Supporting Information

Mn-Etched Zeolitic Imidazolate Framework-67 Nanostructures for Biomimetic Superoxide Anion Sensing

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#Equal contributions.

Experiments

1. Materials. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), manganous chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$), 2-Methylimidazole (2-MeIM), methanol, sodium chloride (NaCl), potassium chloride (KCl), dopamine (DA), ascorbic acid (AA), uric acid (UA) and hydrogen peroxide (H_2O_2) were purchased from Aladdin. Zymosan A (Zym) from Saccharomyces cerevisiae, superoxide dismutase (SOD) from bovine erythrocytes, potassium superoxide (KO_2), and Nafion were bought from Sigma Aldrich. Dulbecco's modified eagle's medium (DMEM) contained with penicillin (80 U mL^{-1}) and streptomycin (0.08 mg mL^{-1}) was purchased from Jiangsu keygen Biotechnology Co., Ltd. Fetal bovine serum was purchased from Bio-Channel Biotechnology Co., Ltd. Phosphate buffered saline (PBS) and trypsin-EDTA (0.25%) were purchased from Cytiva and Life Technologies, respectively. Dimethyl sulfoxide (DMSO) was purchased from Solarbio. Methylthiazolyldiphenyl-tetrazolium bromide (MTT) and 2-(4-Amidinophenyl)-6-indolecarbamidine dihydrochloride (DAPI) were bought from Beyotime Biotechnology.

2. Apparatus and characterizations. The morphology and structure of the prepared materials were characterized by scanning electron microscopy (SEM, FEI quanta FEG 450, USA) and transmission electron microscopy (TEM, FEI G2F20, USA). X-ray diffraction (XRD, Bruker D8 Advance, DE) was utilized to analyze crystal structures of the samples. The element species of the materials were tested by energy-dispersive X-ray spectroscopy (EDS) and the elemental valence states of the materials were measured by X-ray photoelectron spectroscopy (XPS, Thermo 250xi, USA). pH meter was used to adjust the pH value of PBS (SX620, China). The CHI 660E electrochemical work station was applied to evaluate electrochemical behaviors of the materials. Images of cultured cancer cells were taken with Olympus microscope.

3. Fabrication of Mn/ZIF-67-based sensing platform. Mn/ZIF-67 electrodes were prepared to explore the electrochemical behaviors. First, the glassy carbon electrode (GCE, d = 3 mm) was polished with alumina slurry. Then the electrode was respectively ultrasonically cleaned in absolute ethanol and deionized water and dried naturally at room temperature. Next, 5 μL of 5 mg mL^{-1} Mn/ZIF-67 suspension was mixed with 3 μL of 0.1% Nafion solution and then the mixed solution was dropped on the cleaned GCE. Finally, the modified electrode was dried at room temperature. Other electrodes modified with control materials were fabricated using the same methods discussed above.

Supplementary Figures and Tables

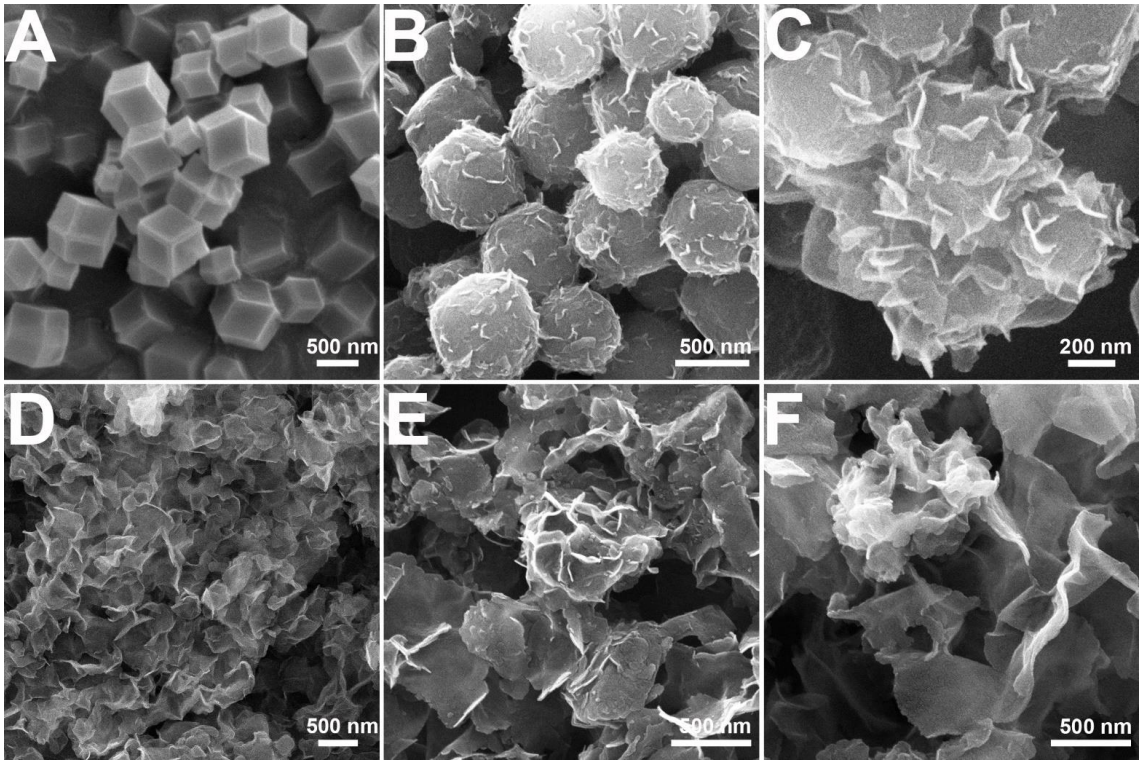

Figure S1. SEM images of ZIF-67 (A), Mn/ZIF-67 (1:1) (B), Mn/ZIF-67 (3:1) (C), Mn/ZIF-67 (5:1) (D), MnCo-LDH/ZIF (7:1) (E) and MnCo-LDH (10:1) (F).

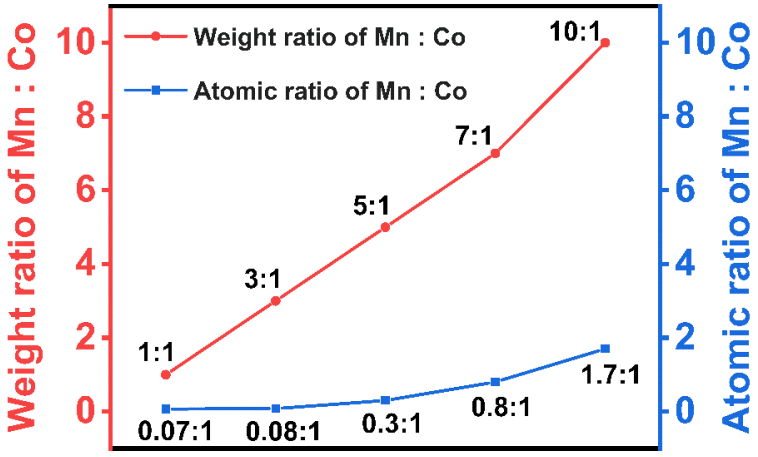

Figure S2. The weight ratio and atomic ratio of Mn : Co of as-prepared materials.

Table S1. BET data of as-prepared materials.

Material	S_{BET} (m^2 g^{-1})	V_T (m^3 g^{-1})
ZIF-67	148.169	0.9977
Mn/ZIF-67 (1:1)	141.135	0.8861
Mn/ZIF-67 (3:1)	149.101	2.7237
Mn/ZIF-67 (5:1)	150.159	2.8732
MnCo-LDH/ZIF (7:1)	148.867	2.7618
MnCo-LDH (10:1)	123.678	2.7373

S_{BET}: Specific surface area

V_T: Total pore volume

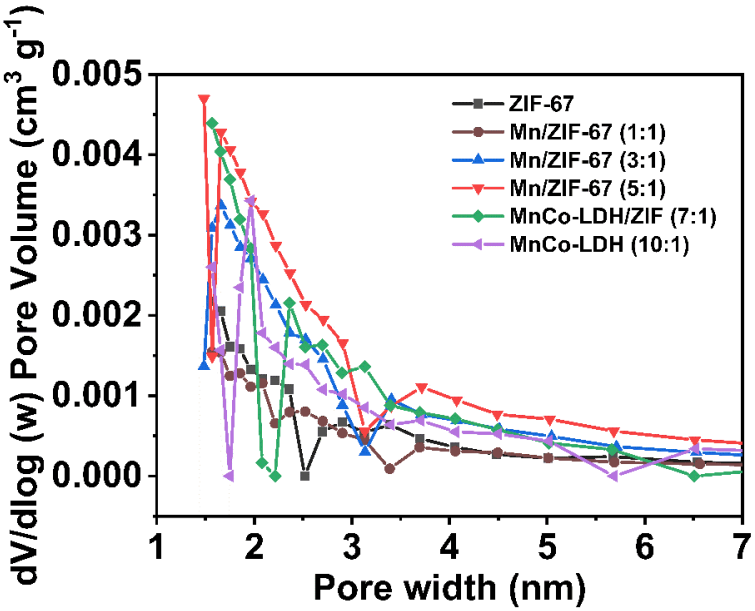

Figure S3. BJH pore size distributions of as-prepared materials.

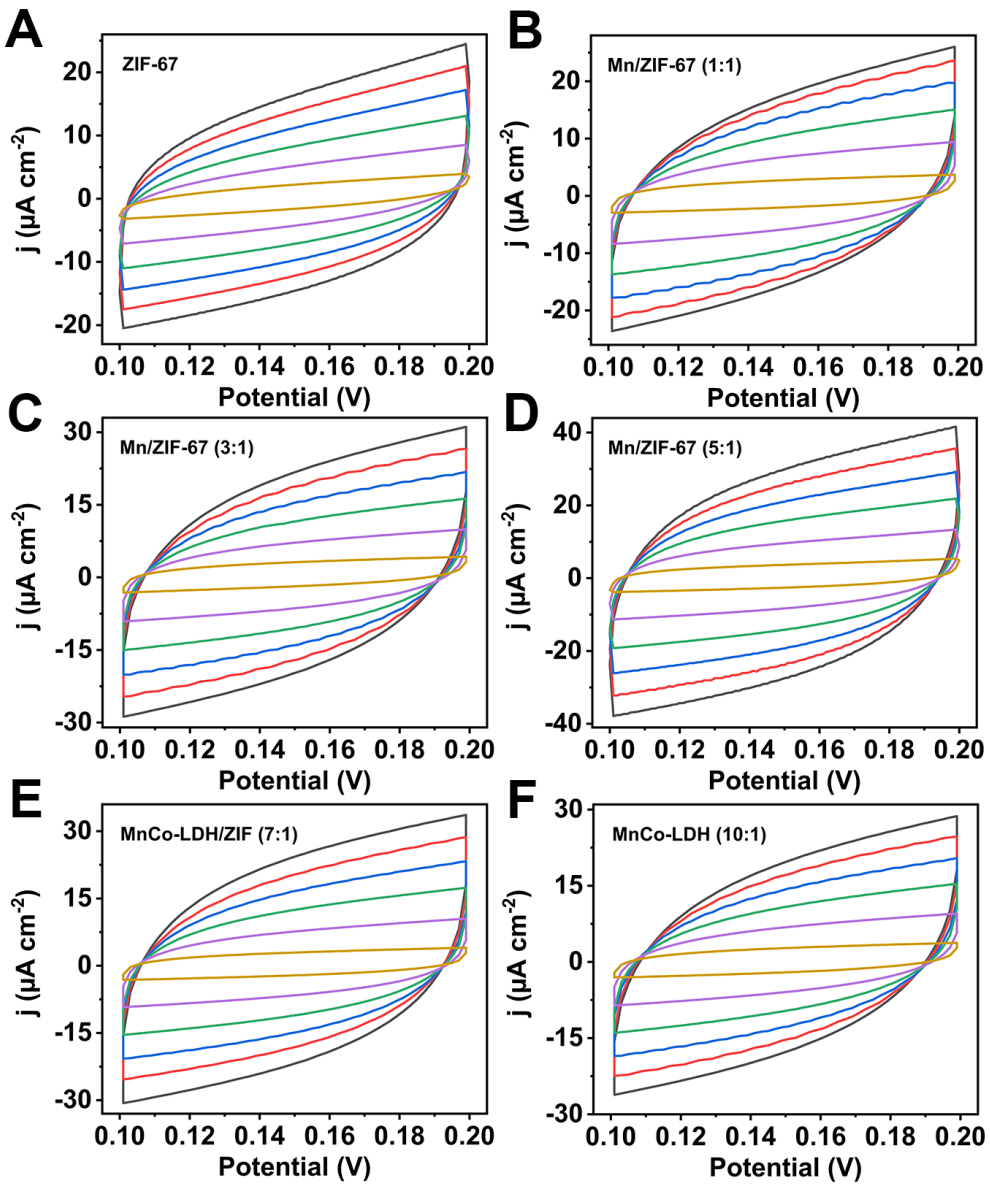

Figure S4. CV curves of ZIF-67 (A), Mn/ZIF-67 (1:1) (B), Mn/ZIF-67 (3:1) (C), Mn/ZIF-67 (5:1) (D), MnCo-LDH/ZIF (7:1) (E) and MnCo-LDH (10:1) (F) in 0.01 M PBS with different scan rates (5-100 mV s^{-1}).

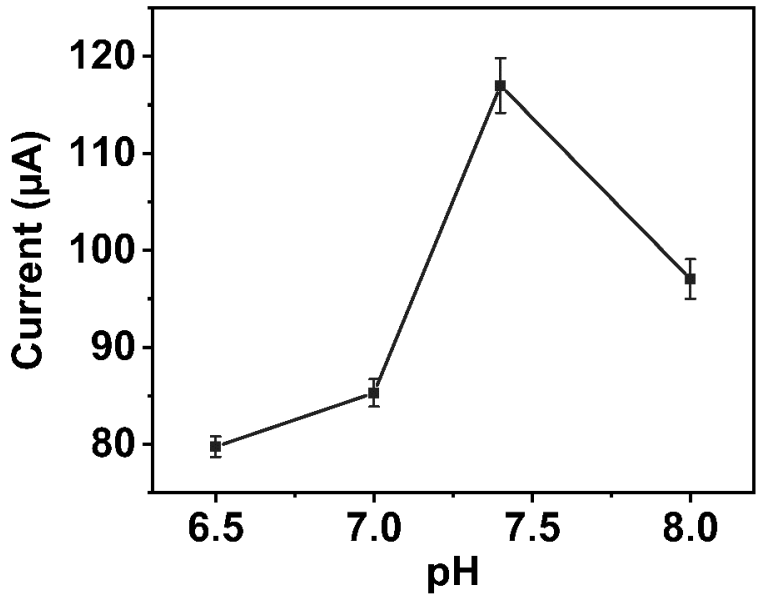

Figure S5. Relationship of peak current and pH (6.5-8.0) in 10 μM $O_2^{\bullet-}$ at 50 mV s^{-1} in range of 0.1~1.0 V.

Table S2. Comparison of various $O_2^{\bullet-}$ sensing platforms.

Sensing materials	Linear range (μM)	Detection limit (nM)	Sensitivity (μA μM^{-1} cm^{-2})	References
$Mn_3(PO_4)_2$/DNA/VACNT	6.5×10^{-2}-4.94 5.915-31.59	30	9.6 20.8	3
$Mn_3(PO_4)_2$/MXene	5.75×10^{-3}-6.98 7.9-25.93	1.63	64.93 38.62	18
$Co_3(PO_4)_2$/I-rGO	2.4×10^{-3}-2.195	1.67	177.14	19
Co_2P/ZnO@PC/CNTs	6.5-4416	2.16×10^3	-	S1
CTS- $Mn_3(PO_4)_2$	5.8×10^{-2}-5	9.7	50.96	S2
Mn-MPSA-MWCNTs	0-1817	127	7.75×10^{-2}	S3
Co based NCs	5×10^{-3}-0.2	1.8	270	S4
Mn/ZIF-67	1.5×10^{-3}-1.471 1.671-10	0.8	439.2195 366.4229	This work

VACNT: vertically aligned carbon nanotube. I-rGO: iodine nanospacerimpregnated reduced graphene oxide. PC: porous carbon polyhedral. CTS: chitosan. MPSA: melamine-phytic acid supermolecular aggregate. MWCNTs: multi-walled carbon nanotubes. NCs: nanocomposites

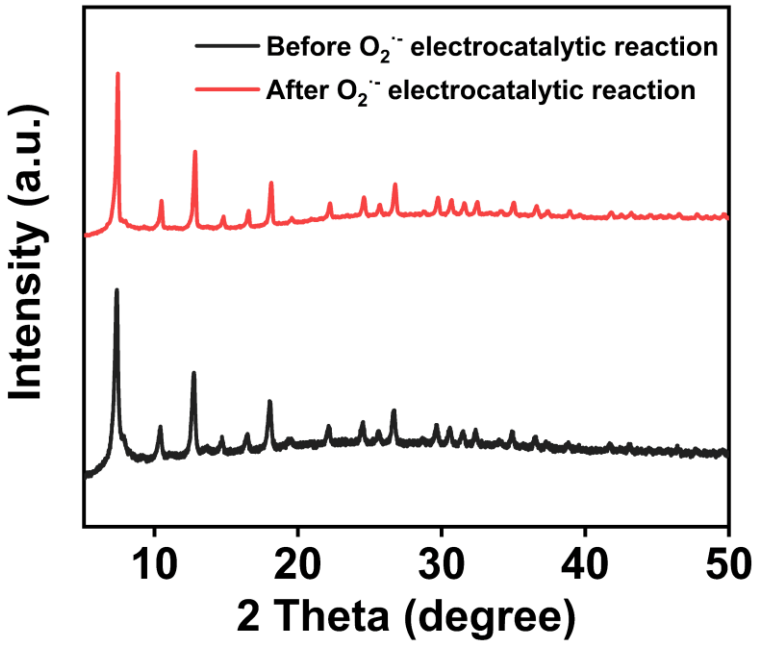

Figure S6. XRD patterns of before and after the electrocatalytic reaction of Mn/ZIF-67.

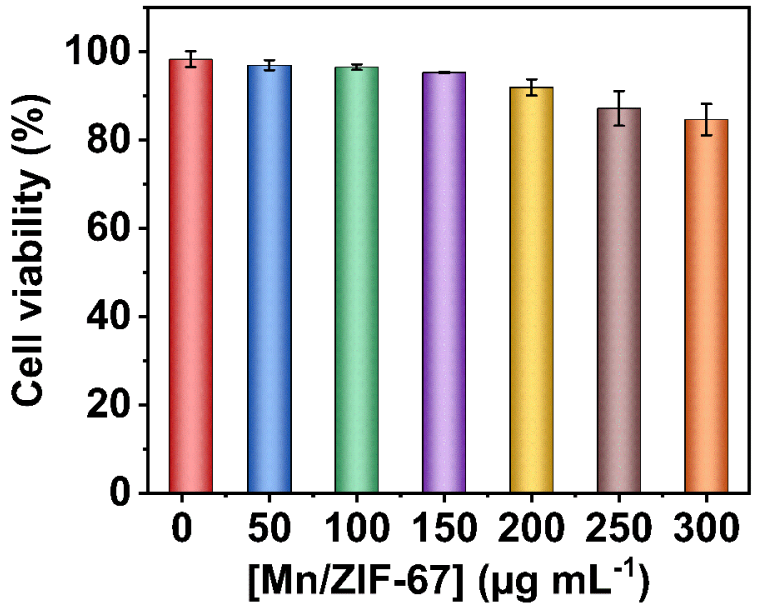

Figure S7. The cell viabilities of A549 cells in various concentrations of Mn/ZIF-67 (5-300 μg mL^{-1}).

References

(S1) Wang, M. Q.; Ye, C.; Bao, S. J.; Zhang, Y.; Xu, M. W.; Li, Z., Bimetal-Organic-Frameworks-Derived Yolk-Shell-Structured Porous Co_2P/ZnO@PC/CNTs Hybrids for Highly Sensitive Non-Enzymatic Detection of Superoxide Anion Released from Living Cells. *Chem. Commun.* **2016**, *52*, 12442-12445.

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