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Supporting Information for

A multivalent mixed-metal strategy for single-Cu^{+}-ion-bridged cluster-based chalcogenide open frameworks for sensitive nonenzymatic detection on glucose

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Experimental Section

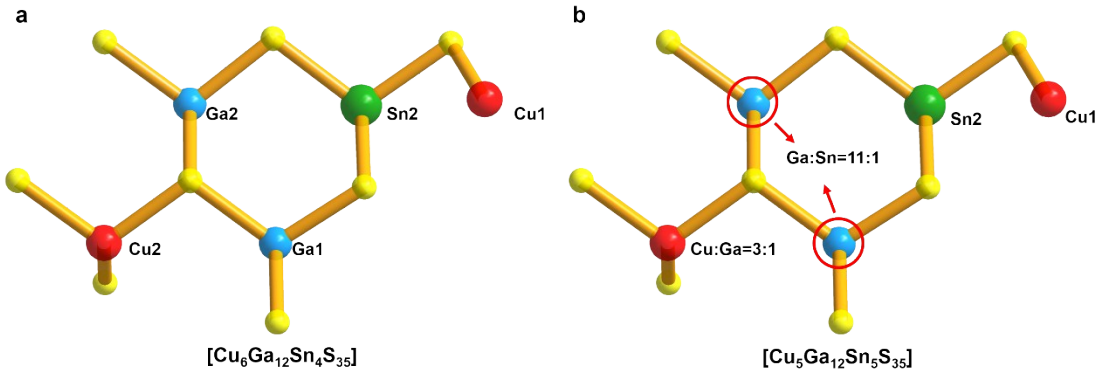
Materials. All analytical grade chemicals employed in this work were commercially available and used without further purification.

Synthesis of MCOF-3. A mixture of cupric acetate monohydrate (96 mg, 0.48 mmol), gallium (III) oxide (62 mg, 0.33 mmol), sulfur powder (96 mg, 3.0 mmol), tin (118 mg, 1 mmol), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 2.0 mL, 16.2 mmol) and H_2O (1.0 mL) was stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 180 ^oC for 10 days, then the autoclave was cooled to room temperature. Dark yellow crystals were obtained. Those raw products were washed three times by ethanol and filtered off. Elemental analysis, *Calcd.* (*wt* %): C, 18.51; N, 6.17; H, 3.13; *Found* (*wt* %): C, 18.10; N, 6.25; H, 3.01.

Synthesis of MCOF-4. A mixture of cupric acetate monohydrate (96 mg, 0.48 mmol), gallium(III) oxide (93 mg, 0.5 mmol), sulfur powder (96 mg, 3 mmol), tin (118 mg, 1 mmol), (*R*)-(-)-2-amino-1-butanol (R-2-AB, 2.0 mL, 21.6 mmol), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU, 2.0 mL, 12.9 mmol) and H_2O (1.0 mL) were stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 180 ^oC for 10 days, then the autoclave was cooled to room temperature. Red block crystals were obtained. Those raw products were washed three times by ethanol and filtered off. Elemental analysis, *Calcd.* (*wt* %): C, 16.66; N, 4.55; H, 3.52; *Found* (*wt* %): C, 16.75; N, 4.65; H, 2.94.

Single Crystal X-ray Diffraction (SCXRD). Single-crystal X-ray diffraction measurements were performed on a Bruker Smart CPAD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated MoKα (λ= 0.71073 Å) radiation at 120 K. The structure was solved by direct method using SHELXS-2014 and the refinement against all reflections of the compound was performed using SHELXL-2014. In these structures, some cations and free solvent molecules were highly disordered and could not be located. The diffuse electron densities resulting from these residual cations and solvent molecules were removed

from the data set using the SQUEEZE routine of PLATON and refined further by using the data generated. In addition, the high angle data (above 1.0 Å resolution for **MCOF-3** and 1.1 Å resolution for **MCOF-4**) was dominated by noise [*I*/sigma < 2.0] and was omitted by collecting relatively low resolution for high-quality crystal data. The experimental formula of **MCOF-3** is **[$Cu_5Ga_{12}Sn_5S_{35}$]**, which is inconsistent with **[$Cu_6Ga_{12}Sn_4S_{35}$]** given in CIF. Owing to the limitation of single-crystal data, the occupancy refinement of Cu/Ga and Ga/Sn cannot be well conducted. Hence, the final formula should be **[$Cu_5Ga_{12}Sn_5S_{35}$]** determined by elemental analysis. According to Pauling's electrostatic valence rule, Scheme S1 was provided to help understand the occupancy of Cu/Ga and Ga/Sn.



Scheme S1. The structure formula provided in CIF (a) and the structure formula determined by elemental analysis (b).

Powder X-ray Diffraction (PXRD). PXRD data were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-Kα (λ=1.54184Å) radiation operated at 30 kV and 10 mA. The samples were ground into fine powders for several minutes before the test.

XPS and AES Measurements. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were collected with a Leeman prodigy spectrometer equipped with a monochromatic Al Kα X-ray source and a concentric hemispherical analyzer.

Elemental Analysis. Energy dispersive spectroscopy (EDS) analysis was performed on scanning electron microscope (SEM) equipped with energy dispersive spectroscopy detector. An accelerating voltage of 25 kV and 40 s accumulation time were applied. EDS results clearly confirmed the presence of Cu, Ga, Sn and S elements. Elemental analysis (EA) of C, H, and N was performed on VARIDEL III elemental analyzer.

Thermogravimetric Analysis (TGA). TGA measurement was performed with a Shimadzu TGA-50 system under nitrogen flow. The TG curve was performed by heating the sample from 20 to 800 °C with heating rate of 10 °C /min.

Fourier Transform Infrared Absorption. Fourier transform-Infrared spectral analysis was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with cesium iodide optics allowing the instrument to observe from 600-4000 cm^{-1}.

Electrochemical Measurements. All of the CV and amperometric tests were conducted using a potentiostat (CHI 660E, Shanghai, Chenhua) in a three-electrode cell (graphite electrode as the counter electrode and A KCl saturated no-leak Ag/AgCl electrode as the reference electrode) at room temperature. The **MCOF-3**/**MCOF-4** electrode served directly as the working electrode for the detection of glucose. The procedure of pretreatment and modification of the working electrode is as follows: it was firstly polished mechanically with 0.05 mm alumina slurry to obtain a mirror-like surface and then rinsed thoroughly with water, ethanol, and water and then allowed to dry. The homogeneous inks were prepared by dispersing 2 mg catalyst and 1 mg carbon black (CB) in mixture of 400 μL water, 100 μL ethanol and 20 μL 5% Nafion (5 *wt*% in propanol, Alfa Aesar) which were denoted as **MCOF-3/CB** and **MCOF-4/CB**. The mixture was then sonicated strongly for 0.5 h to form a uniform ink. 4 μL of as-prepared catalyst ink was coated onto the pre-cleaned working electrode and dried at room temperature for the following electrochemical measurements. The CVs were collected in a 0.1 M NaOH aqueous electrolyte with and without various concentrations of glucose. The amperometric responses of the **MCOF-3/CB** or

MCOF-4/CB electrode to glucose were measured at the applied potential of 0.6 V (*vs.* Ag/AgCl). Langmuir fitting equation ($I = a \times C_{glucose}/(b + C_{glucose})$) was adopted for corresponding calibration of **MCOF-3** and **MCOF-4**. Linear fitting ($I = a \times C_{glucose} + b$) was adopted for corresponding calibration of low concentration (< 50 μM).

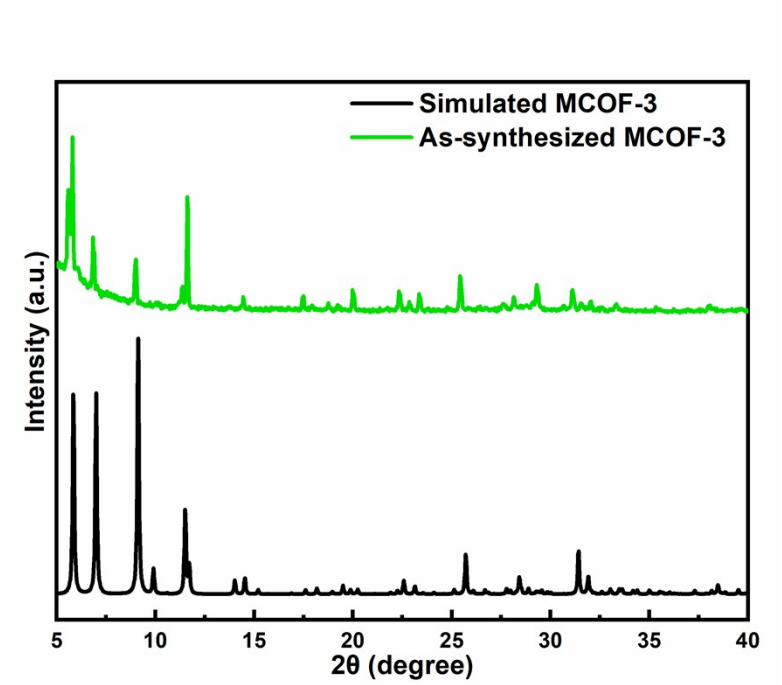


Fig. S1 The simulated and experimental PXRD patterns of **MCOF-3**.

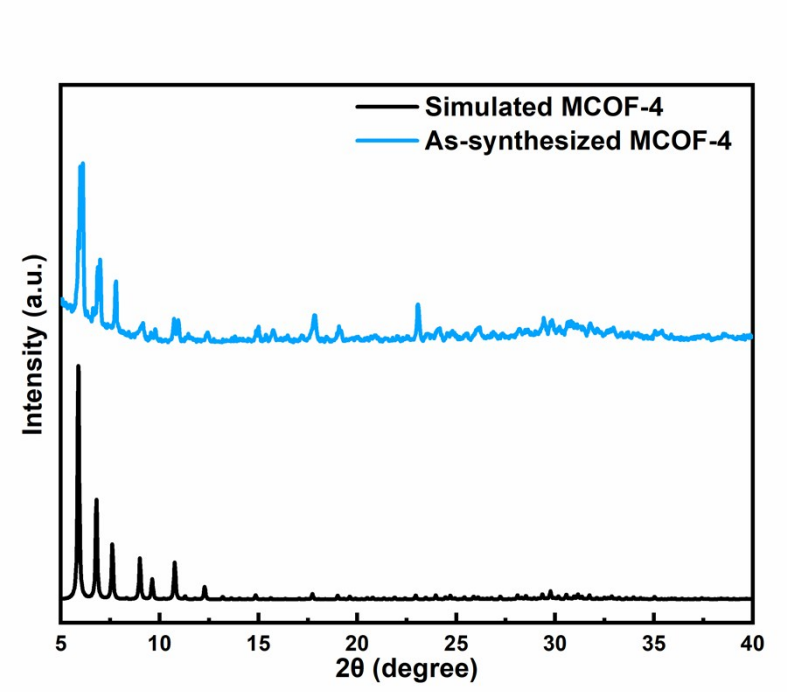


Fig. S2 The simulated and experimental PXRD patterns of **MCOF-4**.

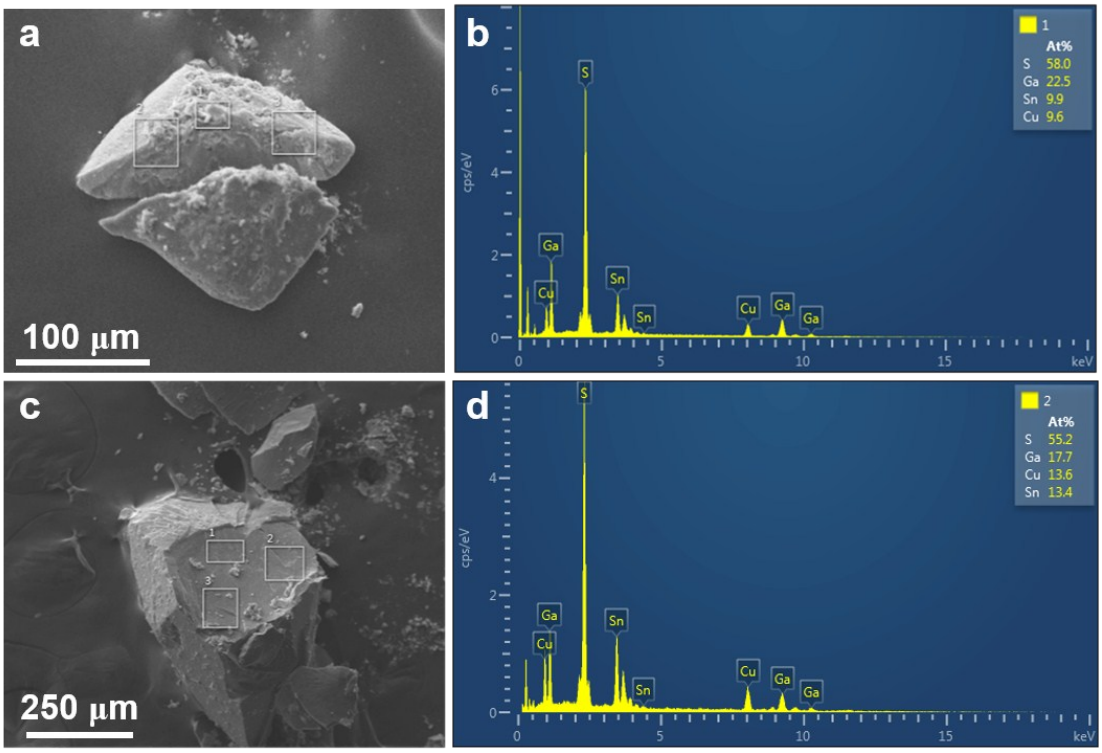


Fig. S3 SEM images of as-synthesized **MCOF-3** (a) and **MCOF-4** (c), and energy dispersive spectroscopy (EDS) of **MCOF-3** (b) (the ratio of Cu/Ga/Sn *Found:*1: 2.34: 1.03.) and **MCOF-4** (d) (the ratio of Cu/Ga/Sn *Found:*1: 1.30: 0.99.).

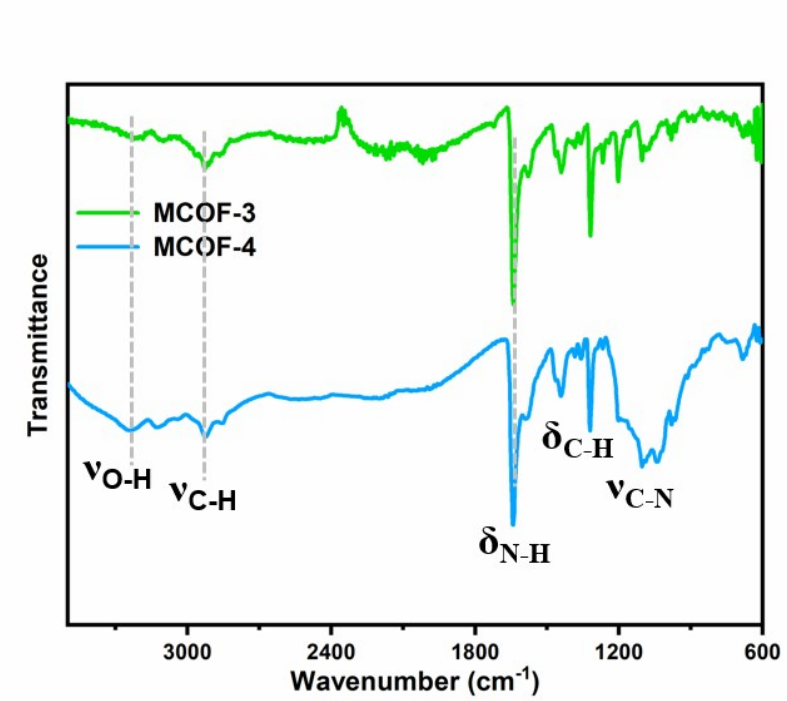


Fig. S4 FT-IR spectra of **MCOF-3** and **MCOF-4**, Important data (cm^{-1}): 3240(w), 2927(w), 1643(s), 1442(m), 1321(m), 1103(m).

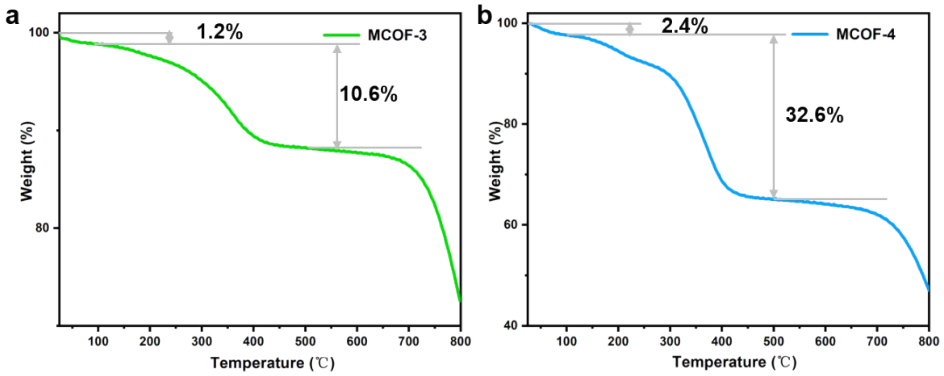


Fig. S5 Thermogravimetric analysis (TGA) curves of **MCOF-3** (a): The initial gradual weight loss of 1.2% between 25-100ºC could be attributed to loss of moisture and solvent of sample. An abrupt weight loss of 10.6% between 100-500 ℃ is attributed to the carbonization of template. TGA curves of **MCOF-4** (b): The initial gradual weight loss of 2.4% between 25-100ºC could be attributed to loss of moisture and solvent of sample. An abrupt weight loss of 32.6% between 100-500 ℃ is attributed to the carbonization of template.

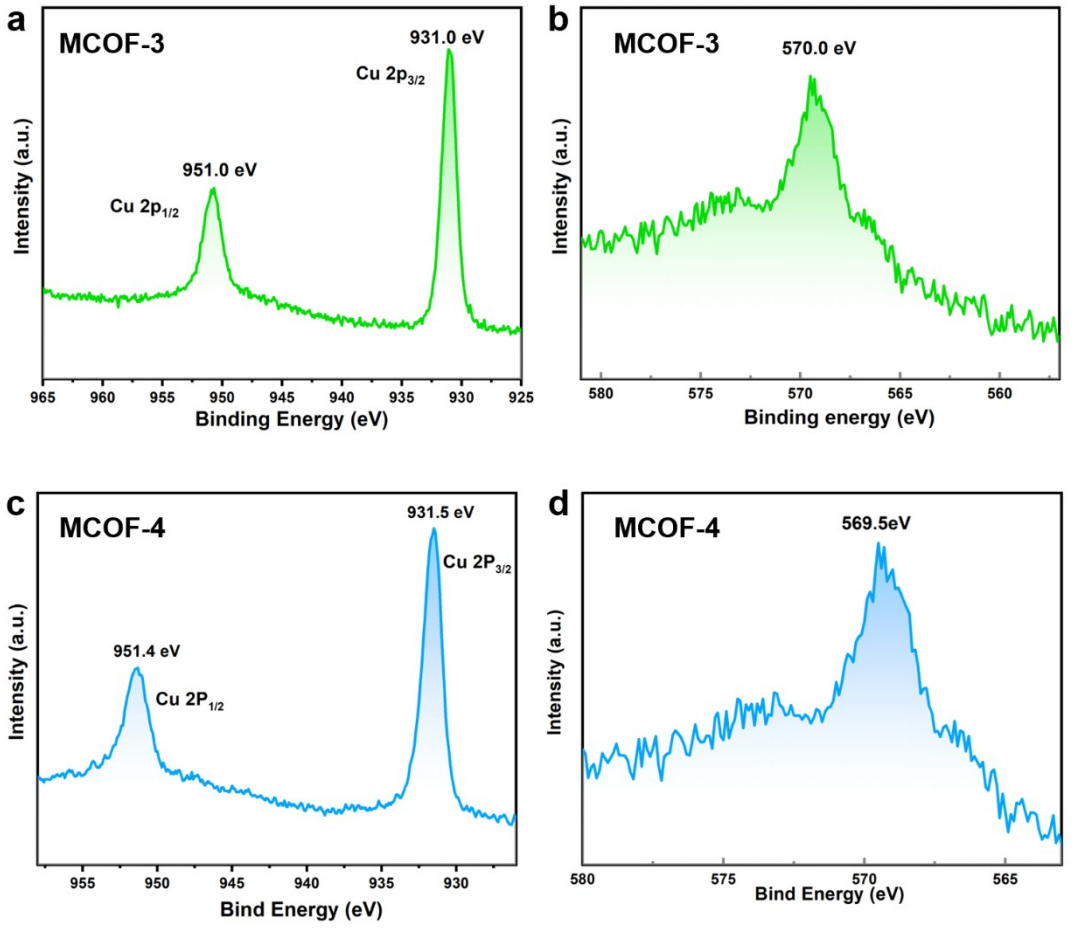


Fig. S6 XPS analysis of **MCOF-3** (a) **and MCOF-4** (c). Auger electron spectra of Cu LM2 in **MCOF-3** (b) and **MCOF-4** (d).

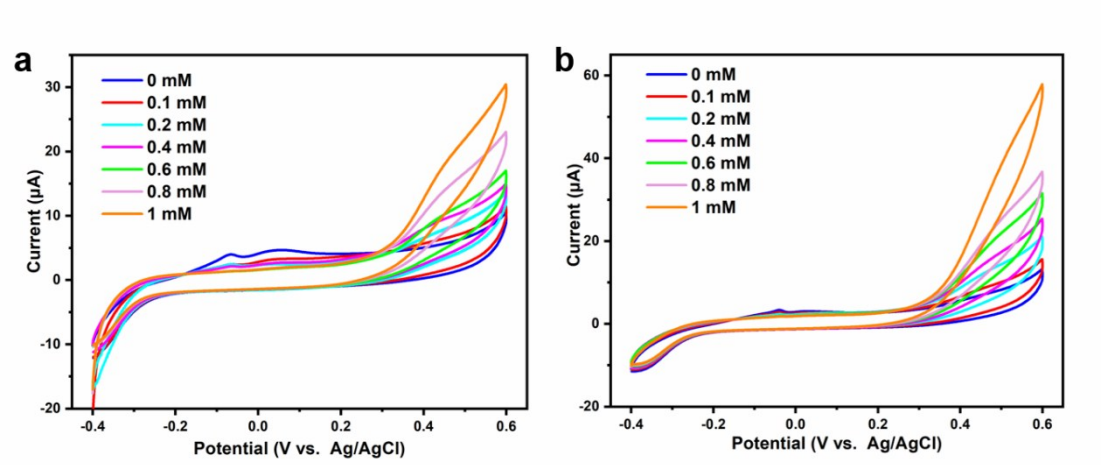


Fig. S7 CVs of the **MCOF-3/CB** (a) and **MCOF-4/CB** (b) in the 0.1 M NaOH solution containing different concentration of glucose (from 0 to 1 mM) at a scan rate of 20 mV s^{-1}.

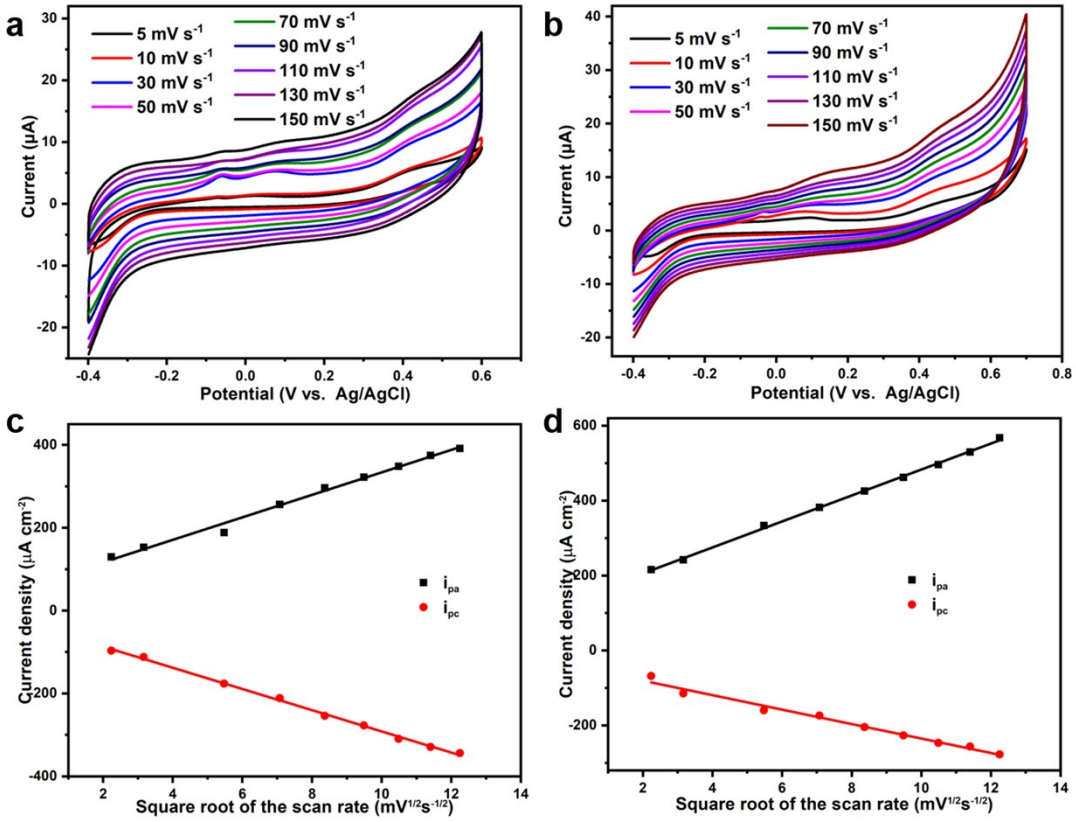


Fig. S8 CVs of **MCOF-3/CB** (a) and **MCOF-4/CB** (b) in the 0.1M NaOH solution containing 0.5 mM glucose at various scan rates; (c) Plots of peak currents as a function of the square root of the scan rate (**MCOF-3**); (d) Plots of peak currents as a function of the square root of the scan rate (**MCOF-4**).

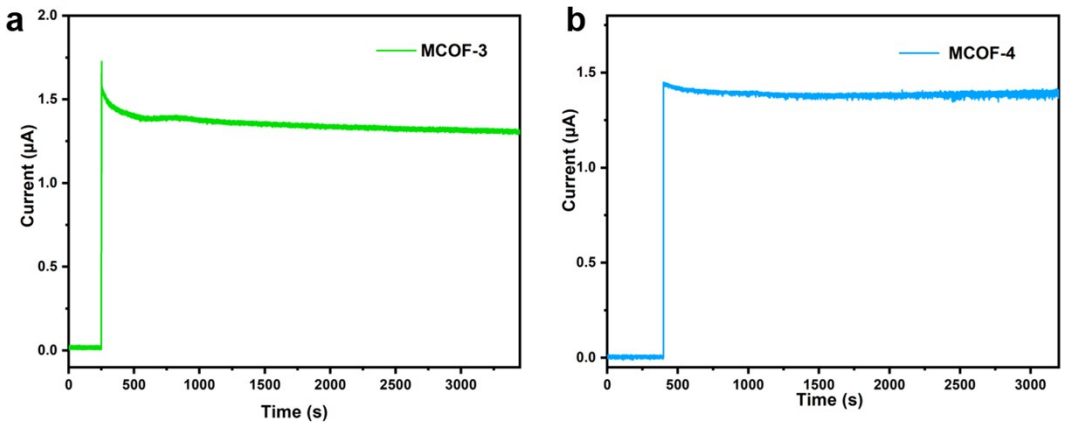


Fig. S9 Amperometric response of **MCOF-3/CB** (a) and **MCOF-4/CB** (b) electrode to 0.1 mM glucose in a 0.1 M NaOH solution at 0.6 V *vs.* Ag/AgCl for a long running time (3500 s).

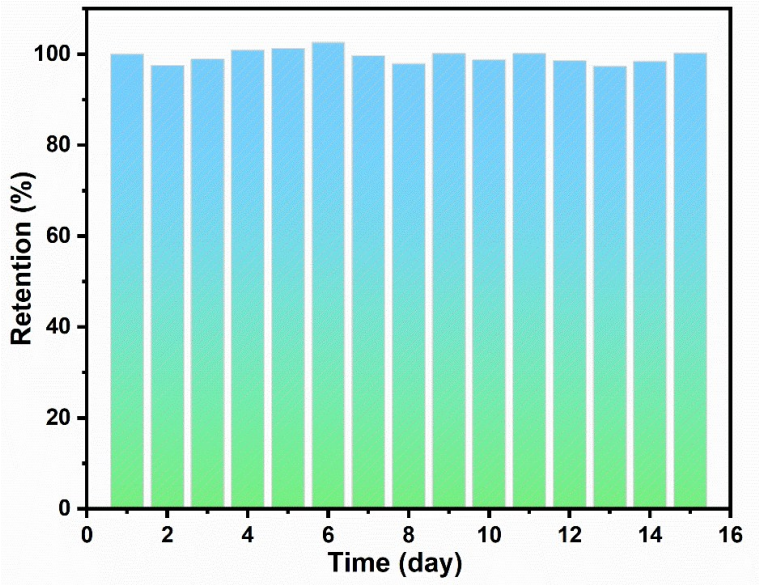


Fig. S10 Long-term stability of **MCOF-4/CB** over 15 days.

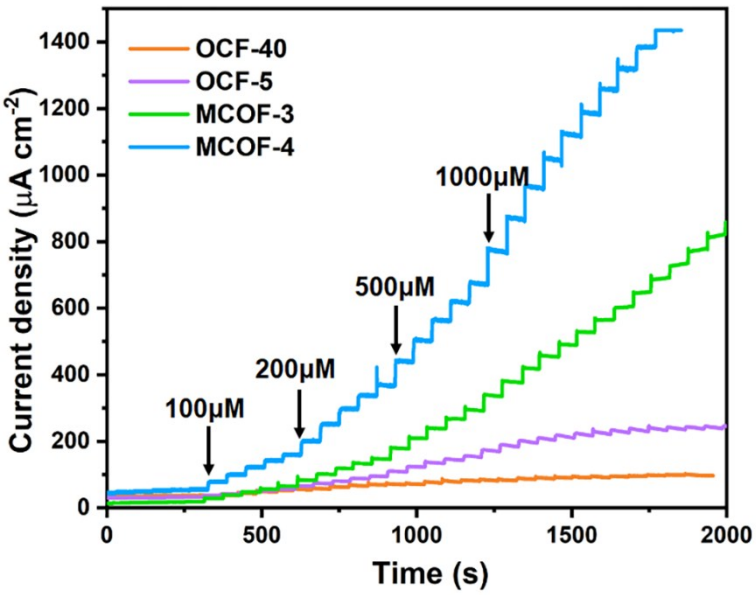


Fig. S11 Amperometric response curves of OCF-40 (isolated T4-CuGaSnS), OCF-5 (T4-CuGaSnS related two-fold interpenetrating *dia* topological structures with S serving as linkers), MCOF-3 (T4-CuGaSnS related three-fold interpenetrating *dia* topological structures with S-Cu-S serving as linkers) and MCOF-4 (P2-CuGaSnS related three-fold interpenetrating *dia* topological structures with S-Cu-S serving as linkers), respectively. Suggesting that accessible single-cuprous ions contributed to the sensitive nonenzymatic detection on glucose.

Table S1 Crystallographic data and structure refinement parameters for **MCOF-3** and **MCOF-4**.

Compound	**MCOF-3**	**MCOF-4**
Formula	$[Cu_5Ga_{12}Sn_5S_{35}](C_7H_{13}N_2)_9(H_2O)_5$	$[Cu_{8.5}Ga_{11}Sn_{8.5}S_{44}](C_9H_{17}N_2)_{4.5}(C_4H_{12}NO)_8(H_2O)_5$
Crystal system	Tetragonal	Trigonal
Z	2	9
Space group	$I4_1/amd$	$R3$
a /Å	25.2441(12)	51.949(4)
b /Å	25.2441(12)	51.949(4)
c /Å	18.8435(11)	31.812(2)
α /°	90	90
β /°	90	90
γ /°	90	120
V (Å^3)	12008.3(13)	74351(11)
D (g·cm^{-1})	1.557	1.498
μ (mm^{-1})	5.108	4.648
F (000)	5224	30897
R_{int}	0.049	0.1357
GOF	1.111	1.012
R_1, wR_2 (I>2σ(I))	0.051, 0.1825	0.0852, 0.2312
R_1, wR_2 (all data)	0.062, 0.2108	0.1200, 0.2741