Supporting information for

A 3D Neutral Chalcogenide Framework Built from Supertetrahedral T3 Cluster and Metal Complex for Electrocatalytic Oxygen Reduction Reaction

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Materials

Gallium oxide (Ga_2O_3, 99.9%, powder), sulfur (S, 99.9%, powder), manganese acetate tetrahydrate ($Mn(AC)_2{\cdot}4H_2O$, 97.0%, powder), tin (Sn, 99.9%, powder), 1,2-diaminocyclohexane ($C_6H_{14}N_2$, 97%, liquid), potassium hydroxide (KOH, 85%, bulk), carbon black (CB, VXC-72), Pt/C(10 wt%, powder), deionized water were all used without further purification.

Synthesis of $[Mn_2Ga_4Sn_4S_{20}]{\cdot}4[Mn(dach)_2]$ (denoted as NCF-4)

S powder (96 mg, 3.00 mmol), Ga_2O_3 (62 mg, 0.33 mmol), Sn powder (115 mg, 0.97 mmol), $Mn(AC)_2{\cdot}4H_2O$ (62 mg, 0.28 mmol), H_2O (0.5 mL) and 1,2-diaminocyclohexane (2 mL) was mixed in a 23 mL Teflon-lined stainless-steel autoclave with stirring for about 30 min at room temperature. Then the vessel was sealed and heated to 180 °C for 7 days. After ultrasonic treatment and wash with ethanol and deionized water, yellowish-brown octahedral crystals were obtained (Yield: ~30% based on Ga_2O_3). Elemental analysis for $[Mn_2Ga_4Sn_4S_{20}]{\cdot}4[Mn(dach)_2]$, calcd (%): C 21.85, H 4.29, N 8.50; found: C 24.27, H 5.01, N 9.15.

Material Characterizations

The as-synthesized crystalline sample was characterized by power X-ray diffraction that was collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-Kα radiation operated at 30 kV and 10 mA. The thermogravimetry (TG) was measured with TG 209 F1 Libra. The single-crystal X-ray diffraction measurements were performed on Agilent diffractometers with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at 296 K. The structure was solved by direct method using SHELXS-97 and the refinement against all reflections of the compound was performed using SHELXL-97. Energy dispersive spectroscopy (EDS) and scanning electron microscope (SEM) were performed on SU1510 with an accelerating voltage 25 kV. A Varian 710-ES inductively coupled plasma optical emission spectrometry (ICP-OES) instrument was used to determine the concentrations of Ga^{3+}/ Mn^{2+}. Room-temperature solid-state UV-Vis diffusion reflectance spectrum of sample was measured on a UV-3600. Fourier transform infrared spectrum of sample was measured on a HYPERION 2000.

Electrochemical measurements

Electrochemical experiments were performed in a typical three-electrode electrochemical system with CHI-750E instrument coupled with a RDE. The three-electrode system is composed of a glassy carbon as working electrode (GRE), a KCl saturated Ag|AgCl electrode as reference, and a Pt wire as counter electrode. The homogeneous inks were prepared by mixing 2 mg compound 1 and 1 mg carbon black (CB) in 400 μL deionized water, 100 μL EtOH and 20 μL Nafion. The inks were sonicated (the frequency is 40KHz, the power is 240W) for 30 min to make them forming more uniform sizes. Then 7 μL inks were coated onto a clean GCE (4 mm in diameter) and dried at room temperture for the following electrochemical measurements. Cyclic voltammetry (CV) was performed at a scanning rate of 50 mV/s after purging high pure O_2 or N_2 gas for 30 min. Linear sweep voltammetry (LSV) was performed with the RDE in the O_2-saturated 0.1 M KOH solution at rotation speeds 1600 rpm with a scan rate of 5 mV/s. All electrochemical experiments were performed at room temperature.

$$n = \frac{4I_{\text{disk}}}{\frac{I_{\text{ring}}}{N} + I_{\text{disk}}}$$

$$H_2O_2\% = \frac{200\frac{I_{\text{ring}}}{N}}{\frac{I_{\text{ring}}}{N} + I_{\text{disk}}}$$

where I_{disk} is the disk electrode current, I_{ring} is the ring electrode current and N is collection efficiency of the ring electrode (Pt). N was determined to be 0.42 according to the literature, in agreement with the value provided by the manufacturer (0.42).

Linear sweep voltammetry (LSV) was performed with the RDE in the O2-saturated 0.1 M KOH solution at rotation speeds varying from 625 to 1600 rpm with a scan rate of 5 mV/s. Koutecky–Levich (K–L) plots were analyzed at various electrode potentials (-0.35, -0.45, -0.55, -0.65 and -0.75 vs. Ag/AgCl). The slopes of their linear fit lines are used to assess the number of electrons (n) transferred per oxygen molecule on the basis of the K–L equation:

$$\frac{1}{j} = \frac{1}{j_{\text{L}}} + \frac{1}{j_{\text{K}}} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_{\text{K}}} \qquad (1)$$

$$B = 0.62nFC_0D_0^{3/2}\nu^{-1/6} \qquad (2)$$

$$J_{\text{K}} = nFkC_0 \qquad (3)$$

where j is the measured current density, j_K and j_L are the kineticand diffusion-limiting current densities, ω is the electrode rotation rate, n is the number of electrons transferred per O_2, F is the Faraday constant, C_0 is the bulk concentration of O_2, D_0 is the diffusion coefficient of O_2, ν is the kinematic viscosity of the electrolyte, and κ is the electron-transfer rate constant.

Table S1. The crystal data and refinement details of **NCF-4**.

	NCF-4
Formula	$Mn_6Ga_4Sn_4S_{20}C_{48}N_{16}H_{112}$
Formula weight	2638.10
Crystal system	tetragonal
Z	4
Space group	$I4_1/a$
a(Å)	23.3697(4)
b(Å)	23.3697(4)
c(Å)	20.7308(9)
β (°)	90
V(Å³)	11322.0(6)
T/K	296
F(000)	5224
μ(mm⁻¹)	2.845
D(g cm⁻³)	1.548
GOF on F^2	1.076
R_1, wR_2 $(I>2\sigma(I))$	0.0434, 0.0910
R_1, wR_2 *(all)*	0.0730, 0.1084

Table S2. The ICP-OES analysis of NCF-4.

Sample	**Time**	**Mn**	**Ga**	**Mn:Ga**
NCF-4	1	1.1249	0.7600	1.48:1
NCF-4	2	1.1208	0.7677	1.46:1
NCF-4	3	1.1320	0.7628	1.48:1
NCF-4	average value	1.1259	0.7635	1.47:1

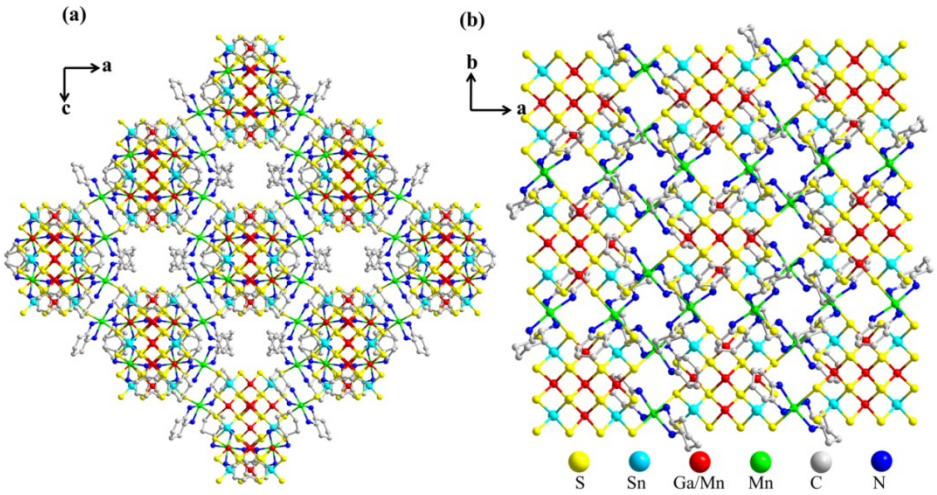

Fig. S1 3D structures of NCF-4 viewed along *b* axis (a) and *c* axis (b).

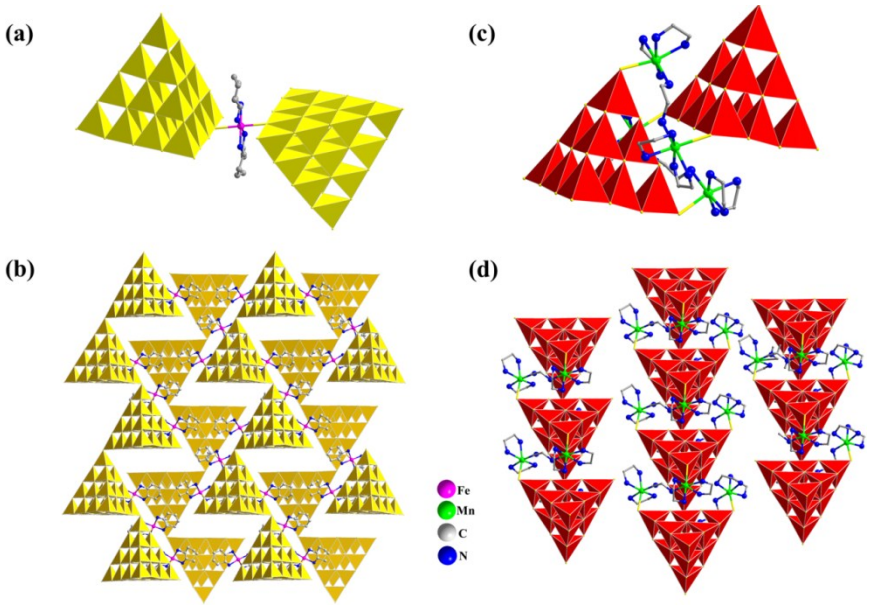

Fig. S2 (a) Inter-clusters T4-Fe edge-edge connection mode by metal complex; (b) 2D polyhedron of T4-Fe viewed along *c* axis; (c) connection mode between $[Mn_2(en)_5]^{4+}$ complex and $[Mn_2Ga_4Sn_4S_{20}]^{8-}$ T3 nanocluster; (d) the packing pattern of $[Mn_2(en)_5][MnGa_2Sn_2S_{10}]$.

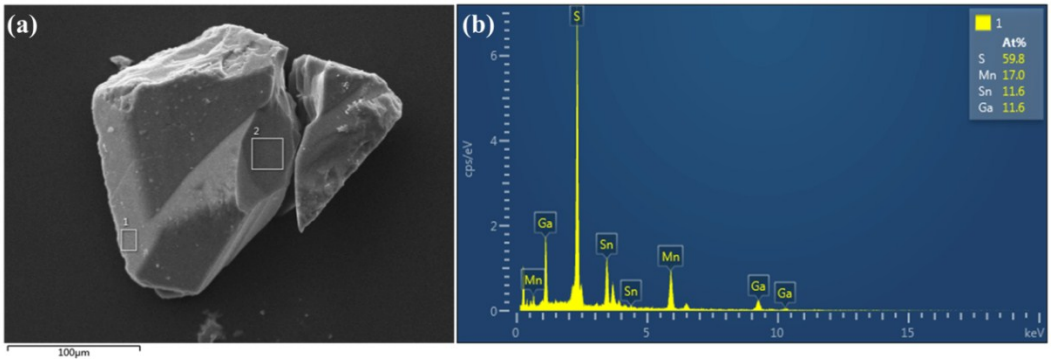

Fig. S3 (a) SEM image of as-synthesized NCF-4, (b) energy dispersive spectroscopy (EDS) of NCF-4.

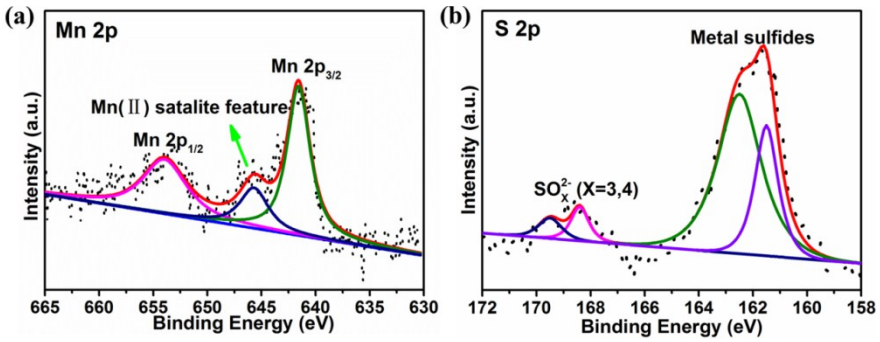

Fig. S4 High-resolution XPS spectra of Mn 2p (a) and S 2p (b) in NCF-4.

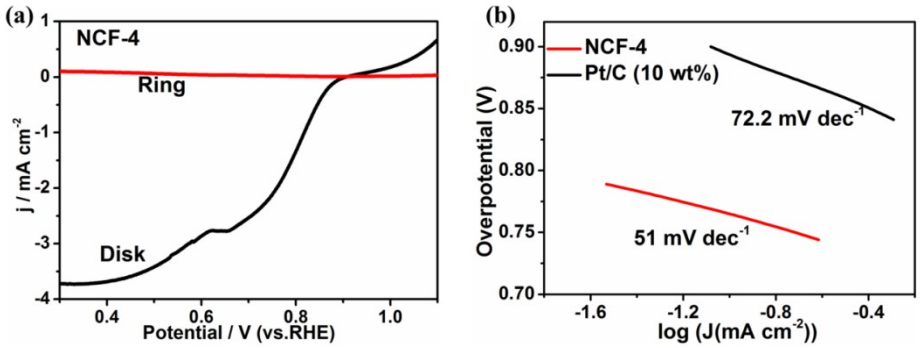

Fig. S5 (a) RRDE curves of NCF-4 in O_2-saturated 0.1 M KOH solution with a sweep rate of 5 mV s^{-1} at a rotation rate of 1600 rpm; (b) the Tafel slope of NCF-4 and Pt/C (10 wt%).

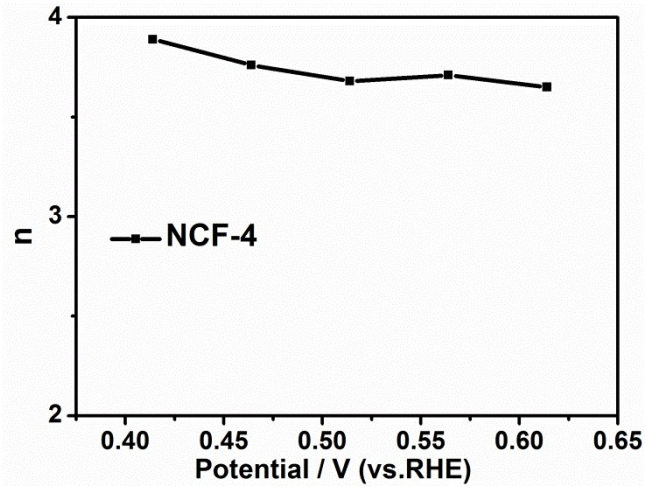

Fig. S6 Electron-transfer numbers (n) of NCF-4 derived from K-L plots at different potentials.

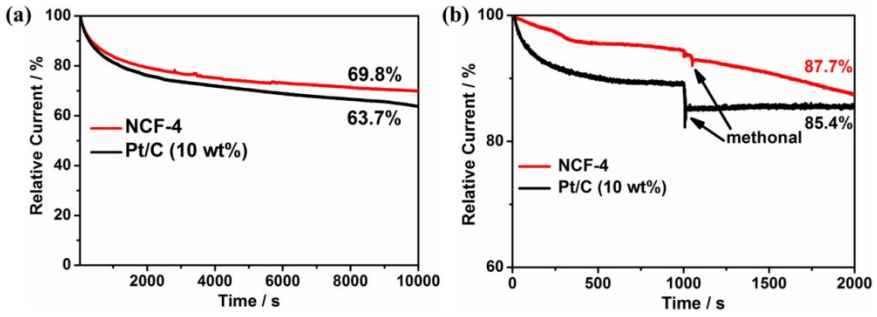

Fig. S7 The durability (a) and methanol crossover effect test (b) of NCF-4 in O_2-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm.

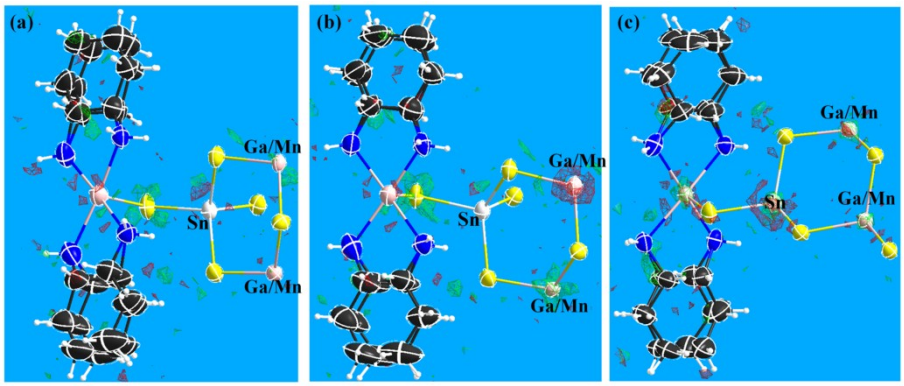

Fig. S8 The electron cloud density distribution map of Ga:Mn : (a) 1:1 (crystal 1); (b) 2:1 (crystal 1); (c) 1.8:1 (crystal 2).

The EDX and ICP-OES measurements give the ratio of Ga:Mn in T3 cluster of about 2:1. However, the crystallographic data give a normal ADP only when the ratio of Mn:Ga is refined to be 1:1 (Fig. S8a), instead of 2:1(Fig. S8b). There exists difference in the ratio of Ga/Mn between the results obtained from EDX/ICP-OES and structure refinement. This is because the structure refinement result from a single crystal can't represent the real ratio of Ga:Mn for the bulky solid sample. When we selected the second crystal for data collection, the refinement of the occupancies at Ga/Mn(11) in T3 cluster give the ratio close to 1.8:1 (as shown in the electron cloud density distribution map in Fig. S8c.), which is close to 2 : 1. After comprehensive consideration, we finally select the result obtained from the EDX and ICP-OES measurement to determine the formula of NCF-4.