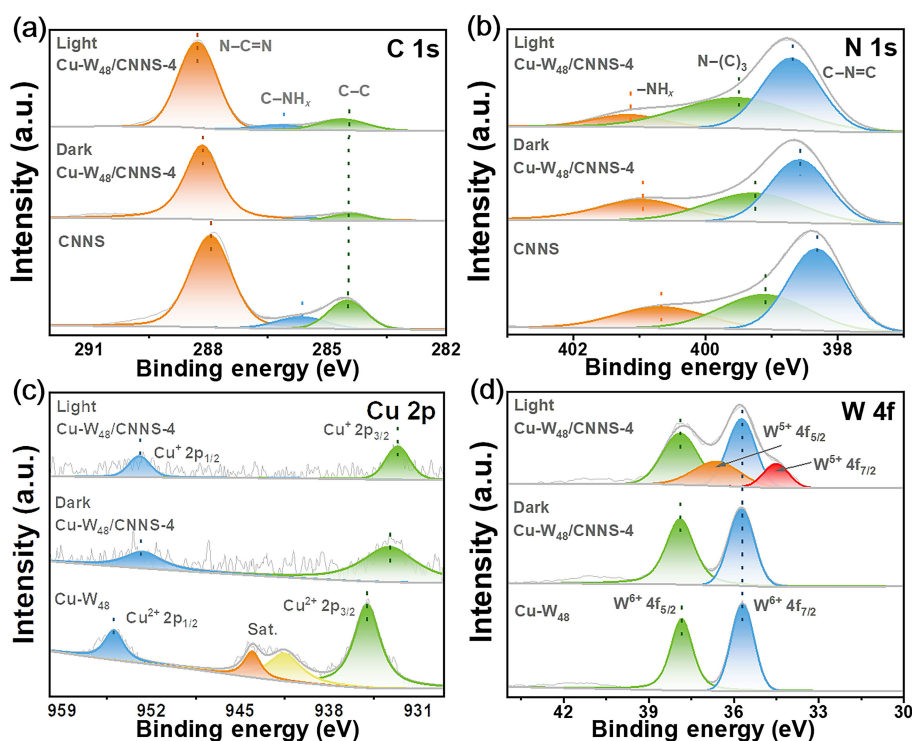


Figure 3 High-resolution-XPS spectra of (a) C 1s, (b) N 1s, (c) Cu 2p, and (d) W 4f in Cu-W₄₈/CNNS-4 under light and dark.

(CNNS) versus normal hydrogen electrode. The valence band (E_{VB}) positions of Cu- W_{48} and CNNS were calculated to be 2.17 and 1.80 V using the equation $E_{\text{VB}} = E_g + E_{\text{CB}}$ (Fig. S15 in the ESM).

3.2 Monoxygenation reaction

Inspired by natural monoxygenases using O_2 as the sole oxidant with sacrificial reductants, the catalytic performance of Cu- W_{48} /CNNS- X composites was evaluated for cyclohexene epoxidation using molecular oxygen at room temperature. Systematic optimization revealed that Cu- W_{48} /CNNS-4 demonstrated exceptional catalytic activity, achieving 96.5% epoxycyclohexane yield with 97.6% selectivity (Fig. 4(a)). The catalytic performance of Cu- W_{48} /CNNS- X improved significantly with increasing Cu- W_{48} loading when X ranged of 1–4 (Table S1 in the ESM). Upon further increasing the Cu- W_{48} loading amount, the clusters agglomerated, leading to a decrease in catalytic activity (the yield of epoxycyclohexane decreased from 96.5% to 49.5%). Therefore, Cu- W_{48} /CNNS-4 was identified as the optimal catalyst composition. Control experiments provided critical mechanistic insights (Fig. 4(b)). The significantly lower yields from Cu^{2+} /CNNS (18.5%) and W_{48} /CNNS (24.0%) underscored the precisely coordinated Cu centers in Cu- W_{48} for O_2 activation. Similarly, W_{18} /CNNS (31.6%) and W_{30} /CNNS (14.1%) showed inferior performance, further confirming the unique advantage of the Cu- W_{48} cluster as an artificial monoxygenase. For cyclohexene monoxygenation, the Cu- W_{48} /CNNS-4 catalyst demonstrated superior activity over both pristine CNNS and Cu- W_{48} (Fig. 4(c)).

Notably, a physical mixture of Cu- W_{48} and CNNS (CNNS&Cu- W_{48}) yielded only 41.2% (Fig. S16 in the ESM), emphasizing the crucial importance of achieving monodisperse Cu- W_{48} on the CNNS support. The catalyst exhibited excellent recyclability, maintaining high activity and selectivity through seven cycles (Fig. 4(d)). After the cycling tests, the structural integrity of Cu- W_{48} /CNNS-4 was verified by TEM images, in which no observable nanoparticle aggregation was detected (Fig. S17 in the ESM). After photocatalysis, the PXRD patterns and FT-IR spectrum of the recovered catalyst were similar to Cu- W_{48} /CNNS-4 (Fig. S18 in the ESM). The ICP analysis revealed that the Cu- W_{48} content in Cu- W_{48} /CNNS-4 after the catalytic reaction was comparable to its initial value (Table S2 in the ESM). These results demonstrated the stability of Cu- W_{48} /CNNS-4. As a result, Cu- W_{48} /CNNS-4 is a robust and highly efficient catalyst, which exhibited the highest yield for photocatalytic cyclohexene oxidation under milder conditions (Table S3 in the ESM). To better understand the catalytic process, a series of control experiments were performed. Only very small amounts of epoxycyclohexane were observed under dark conditions or under the N_2 atmosphere, indicating that both light and oxygen are indispensable for efficient photooxidation (Fig. S19 in the ESM).

The photo-oxidation reaction was completely inhibited when β -carotene was used as a $^1O_2$ scavenger, indicating that $^1O_2$ played a key role in the catalytic process. By addition of 1,4-benzoquinone as the O_2^- scavenger, the product yield decreased to 1.9%, suggesting the key role of O_2^- in the catalytic process. Trapping experiments

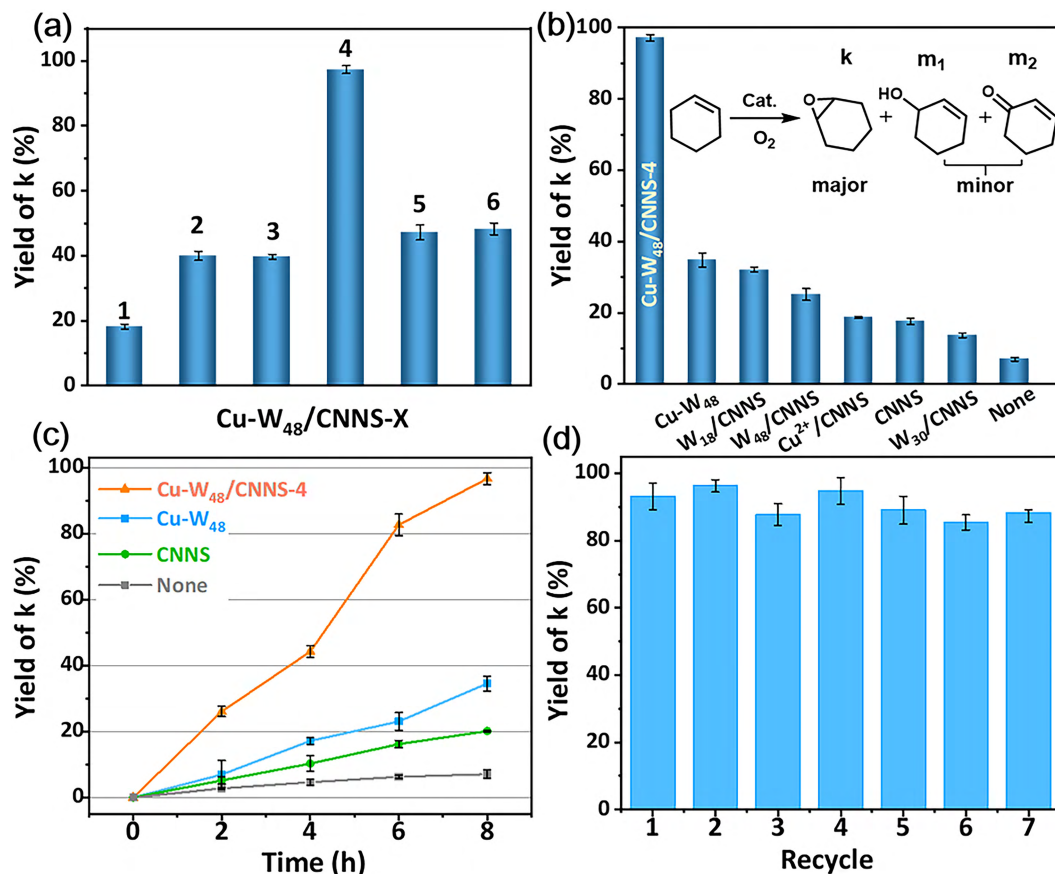


Figure 4 (a) Photocatalytic epoxidation of cyclohexene of Cu- W_{48} /CNNS- X . (b) Epoxycyclohexane yield with Cu- W_{48} /CNNS-4 and control samples (k: epoxycyclohexane, m₁: cyclohexenol, m₂: cyclohexenone). (c) Epoxycyclohexane yield with time for Cu- W_{48} /CNNS-4 and control experiments. (d) Recycle experiments with Cu- W_{48} /CNNS-4 as the catalyst.

revealed the role of holes and electrons, with KI and AgNO₃ yielding conversions of 1.7% and 20%, respectively. ESR studies further confirmed the characteristic signals of ¹O₂ and O₂^{•−}. Under illumination, distinct O₂^{•−} characteristic signals were observed using DMPO as a scavenger, while ¹O₂ characteristic signals were detected using 4-oxo-TMP as the trapping agent. No O₂^{•−} signal was detected under dark conditions. However, a distinct signal emerged after 3 min of illumination, and subsequently disappeared upon addition of cyclohexene. Concurrently, the ¹O₂ signal exhibited significant enhancement under light exposure, similarly diminishing after cyclohexene addition. These findings indicate that both ¹O₂ and O₂^{•−} participated as key reactive species in this photo-oxidation reaction. (Fig. S20 in the ESM).

The catalyst was subsequently employed to evaluate various photo-oxidation reactions (entries 1–8) under the optimized conditions (Table 1). Remarkably, Cu-W₄₈/CNNS-4 demonstrated excellent catalytic performance in the epoxidation of various olefins under an oxygen atmosphere (entries 1–3), and the yield reached 97% for epoxycyclohexane (entry 1). Remarkably, the oxidation of ethylbenzene afforded acetophenone with 66% yield (entry 4), and the Cu-W₄₈/CNNS-4 catalyst exhibited outstanding activity in the carbonylation of benzyl, resulting in an 81% yield of 1-indanone (entry 5). This composite catalyst also showed broad applicability and high activity for the oxidation of thioethers and alcohols (entries 6–8). These findings indicated that POM-based artificial monooxygenases possess effective oxidative capabilities under mild reaction conditions with molecular oxygen as the oxidant.

Reaction conditions: substrate (0.5 mmol), catalyst (4 mg), 1,2-dichloroethane (6 mL), and isobutyraldehyde (1.0 mmol), O₂ atmosphere, room temperature, reaction time: 8 h. The yields determined by GC-MS.

To investigate the charge separation and transfer behaviour in the photocatalytic system, photoluminescence (PL) spectroscopy was performed on both Cu-W₄₈/CNNS-4 and CNNS. Steady-state PL spectra of CNNS revealed a prominent emission peak at 445 nm (Fig. S21(a) in the ESM), representing the recombination of photogenerated electron-hole pairs. The PL spectra of Cu-W₄₈/CNNS-4 exhibited much lower fluorescence intensity compared to that of bare CNNS. The reduced fluorescence intensity indicates effective separation of photogenerated electrons and holes through the incorporation of Cu-W₄₈ clusters [43]. Time-resolved fluorescence spectra provided further insight into the charge carrier dynamics. The average PL lifetime of Cu-W₄₈/CNNS-4 (5.65 ns) was substantially shorter than that of CNNS (6.86 ns), indicating more efficient charge transfer processes in the composite system

Table 1 Cu-W₄₈/CNNS-4 catalyzed monooxygenation reactions^a

Entry	Substrate	Product	Conversion (Yield)	Entry	Substrate	Product	Conversion (Yield)
1			98% (97%)	5			86% (81%)
2			90% (86%)	6			> 99% (97%)
3			97% (93%)	7			> 99% (91%)
4			80% (66%)	8			98% (82%)

^aReaction conditions: substrate (0.5 mmol), catalyst (4 mg), 1,2-dichloroethane (6 mL), and isobutyraldehyde (1.0 mmol), O₂ atmosphere, room temperature, reaction time: 8 h. The yields determined by GC-MS.

(Fig. S21(b) in the ESM). These spectroscopic findings, combined with XPS analysis, further confirm efficient electron transfer from CNNS to Cu-W₄₈, which accounted for the superior photocatalytic performance of the hybrid material.

To further elucidate the charge separation dynamics, electrochemical impedance spectroscopy (EIS) measurements were performed, revealing a significantly smaller arc radius in the Nyquist plot for Cu-W₄₈/CNNS-4 compared with CNNS (Fig. S21(c) in the ESM). In addition, Cu-W₄₈/CNNS-4 exhibited higher photocurrent density than CNNS (Fig. S21(d) in the ESM), confirming its superior charge separation/transfer capabilities. These electrochemical characteristics verify the outstanding photocatalytic performance of Cu-W₄₈/CNNS-4. Electron spin resonance (ESR) spectroscopy provided further insight into the charge carrier behaviour. The Lorentzian lines in the electron spin resonance spectra of CNNS and Cu-W₄₈/CNNS-4 were observed at $g = 2.004$, indicating the formation of unpaired electrons induced by nitrogen vacancies (Fig. S22 in the ESM) [44]. The ESR signals at $g_{\perp} = 2.047$ and $g_{\parallel} = 2.268$ were attributed to Cu²⁺, and their intensities gradually decreased with increasing illumination time. Compared to CNNS ($g = 2.004$), the enhanced intensity of the Lorentzian line signal in Cu-W₄₈/CNNS-4 indicates an increased concentration of nitrogen defects and a higher density of free electrons in Cu-W₄₈/CNNS-4. These spectroscopic results suggest that Cu-W₄₈ incorporation effectively promoted the separation of photoinduced charge carriers (electrons and holes) in CNNS.

3.3 Monooxygenation reaction mechanism and density functional theory

To gain further insight into the catalytic mechanism of the Cu-W₄₈, density functional theory (DFT) calculations were employed to study the reaction pathways on the Cu₄ cluster and mononuclear Cu₁ site, respectively. First, the coordinated hydroxyl and water ligands were removed from Cu₄ and Cu₁ sites, thereby facilitating O₂ adsorption (Fig. S23 in the ESM). The dehydroxylated tetranuclear copper cluster [Cu₄(OH)₃] and mononuclear [Cu^{II}] sites subsequently adsorbed O₂ for oxygen activation, and the reaction processes on [Cu₄(OH)₃] and [Cu] sites were illustrated in Figs. 5(a) and 5(b).

The oxygen activation mechanism of natural monooxygenases (Methane monooxygenases and cytochromes P450) provides a framework for proposing catalytic processes for Cu₁ and Cu₄ sites [45]. The resulting tetranuclear copper cluster [Cu₂(OH)₃Cu^{II}] contains two unbridged Cu^{II} centers to form [Cu₂(OH)₃Cu^{II}] (1a). The two Cu^I in the tetranuclear copper cluster can activate O₂ to form [Cu₂(OH)₃Cu^{III}2(O₂)] (1b). One oxygen atom is then removed by a sacrificial reducing agent. Further, the resulting [Cu₂(OH)₃Cu^{II}2O] (1c) monoxide-bridged binuclear copper center subsequently interacted with cyclohexene to form the final reaction intermediate (1d), which can release the final product easily. For the Cu₁ site, the activation of O₂ is contingent upon the provision of electrons by a sacrificial agent. This process generates a copper-oxygen intermediate (2b) in which O₂ is coordinated. The intermediate undergoes a series of reactions, beginning with the cleavage of the O=O bond, forming a Cu₁-O-radical intermediate (2c). This intermediate subsequently undergoes a radical rebound mechanism, resulting in the generation of an epoxidized product (2d). Concurrently, the Cu₁ active center is regenerated to its initial oxidation state (2a) via an electron transfer cycle.

In situ FT-IR spectroscopy was employed to monitor the interaction between cyclohexene and Cu-W₄₈/CNNS-4 during the

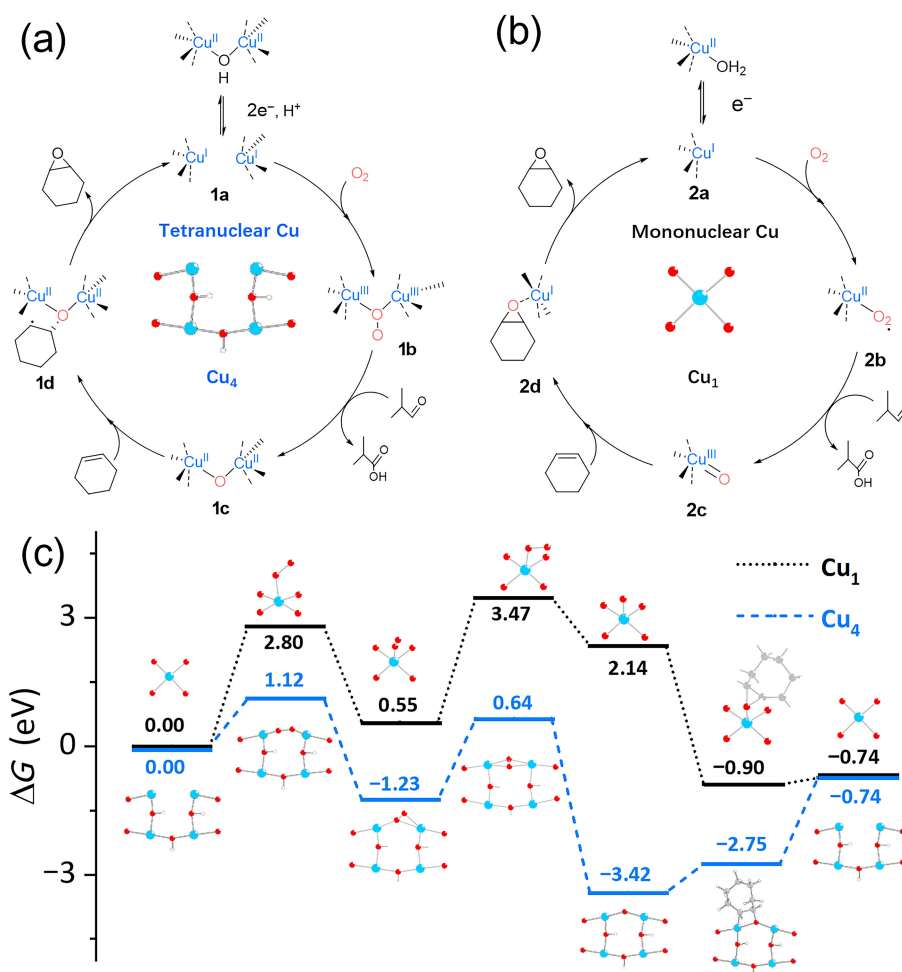


Figure 5 Proposed mechanisms for cyclohexene oxidation over (a) Cu₄ (left) and (b) Cu₁ (right) sites. (c) DFT calculated free energy profiles of cyclohexene oxidation catalyzed by mononuclear systems (Cu₁; black line) and tetranuclear copper (Cu₄; blue line).

photooxidation process. As shown in Fig. S24 in the ESM, the characteristic absorption bands observed at 1380–1420, 2870–2910, and 2950–2995 cm⁻¹ correspond to the C–H and =C–H of cyclohexene, respectively. With prolonged irradiation, the intensities of these bands gradually decreased. Concurrently, an increase in the signal intensities associated with C–O–C (1230 cm⁻¹) was detected, indicating the consumption of cyclohexene and the formation of epoxycyclohexane.

As shown in Fig. 5(c), the energy profile demonstrates a significant difference in the free energy barriers for O₂ activation between the Cu₄ and Cu₁ sites. Specifically, the Cu₄ site exhibits a substantially lower barrier (1.12 eV) compared to the Cu₁ site (2.80 eV), and this difference arises from the formation of a [Cu₂(μ₂-O₂)] bridge by the synergistic interaction between the binuclear sites and their unique coordination geometry. Detailed analysis of the geometric evolution of adsorbed O₂ indicates that the intermediate state at the Cu₄ site is more stable, with a free energy of -1.23 eV. Subsequently, isobutyraldehyde captures the distal oxygen atom of the adsorbed O₂ molecule, leading to O=O bond cleavage. This step is highly exergonic at the Cu₄ site ($\Delta G = -4.06$ eV, from 0.64 to -3.42 eV), whereas the corresponding free energy change at the Cu₁ site is significantly less favorable ($\Delta G = -1.33$ eV, from 3.47 to 2.14 eV). The remaining oxygen species then participated in cyclohexene oxidation. The comparative analysis of free energy barriers between the Cu₄ and Cu₁ sites underscores the critical

importance of efficient O₂ adsorption at the active site. Notably, the oxygen activation barrier at the Cu₁ site is markedly higher than that at the Cu₄ site, indicating that the exposed binuclear copper centers in Cu-W₄₈ synergistically enhance O₂ adsorption and activation. Thus, the Cu₄ site is the preferred location for cyclohexene oxidation, owing to its lower activation energy and more thermodynamically favorable reaction pathway.

4 Conclusions

In summary, the single-cluster catalyst Cu-W₄₈/CNNS has been developed by precisely immobilizing wheel-shaped POM Cu-W₄₈ on CNNS. The Cu₄ unit in Cu-W₄₈ enables efficient O₂ activation and selective monooxygenation. The optimized Cu-W₄₈/CNNS-4 catalyst exhibits exceptional performance in the epoxidation of cyclohexene, achieving a remarkable 96.5% yield and 97.6% selectivity under mild conditions. Mechanistic studies reveal that the binuclear Cu₂ subunits within the Cu₄ cluster play a pivotal role in oxygen activation, significantly lowering the energy barrier compared with mononuclear Cu sites. The synergistic interaction between the Cu₂ subunits and W₄₈ framework facilitates the formation of a [Cu₂(μ₂-O₂)] intermediate, promoting efficient O=O bond cleavage and subsequent substrate oxidation. Furthermore, electron transfer from CNNS to Cu-W₄₈ enhances charge separation, further boosting catalytic efficiency. Remarkably, Cu-

W₄₈/CNNS-4 demonstrates broad applicability in diverse monooxygenation reactions, including aromatic hydrocarbon oxidation, thioether oxidation, and alcohol oxidation, highlighting its potential as a multinuclear metal-cluster catalyst. This work not only provides a rational design strategy for atomically precise multinuclear cluster catalysts by integrating transition-metal-oxo clusters into POM scaffolds, but also opens new avenues for developing high-efficiency catalytic systems.

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Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

W.-X. S., S. Y., and Z.-M. Z. conceived and designed this project. Z.-R. Z. performed the experiments. Z.-R. Z., P. Z., and M.-Y. C. analyzed the data. W.-X. S. carried out the DFT calculation. Z.-R. Z., S. Y., D. L. K., Z.-M. Z., T.-B. L., and W.-X. S. wrote and revised the article.

Use of AI statement

None.

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