

Supporting Information for

**Bio-inspired Design of a Cu-Zn-Imidazolate Mesoporous Silica Catalyst
System for Superoxide Dismutation**

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Supporting Information Available: The list of Abbreviations, syntheses of mesoporous silicas, results of physical measurements (ICP-MS, nitrogen adsorption isotherms, XRD spectra and EPR spectra) and IC₅₀ values of mimic materials.

Abbreviation

CuIm	Equivalent mixture of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and imidazolate anion
CZS	(diethylenetriamine) $\text{Cu}-\mu$ -imidazolate- $\text{Zn}(\text{tris}(2\text{-aminoethyl})\text{amine})$ perchlorate or $[(\text{N}3)\text{Cu}-\mu\text{-Im}-\text{Zn}(\text{N}4)](\text{ClO}_4)_3 \cdot \text{CH}_3\text{OH}$
CuZnSOD	Copper zinc superoxide dismutase
Im	Imidazole
MPS	Mesoporous silica
MSN-N3	N3(diethylenetriamine) silanol group supported on MSN
MSN-N3-CuIm	CuIm immobilized on MSN-N3 covalently
MSN-CZS-c	ZnN4 binding to MSN-CuIm covalently
MSN-CZS- <i>i</i> _{sol}	Cu(II) and Zn(II) residue in MeOH after MSN loading CZS complex via ionic exchange
N3	Diethylenetriamine
N4	Tris(2-aminoethyl)amine
NBT	Nitro blue tetrazolium
$\text{O}_2^{\cdot -}$	Superoxide anion radicals
SBA-15-CuIm	CuIm immobilized on SBA-15-N3 covalently
SBA-15-CZS-c	ZnN4 binding to SBA-15-CuIm covalently
SBA-15-CZS- <i>i</i> _{sol}	SBA-15 loading with CZS complex via ionic exchange in solution
TMAC	N-trimethoxysilylpropyl-N,N,N-trimethyl-ammonium chloride
X-CZS-i	CZS immobilized in X mesoporous silica, such as MSN, SBA-15, MCM-41-SH, Al-MCM-41 and Al-SBA-15 via ionic exchange

Experimental Section: Syntheses of Mesoporous Silicas.

Synthesis of MSN. MSN is nano-sized MCM-41. The size range of MSN could be between 30 to 300 nm.¹ It suspended in water very well and can be used as nanocarrier. The protocol of preparation was given previously.² Briefly, we synthesized MSN under low concentration of tetraethoxysilane (TEOS), surfactant and NH_4OH as base in a two-step preparation process. First,

0.58 g of cetyltrimethyl-ammonium bromide ($C_{16}TAB$) was dissolved in 300 g of 0.51 M NH_4OH at 50 °C, and 5 mL of 0.21 M dilute TEOS (in ethanol) was added. After stirring for 5 h, 5 mL of 0.88 M TEOS was added, followed by stirring for another 1 h. The solution was then aged at 50 °C for 24 h. Precipitate were separated by centrifuging at 18000 rpm for 20 min, washing, and re-dispersing with ethanol several times. Surfactant templates were removed by extraction in acidic ethanol (1 g of HCl/50 mL of ethanol at reflux temperature for 24 h) and solids was re-dispersed in ethanol.

Synthesis of particulate SBA-15 and Al-SBA-15. A typical synthesis procedure using the triblock copolymer Pluronic P-123 as template was given previously.³ Briefly, we summarize as follows: 1.4 g of P-123 was first dissolved in 50 mL deionized water at 45 °C. Second, 5.5 g sodium silicate solution (27% SiO_2) was adjusted to a pH value of 5.0 by titration with 1.2 M sulfuric acid under stirring at 45 °C. Then two solutions were mixed and aged for 3 h. After the gel was hydrothermally treated at 100 °C for 24 h in a static autoclave, the mixture was filtered, washed with deionized water and calcined at 560 °C in air for 6 h. The Al-SBA-15 was synthesized by adding sodium aluminate (54% Al_2O_3) to the solution of P-123 in the first step as mentioned above. The molar composition was (37) SiO_2 : (1) Al_2O_3 .

Synthesis of particulate Al-MCM-41- N^+ . First, a proper amount of 1.2 M sulfuric acid was added to sodium silicate solution (27% SiO_2) to adjust its pH value to 9. The solution was added

to a C₁₆TAB solution with sodium aluminate (54% Al₂O₃) under stirring at 45 °C and a gel mixture was formed. The molar composition was (37) SiO₂: (1) Al₂O₃. Aged for 3 h, the gel was then hydrothermally treated at 100 °C for 24 h in a static autoclave. The as-synthesized product was filtered and washed thoroughly with deionized water. Then the dried product was calcined at 560 °C in air for 6 h to remove the organic templates.⁴

The positive charged Al-MCM-41-N⁺ was synthesized as follows: 0.0156 mL of N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (TMAC) was added to 0.3 g of Al-MCM-41 with 20 mL ethanol and stirred at reflux temperature for 24 h. The solids were separated by filtration, washing, and re-dispersing with ethanol several times to remove the TMAC residues.

Synthesis of MCM-41-SH. The materials MCM-41-SH provides stronger surface acidity because its silicon source is beta-zeolite seed.^{5, 6} It was synthesized with short surfactant (myristyltrimethylammonium bromide (C₁₄TAB)) as template, and put small quaternary ammonium ions (TEAOH) together in order to separately develop a zeolitic nanocluster as the silica precursor. Originally, sodium aluminate, sodium hydroxide, and tetraethylammonium hydroxide (20% wt% aqueous solution) were put together in a vessel. The fumed silica source was added to the mixture and stirred for 4 h. Then, the solution was transferred to autoclave and hydrothermal at 100 °C for 18 h to yield zeolite precursors. C₁₄TAB was dissolved in deionized

water followed by adding zeolite precursors, and transferred to autoclave to be treated hydrothermally at 120 °C for about 48 h. Then, the solution was cooled to room temperature and adjusted pH to 10. The resulting mixture was hydrothermally treated again at 120 °C for 48 h. Finally, the solid sample was filtered, washed with deionized water and calcined at 580 °C for 3 h to remove C₁₄TAB. The molar ratio was (37) SiO₂: (1) Al₂O₃.

References

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Table S1. Composition of Cu(II) and Zn(II) Ions by ICP-MS

After ionic exchange	Cu/Zn	Amount of Cu(Zn) ^a
MSN-CZS-i _{sol} ^b	2.27	1526.12 (691.31)
SBA-15-CZS-i _{sol} ^b	3.78	1925 (524)

^a The unit of amount is ppb. ^b MSN-CZS-i and SBA-15-CZS-i were obtained in MeOH after loading CZS complex via ionic exchange.

Table S2. IC₅₀ Values of CZS Vomplex and Encapsulated Mimic Materials Before and After Hydrothermal Treatment for 24 h Measured by UV-Visible at 560 nm with Adjusting pH to 7.4

Sample	IC ₅₀ (μM)			
	hydrothermal 0 h		hydrothermal 24 h	
CZS	59		62	
	59	58.6±0.6	59	60.0±1.5
	58		61	
MSN-CZS-i	36		45	
	37	36.5±0.5	47	45.0±2.0
	36.5		43	
SBA-15-CZS-i	47		54.2	
	46	47.0±1.0	56.7	55.1±1.4
	48		54.5	
Al-SBA-15-CZS-i	30		37	
	28	28.3±1.5	34	34.6±2.1
	27		33	
MCM-41-SH-CZS-i	18.5		25.4	
	18.5	18.3±0.6	26	25.8±0.4
	18		26.2	
Al-MCM-41-N ⁺ -CZS-i	2.3		7.8	
	1.9	1.9±0.3	7	8.4±0.6
	1.7		8.1	
MSN-CZS-c	44		43	
	43.5	43.8±0.3	45	45.6±3.1
	44		49	
SBA-15-CZS-c	56		60	
	55	55.3±0.6	63	61.0±1.7
	55		60	
MSN- N3-CuIm	117		124	
	118	117.7±0.6	127	124.0±3.0
	118		121	
SBA-15- N3-CuIm	122		122	
	119	120.0±1.7	124	122.7±1.2
	119		122	

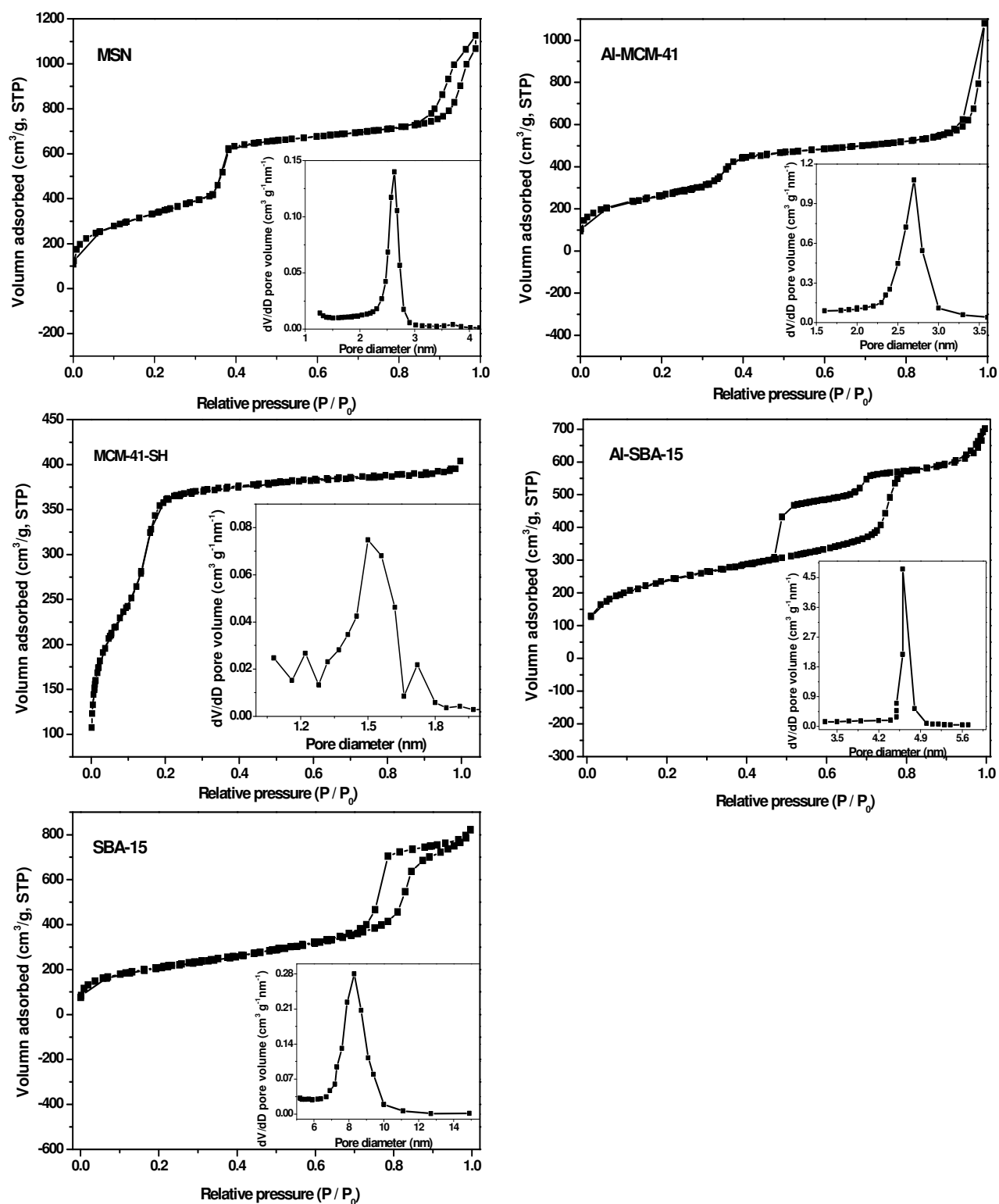


Figure S1. Nitrogen adsorption isotherms of various MPS samples (inset: BJH pore size distribution).

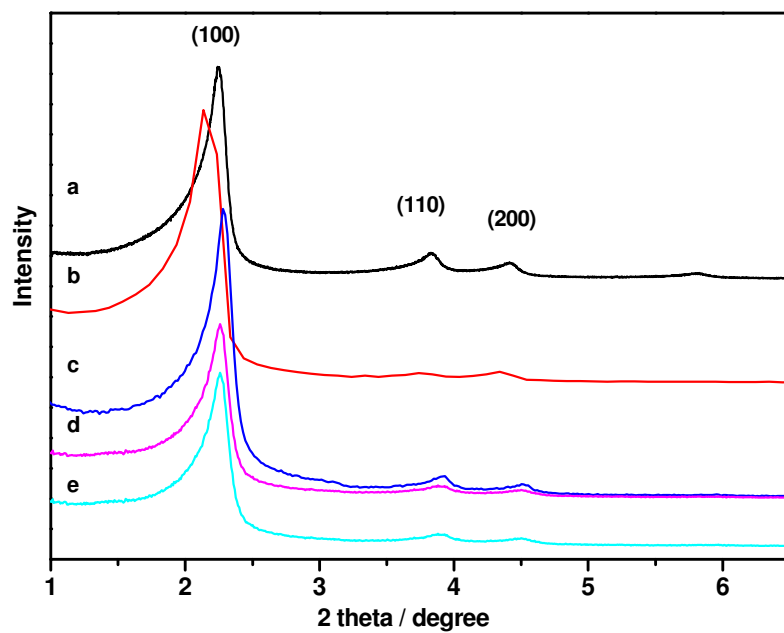


Figure S2. Small-angle powder XRD patterns of (a) MSN, (b) MSN-N3, (c) MSN-N3-CuIm, (d) MSN-CZS-c and (e) MSN-CZS-i.

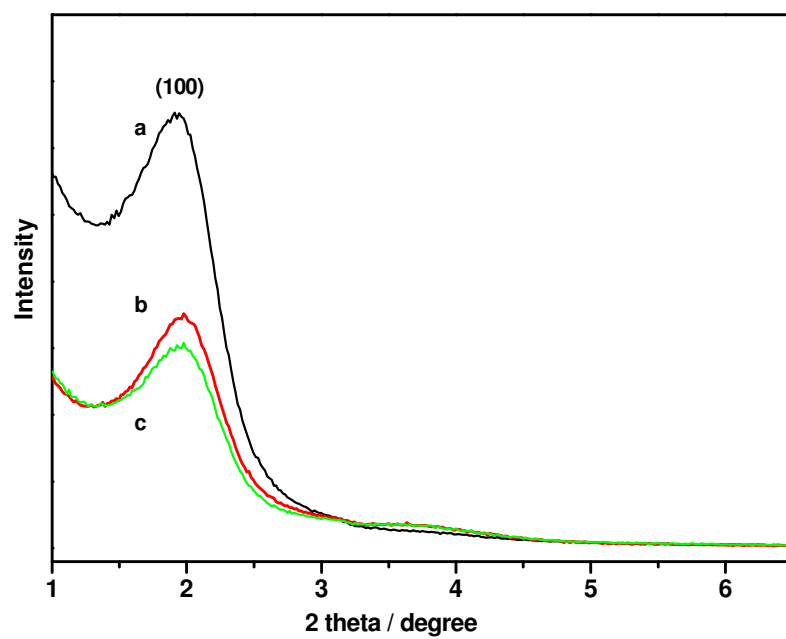


Figure S3. Small-angle powder XRD patterns of (a) Al-MCM-41, (b) Al-MCM-41-N⁺ and (c) Al-MCM-41-N⁺-CZS-i.

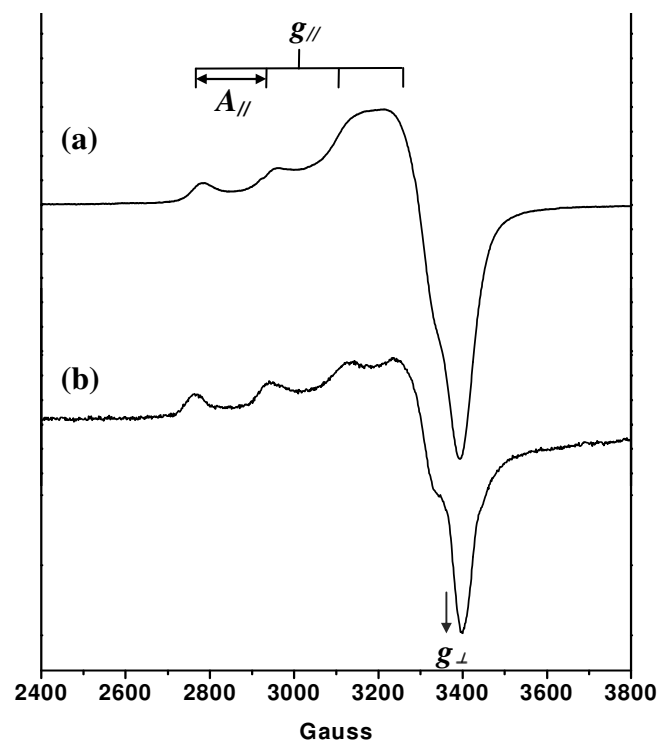


Figure S4. X-band EPR spectra of (a) MSN-N3-CuIm and (b) SBA-15-N3-CuIm at 77 K.