

Electronic Supplementary Information

Polyoxometalate-like sub-nanometer molybdenum(VI)-oxo clusters for sensitive, selective and stable H₂O₂ sensing

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1. Instrumentation

Electrochemistry and electrochemical sensing experiments were performed on a CHI 730E (CH Instruments Inc.) and PalmSens4 (PalmSens BV, Netherlands) potentiostat.

General remarks: All chemicals were purchased from Sigma Aldrich, ABCR or ACROS and were of reagent grade. The chemicals were used without further purification unless stated otherwise.

2. Experimental section

2.1 Synthesis of samples 1, 2 and 3

Synthesis of composite 1-1. Composite 1-1 was synthesized using commercial silica gel powder with pore size of 150 Å (Sigma-Aldrich) as a hard template. Typically, 2.555 g (1.4 mmol) of phosphomolybdic acid hydrate ($[\text{H}_3\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ (=PMo₁₂) Alfa Aesar) was dissolved in 5 g of water, then 1.25 g (3.63 mmol) of sucrose (Merck Millipore (Calbiochem)) was added and dissolved. Finally, 1.0 g of silica powder was dispersed in the above solution and stirred overnight at room temperature. The mixture was heated in air to 100 °C for 6 h and subsequently to 160 °C for another 6 h. This impregnation process was repeated with a second solution containing 0.8 g (2.32 mmol) of sucrose and 1.643 g (0.9 mmol) of PMo₁₂ in 5 g of water. The air-dried materials were carbonized at 900 °C for 5 h under Ar at a heating rate of 5 °C/min. To remove the silica template, the as-prepared composites were stirred in 50 ml of 10% aqueous hydrofluoric acid (HF_{aq}, ≥48%, Sigma-Aldrich) for 48 h, then washed with water and ethanol three times respectively, and finally dried at 100 °C overnight. Note that hydrofluoric acid is toxic and necessary handling precautions need to be taken.

Synthesis of composite 1-2. 0.1 g of 1-1 was dispersed in 10 ml of 10% aqueous HNO₃ (~65%, ACROS) and stirred for 5 hours at 50 °C. The powder was filtered off, washed with water (4x) and dried at 100 °C overnight, giving solid, dry composite 1-2.

Synthesis of composite 1. Composite **1-2** (25 mg) was mixed with 0.25 g of 50 wt% aqueous cyanamide solution as a nitrogen source (99 %, Aldrich) and 0.25 g water. The mixture was stirred overnight and left to dry at 30 °C in air for 48 h. The dried powder was firstly calcined at 550 °C for 4 h (heating rate 4 °C/min) and then at 650 °C for 3 h (heating rate 4 °C/min) in Ar to obtain composite **1**.

Synthesis of composite 2 and 3. Mesoporous carbon (**MC**), oxidized mesoporous carbon (**OMC**) and nitrogen-doped mesoporous carbon (**NMC**, hereafter: **2**) references were prepared following the same method as **1** by using concentrated sulfuric acid (96%, ACROS) as carbonization catalyst. Composite **3** was prepared by physical mixing (prolonged manual grinding) of **2** with commercial **MoO₃** (99.5%, Alfa Aesar, the loading amount of Mo was similar to the loading of **1** (10.4 wt%)).

2.2 H₂O₂ sensing application

1) H₂O₂ sensor based on 1-modified glassy carbon (GC) electrode. 2 mg of the finely ground catalyst (**1** or reference samples **2**, **3**) was dispersed in 400 μL anhydrous ethanol ([catalyst] = 5 mg mL⁻¹) by sonication for 1 h to form a homogeneous ink. 7.5 μL of the above catalyst ink **1** was loaded onto a glassy carbon rotating disk electrode (RDE, the loading of the catalysts was 0.3 mg cm⁻²). Cyclic voltammetric (CV) and amperometric measurements were performed on a CHI 730E potentiostat. A standard three-electrode cell was used and was operated at room temperature. A platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The prepared thin-film modified RDE was used as the working electrode. The electrolyte, consisting of a solution of 0.1 M phosphate buffer solution (PBS, pH 7.0), was saturated with ultrahigh-purity Ar for 30 min before CV measurements and an Ar atmosphere was kept over the solution in the cell during amperometric measurements. In steady-state chronoamperometric (CA) experiment, the potential was set as at -0.3 V vs. SCE with an electrode rotating speed of 1600 rpm, and the current-time curves were recorded after a constant background current had been established.

2) H₂O₂ sensor based on 1-modified Screen-Printed Electrode (SPE). CV and CA measurements were conducted by an electrochemical station (PalmSens4, PalmSens BV, Netherlands) with a three-electrode-system on a SPE (DRP-110, DropSens). The working electrode (diameter = 4 mm, catalyst loading = 0.3 mg cm⁻²) and the counter electrode of the SPE were made by carbon, reference electrode was made by silver. Different amounts of H₂O₂ was added to PBS saturated with N₂ to get a series of solutions with different concentrations. In the CV and CA measurements, 50 μL of H₂O₂ solution was dropped on the surface of SPE as the electrolyte. CV measurements were taken at the potential range between -1.0 V and 0.5 V. CA measurements were taken at -0.6 V with the H₂O₂ solutions added and substituted successively.

3. Supplementary Figures and Tables

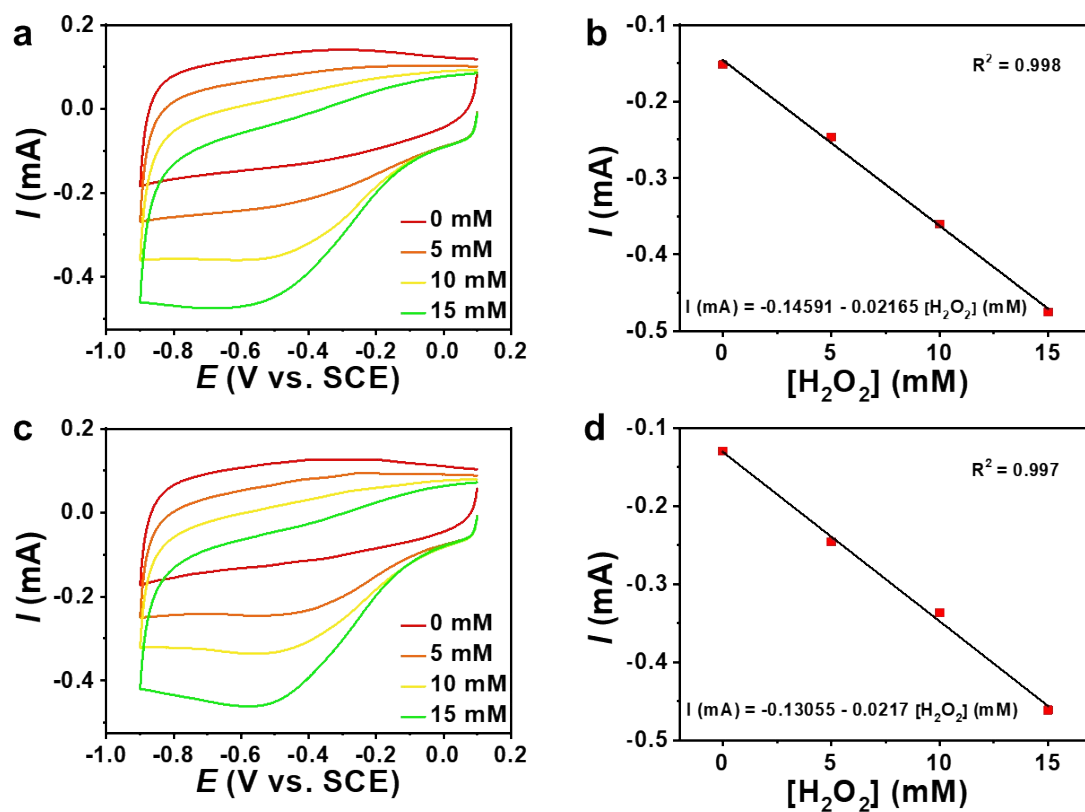


Figure S1. Electrochemical study of the H₂O₂ detection by **2** and **3** deposited on a rotating disk electrode (RDE). a) CVs of the **2**-modified RDE (0.3 mg/cm²) in 0.1 M aqueous PBS (pH = 7) at 50 mV s⁻¹; [H₂O₂] = 0 to 15 mM. b) The corresponding calibration plot based on Fig. S1a, currents determined at -0.65 V vs. SCE. c) CVs of the **3**-modified RDE (0.3 mg/cm²) in 0.1 M aqueous PBS (pH = 7) at 50 mV s⁻¹; [H₂O₂] = 0 to 15 mM. d) The corresponding calibration plot based on Fig. S1c, currents determined at -0.56 V vs. SCE.

Table S1. Comparison of the performance of different H₂O₂ biosensors based on metal/metal oxide clusters.

Material	Electrolyte	Detection limit (M)	Linear range (M)	Sensitivity ($\mu\text{A mM}^{-1} \cdot \text{cm}^{-2}$)	Response time (s)	Reference
[Mo-oxo] _n /NPC	0.1 M PBS (pH 7.0)	2.3×10^{-7}	$5 \times 10^{-8} - 5 \times 10^{-3}$	2211.8	2	This work
Pt-PdBNC	0.1 M PBS (pH 6.9)	8.7×10^{-7}	$5 \times 10^{-6} - 6 \times 10^{-3}$	804	2	1
SnO ₂ -rGO	0.1 M PBS (pH 7.4)	4.78×10^{-7}	$5 \times 10^{-7} - 8 \times 10^{-4}$	406	2	2
HRP-Au NCs	50 mM glycine buffer (pH 9.0)	3.0×10^{-8}	$1 \times 10^{-7} - 1 \times 10^{-4}$	-	-	3
TMB/Fe28	HCl (pH 2.0)	5.24×10^{-7}	$2.62 \times 10^{-5} - 1.57 \times 10^{-4}$	-	-	4
BSA-Ag NCs		3.0×10^{-7}	$6 \times 10^{-7} - 1 \times 10^{-4}$	-	-	5
Pd nanocluster	Britton-Robinson buffer (pH 7)	-	-	102.1 ± 2.32	-	6

Notes: Pt-Pd bimetallic nanoclusters (Pt-PdBNC); Horseradish peroxidase-gold nanoclusters (HRP-Au NCs); 3,3',5,5'-tetramethylbenzidine (TMB); bovine serum albumin (BSA)-stabilized silver nanoclusters (BSA-Ag NCs).

Sensing Performance of H₂O₂ with 1-modified SPE Cyclic voltammetry (CV) was applied to study the electroactivity of **1** towards H₂O₂. The test was taken on a screen printed electrode (SPE), and 50 μL H₂O₂ solution was dropped on the SPE. Figure S1 shows the CV curves in the different concentrations and absence of H₂O₂. After the addition of 1, 2 and 3 mM H₂O₂, the cathodic peak current (between -0.5 V and -0.7 V vs. RHE) increases and the anodic peak current (between -0.1 V and 0.1 V vs. RHE) decreases with the increasing of concentration of H₂O₂, which indicates the reversibility of the catalytic process. The cathodic peak current is higher than anodic peak current. Therefore, CA test was conducted at a constant potential -0.6 V vs. Ag. As shown in Figure S2, the minimum and maximum detected concentration of H₂O₂ are 10 μM and 100 mM, respectively. Although current response of sensor is rapid (ca. 2 s), 700 s sensing time is applied to each concentration of H₂O₂ for achieving steady current. The sudden increase of current can be attributed to the addition of H₂O₂ solution, which contains dissolved oxygen. The instant currents at 650 s of 700 s are selected as the data of respective concentration of H₂O₂, the relevant linear response was shown in Figure S3. The newly-synthesized **1** exhibits good linear response and the linear equation is $\lg(I(\text{mA})) = 1.102 \lg(C(\text{mM})) - 2.842$ ($R^2 = 0.995$). To further study the stability of **1**, the CA test was conducted by the same sensor after storage under ambient conditions for 2 months. It shows similar response with the linear equation of $\lg(I(\text{mA})) = 1.043 \lg(C(\text{mM})) - 2.731$ ($R^2=0.997$). Those results indicate that **1** offers sensitive, fast and stable response to H₂O₂.

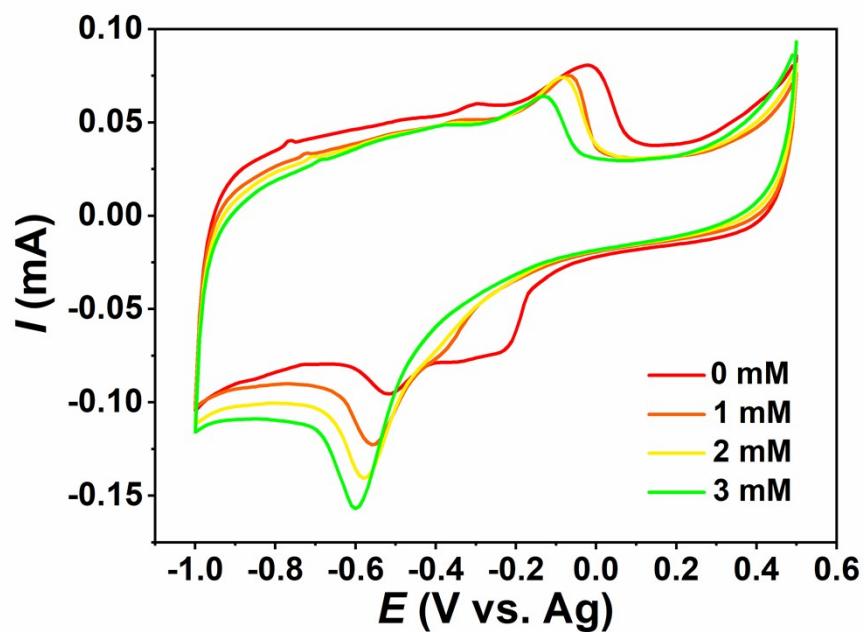


Figure S2. CVs of the 1-(0.3 mg/cm²) modified SPE in aqueous PBS (pH = 7) at 50 mV s⁻¹ in the presence of H₂O₂ concentrations of 0 to 3 mM.

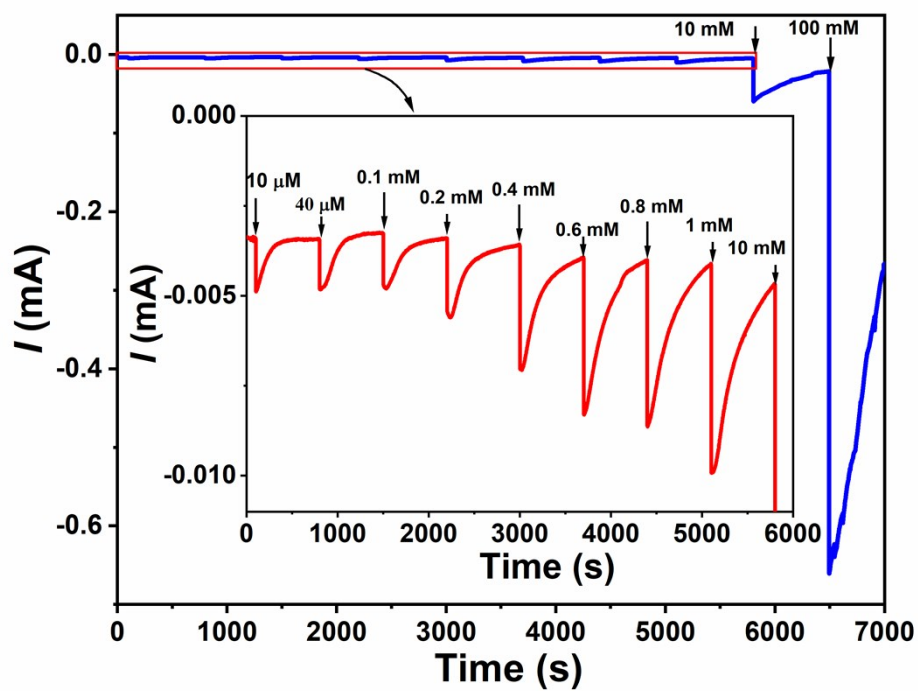


Figure S3. Typical amperometric responses of the 1-modified SPE upon addition of aliquots of H₂O₂ at -0.6 V vs. Ag in aqueous PBS (pH = 7).

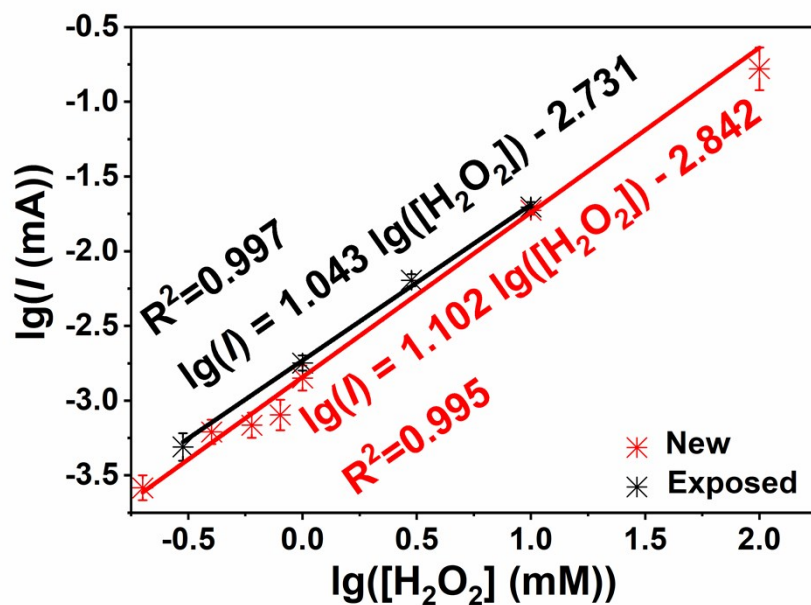


Figure S4. The corresponding calibration plot of steady-state currents against concentrations of H_2O_2 based on Figure S3.

Reference

- 1 X. Niu, C. Chen, H. Zhao, Y. Chai and M. Lan, *Biosens. Bioelectron.*, 2012, **36**, 262–266.
- 2 C. Zhang, L. Li, J. Ju and W. Chen, *Electrochim. Acta*, 2016, **210**, 181–189.
- 3 F. Wen, Y. Dong, L. Feng, S. Wang, S. Zhang and X. Zhang, *Anal. Chem.*, 2011, **83**, 1193–1196.
- 4 M. J. Wei, J. Q. Fu, B. Li, K. Z. Shao, H. Y. Zang, X. H. Wang and Z. M. Su, *New J. Chem.*, 2019, **43**, 13430–13436.
- 5 G. Yue, S. Li, W. Liu, F. Ding, P. Zou, X. Wang, Q. Zhao and H. Rao, *Sensors Actuators, B Chem.*, 2019, **287**, 408–415.
- 6 C. Hegarty, S. McKillop, T. Dooher, D. Dixon and J. Davis, *IEEE Sensors Lett.*, 2019, **3**, 1–4.