

Modular assembly of polyoxometalate clusters at the sub-1 nm scale

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Supplementary Information

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Supplementary Methods

1. Experimental Section

1.1 Synthesis of starting material $\text{Na}_7\text{PW}_{11}\text{O}_{39}$

Dissolve sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) in distilled water. Prepare a diluted phosphoric acid (H_3PO_4) solution in a separate container. Gradually add the phosphoric acid solution into the Na_2WO_4 solution while stirring. Adjust the pH of the solution to 1.5-2 by adding nitric acid (HNO_3) or sodium nitrate (NaNO_3). Heat the solution to 90 °C and stir for 4 hours to facilitate cluster formation. Allow the solution to cool to room temperature, during which $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ precipitates out as crystals or powder. Filter the precipitate and wash it with distilled water or diluted nitric acid to remove impurities.

Dry the filtered product in an oven at 50 °C until dried. Store the final product (a white or pale-yellow powder) in a dry container to prevent moisture absorption. **Notes:** pH Control: Ensure the pH remains within 1.5-2 for proper cluster formation. Handle acids and tungstate compounds with care, as they are corrosive and potentially toxic. Use proper protective equipment.

1.2 Synthesis of starting material $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$

Tetrabutyl ammonium hexamolybdate ($[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$) has been prepared according to the following procedure: 58 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were stirred with 100 mL of dimethyl formamide. Acetic anhydride (48 mL) was slowly added, then acidification was performed with 33 mL of concentrated (12 M) hydrochloric acid, resulting in a heating of the solution. The hot solution was filtered and the yellow filtrate was precipitated with a solution of 1 M tetra butylammonium bromide in dimethylformamide (100 mL). The resulting yellow salt (42 g) was filtered, washed with ethanol and ether, and finally recrystallized from acetone.

1.3 Synthesis of Ag nanoclusters

0.15 g silver nitrate and 10 mL oleic acid (OA) were added into a 10 mL Teflon-autoclave and stirred, and the system was then heated at 100 °C for 3 h. The resulting was washed with ethanol, and finally redispersed in cyclohexane for storage.

2. Molecular Dynamics (MD) Simulations

2.1 Simulations of Ca-POM nanowires

The point charge of organic molecules can be obtained by First-principles density functional theory (DFT) simulation using Gaussian 16 code.²² The 6-311g++ basis with B3LYP functions were applied to the systems.^{23,24} The PRODRG was used to parameterize the models.²⁵ The model for $\text{PW}_{12}\text{O}_{40}^{3-}$,

oleyamine, and protonated oleyamine can be obtained from the previous work.^{26,27} The GROMACS 4.67 package was applied to the molecular dynamics (MD) simulations.²⁸ For oxygen, carbon, phosphorus, calcium, hydrogen atoms, and so on, the GROMOS96 force fields were used.²⁹

To study the structure of nanowires, six $\text{PW}_{12}\text{O}_{40}^{3-}$ were placed in an $8 \times 8 \times 9.6 \text{ nm}^3$ simulation box, aligned as straight line. Six Ca^{2+} , six protonated oleyamine and 36 oleyamine molecules were put into the vacuum box around the $\text{PW}_{12}\text{O}_{40}^{3-}$ randomly. The amounts of molecules were obtained from experimental results. The positions of these $\text{PW}_{12}\text{O}_{40}^{3-}$ were frozen and other molecules can move freely during the simulation at first, and then all the molecules can move freely. The cutoff distance for short-range non-bonded interactions was chosen to be 12 Å and long-range electrostatic and Berendsen bath coupling scheme were used.³⁰ The NVT Ensemble were applied, and the simulations were run over 400 ps in steps of 2 fs. To check the assembly process, four Ca^{2+} , four protonated oleyamine and 24 oleyamine molecules were put into the vacuum box around the $\text{PW}_{12}\text{O}_{40}^{3-}$ randomly. All the molecules could move freely.

2.2 Simulations of $\text{NiS}_x\text{-NiO}_x\text{-POM}$

The aim of utilizing molecular dynamics simulations is to understand the mechanism of the nucleation process of polyoxometalate (POMs) co-assembled with $\text{NiS}_x\text{-NiO}_x$ to form uniform binary cluster-nuclei co-assembled materials, using the GROMACS 4.07 simulation package⁵ and GROMOS96 force fields⁶. Molecular dynamics simulation enables us to trace the nanoscale events and at the same time provides molecular details. For this purpose, we utilize all-atomic models for our simulations.

Computational details

Lennard-Jones parameters

The GROMACS 4.07 simulation package and GROMOS96 force field were used for all our MD simulations. Two neighboring atoms interact with each other through van der Waals interactions, which is treated using a 12-6 Lennard-Jones (LJ) potential summed over all pairs of atoms i and j . The LJ potential may also be written in the following form:

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij}((\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6) \quad (\text{S1})$$

where r_{ij} is the distance between the interacting pairs of atoms, σ_{ij} and ε_{ij} are the LJ parameters between atoms. The GROMACS LJ potential parameters $C_i^{(6)}$ and $C_i^{(12)}$ can be defined using the combination rules:

$$C_i^{(6)} = 4 \varepsilon_i \sigma_i^6 \quad (\text{S2})$$

$$C_i^{(12)} = 4 \varepsilon_i \sigma_i^{12} \quad (\text{S3})$$

The combinations for different atom-types can be computed according to the combination rule:

$$C_{ij}^{(6)} = (C_i^{(6)} C_j^{(6)})^{1/2} \quad (\text{S4})$$

$$C_{ij}^{(12)} = (C_i^{(12)} C_j^{(12)})^{1/2} \quad (\text{S5})$$

There are three kinds of POM clusters introduced to intervene the nucleation process of materials, which are $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{Mo}_8\text{O}_{26}$, (denoted as $[\text{TBA}]_4\text{Mo}_8\text{O}_{26}$), $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Mo}_6\text{O}_{19}$, (denoted as $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$) and $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (denoted as PMA)). The uniform binary cluster-nuclei co-assembled materials are $\text{NiS}_x\text{-NiO}_x\text{-Mo}_8\text{O}_{26}$, $\text{NiS}_x\text{-NiO}_x\text{-Mo}_6\text{O}_{19}$ and $\text{NiS}_x\text{-NiO}_x\text{-PMA}$.

Supplementary Table

Supplementary Table 1 | Summary of the works related to the preparation of PCAMs sub-nanometer materials by solvothermal methods and two-phase methods.

Ref.	Materials	Publication	Title	Application
1	1D Ca-POM nanowire	Science	Locking volatile organic molecules by subnanometer inorganic nanowire-based organogels	Organogel
2	2D clusterphene	Nat. Chem.	Self-assembly of polyoxometalate clusters into two-dimensional clusterphene structures featuring hexagonal pores.	Catalyze the epoxidation of olefin
3	2D Cluster-nuclei co-assembly nanosheet	Nat. Chem.	Incorporation of clusters within inorganic materials through their addition during nucleation steps	Catalyze oxidative desulfurization of gasoline
4	2D polyoxoniobate-based clusterphene	Nat. Synth.	Synthesis of two-dimensional polyoxoniobate-based clusterphenes with in-plane electron delocalization	Photo-catalyze of benzyl alcohol oxidation
5	2D POM-assembled superstructures	Nat. Synth.	Phase engineering of polyoxometalate assembled superstructures	Catalyze the epoxidation of olefin
6	Crystalline covalent network	Sci. Adv.	A monolayer crystalline covalent network of polyoxometalate clusters	Catalyze the oxidation of benzyl alcohol
7	Ag-POM coassembly nanowires	Adv. Mater.	Visible light induced Ag-polyoxometalate coassembly into single-cluster nanowires	Electrochemical sensing/Catalytic gasoline desulfurization
8	POM single-cluster ring	Sci. Adv.	Single molecule-mediated assembly of polyoxometalate single-cluster rings and their three-dimensional superstructures	Catalyze the epoxidation of olefin/ Electrochemical sensing performance
9	POM chiral assemblies	J. Am. Chem. Soc.	Tuning the chirality evolution in achiral subnanometer systems by judicious control of molecule interactions.	Circularly polarized light photodetector
10	Au-POM nanowire	Small	Au-polyoxometalates A-B-A-B	Catalyze the

			type copolymer-analogue sub-1 nm nanowires	CO ₂ reduction reaction
11	NiO-POM heterostructure	J. Am. Chem. Soc.	Electron-delocalization-stabilized photoelectrocatalytic coupling of methane by NiO-polyoxometalate sub-1 nm heterostructures	Photoelectrocatalytic coupling of methane
12	Hybrid MoO ₃ -POM nanobelt	J. Am. Chem. Soc.	Hybrid MoO ₃ -polyoxometallate sub-1 nm nanobelt superstructures	Photothermal conversion/Catalyze the oxidation of thioether
13	Macroscopic helical structure	J. Am. Chem. Soc.	Chirality evolution from sub-1 nanometer nanowires to the macroscopic helical structure	Circularly polarized luminescence
14	Bi ₂ O ₃ -PMoO SNWs	Adv. Func. Mater.	Polyoxometalates facilitating synthesis of subnanometer nanowires	Flexible films used to solar steam generation and seawater desalination
15	TiO ₂ /ZrO ₂ -POM nanobelt heterostructure	Adv. Mater.	Subnanometer nanobelts based on titanium dioxide/zirconium dioxide-polyoxometalate heterostructures	Catalyze the oxidative desulfurization reaction
16	2D single cluster superlattice/Single cluster nanowire	Adv. Func. Mater.	Temperature-responsive self-assembly of single polyoxometalates clusters driven by hydrogen bonds	Catalyze the epoxidation of olefin
17	CuO-PMA-Ag nanosheet heterostructure	Chem. Sci.	Ternary hybrid CuO-PMA-Ag sub-1 nm nanosheet heterostructures	Catalyze the epoxidation of olefin
18	ZnO-POM nanosheets	J. Am. Chem. Soc.	ZnO-POM cluster sub-1 nm nanosheets as robust catalysts for the oxidation of thioethers at room temperature	Catalyze the oxidation of thioether
19	Single-walled cluster nanotube	J. Am. Chem. Soc.	Single-walled cluster nanotubes for single-atom catalysts with precise structures	Catalyze the alcoholysis of dimethylphenylsilane
20	Mechanically tunable organogels	Nat. Commun.	Mechanically tunable organogels from highly charged polyoxometalate clusters loaded with fluorescent dyes	Organogel
21	Versatile inorganic nanowire	J. Am. Chem. Soc.	Versatile inorganic subnanometer nanowire adhesive	Adhesive

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