Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Porous manganese-cobalt oxide microsphere with tunable oxidase mimicking activity for sulfide ion colorimetric detection

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Experimental section

Chemical and Materials

Potassium hexacyanocobaltate(III) ($K_3[Co(CN)_6]$), $MnCl_2·4H_2O$, $Na_2S·9H_2O$, NaAc, NaBr were purchased from Aladdin Ltd. (Shanghai, China). 3,3',5,5'-Tetramethylbenzidine dihydrochloride hydrate ($TMB·2HCl·xH_2O$) were obtained from Shanghai Yuanye Bio-Technology Co., Ltd. $CoCl_2·6H_2O$, HAc, $MgSO_4·H_2O$, $KMnO_4$, NaCl, NaF, Na_2CO_3, $NaNO_3$, Na_2SO_4 were provided by Chengdu Kelong Chemical Reagent Factory. L(+)-Ascorbic acid (AA), 1,4-Benzoquinone (p-BQ), Thiourea were provided by Beijing Innochem Science&Technology Co., Ltd. Na_3PO_4 were purchased from Beibei Chemical Reagent Factory. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Milli-Q system.

Synthesis of $Mn_xCo_{1-x}O$

For Mn-Co PBA precursor synthesis, 0.9 mmol citrate and 0.6 mmol $MnSO_4·H_2O$ were dissolved in 20 mL deionized water under vigorous stirring at room temperature and denoted as solution A. Meanwhile, 0.4 mmol $K_3[Co(CN)_6]$ was added into 20 mL deionized water to form solution B. After that, solution B was slowly added into solution A with 5 min stirring. Then, the mixture was left at room temperature for 24 h. After centrifugation and washing by ethanol, the product was subsequently dried at 70 ℃ in air for 12 h and labeled as $Mn_{0.6}$-$Co_{0.4}$ PBA. To obtain $Mn_{0.6}Co_{0.4}O$, $Mn_{0.6}$-$Co_{0.4}$ PBA precursor was annealed in air at a temperature of 400 ℃ for 1 h.

$Mn_xCo_{1-x}O$ was synthesized with the same procedure except that the dosages of $MnSO_4 \cdot H_2O$ and $K_3[Co(CN)_6]$ source precursor were different. The detail dose was listed in following Tab S1.

Synthesis of Co_3O_4

Co_3O_4 were synthesized with the same procedure as $Mn_{0.6}Co_{0.4}O$ except that 0.6 mmol $MnSO_4 \cdot H_2O$ was substituted with 0.6 mmol $CoCl_2 \cdot 6H_2O$.

Synthesis of MnO_2

In a typical procedure, 2.0 mmol $MnCl_2 \cdot 4H_2O$ and 3.0 mmol $KMnO_4$ was first ground in an agate mortar at room temperature for about half an hour, then put it in a water bath at a temperature of 65 ℃ for 5 hours to make the reaction proceed thoroughly, and then washed with distilled water and dried in a vacuum desiccater at 80℃ for 4 hours. The final products were black powders of MnO_2.

Kinetic analysis

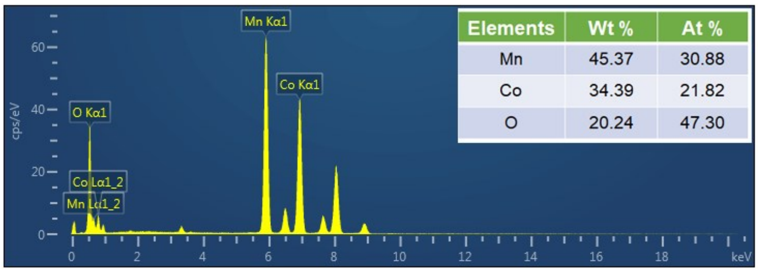
Kinetic measurements were carried out by monitoring the absorbance change at 652 nm. The experiments were carried out at room temperature with 50 mM TMB in NaAc-HAc buffer (0.2 M, pH 5) in presence of 8 μg/mL $Mn_xCo_{1-x}O$ (or Co_3O_4, MnO_2). The Michaelis-Menten behavior of the $Mn_{0.6}Co_{0.4}O$ was investigated by monitoring the absorbance of oxTMB at 652 nm with UV-vis spectrophotometer. The experiments were carried out at 20℃ with different concentrations of TMB in NaAc-HAc buffer (0.2 M, pH 5) in presence of 8 μg/mL $Mn_{0.6}Co_{0.4}O$. Lineweaver-Burk plots, $1/v = (K_m/V_{max})(1/[S]+1/V_{max})$, was used to calculate the Michaelis-Menten constant, where *v* represents the initial velocity, V_{max} stands for the maximal reaction velocity, [S] is the concentration of substrate and K_m is the Michaelis constant.

Sulfide ion detection

A typical colorimetric analysis for S^{2-} was realized as followings. Firstly, 16 mL $Mn_{0.6}Co_{0.4}O$ (500 mg/mL) and 10 mL TMB (5 mM) were added into 965 mL 0.2 M NaAc-HAc buffer (pH 5) and mixed thoroughly. After that, the mixture was incubated at 20°C for 10 min. Then, 10 mL S^{2-} with different concentration was added and mixed. The mixed solution was incubated for 5 min at 20℃ again. Finally, the absorbance spectrum of the solution was monitored.

Characterizations

X-ray diffraction (XRD) patterns of Mn-Co PBA precursor data and resulting $Mn_xCo_{1-x}O$ were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). The morphology of all materials was obtained from transmission electron microscopy (TEM) measurements (HITACHI H-8100 electron microscopy, Hitachi, Tokyo, Japan) and scanning electron microscopy (SEM) (FE-SEM, JSM-7800) at an accelerating voltage of 6 kV. XPS measurements were performed on a Thermo ESCALAB 250XI X-ray photoelectron spectrometer using Mg as the exciting source. SSA and pore size were analyzed using a Beishide BSD-PS1 at liquid N_2 temperature. Absorption spectra were recorded with a UV2550 UV-Vis Spectrophotometer (Shimadzu, Japan).



Elements	Wt %	At %
Mn	45.37	30.88
Co	34.39	21.82
O	20.24	47.30

Fig. S1. EDS spectrum of $Mn_{0.6}Co_{0.4}O$.

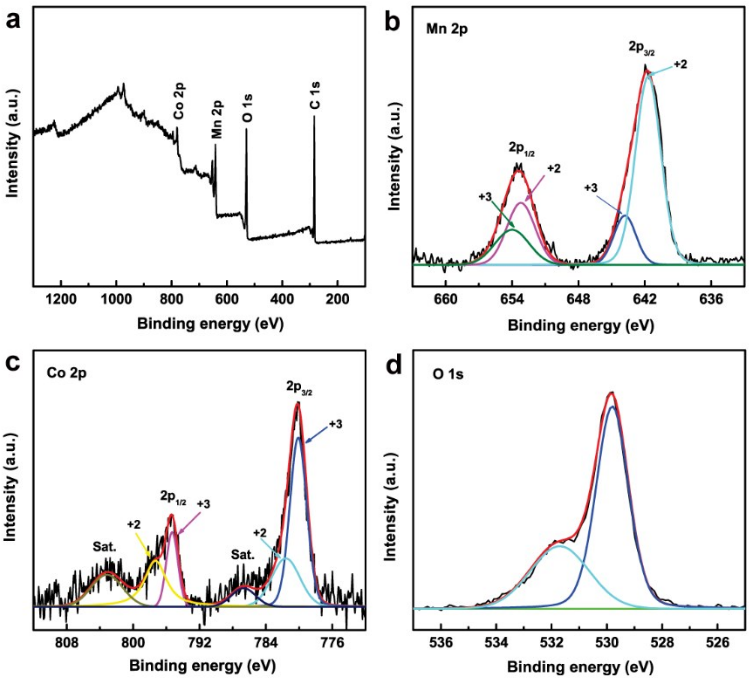


Fig. S2. (a) XPS full spectra, (b) Mn 2p, (c) Co 2p, and (d) O 1s spectra of $Mn_{0.6}Co_{0.4}O$.

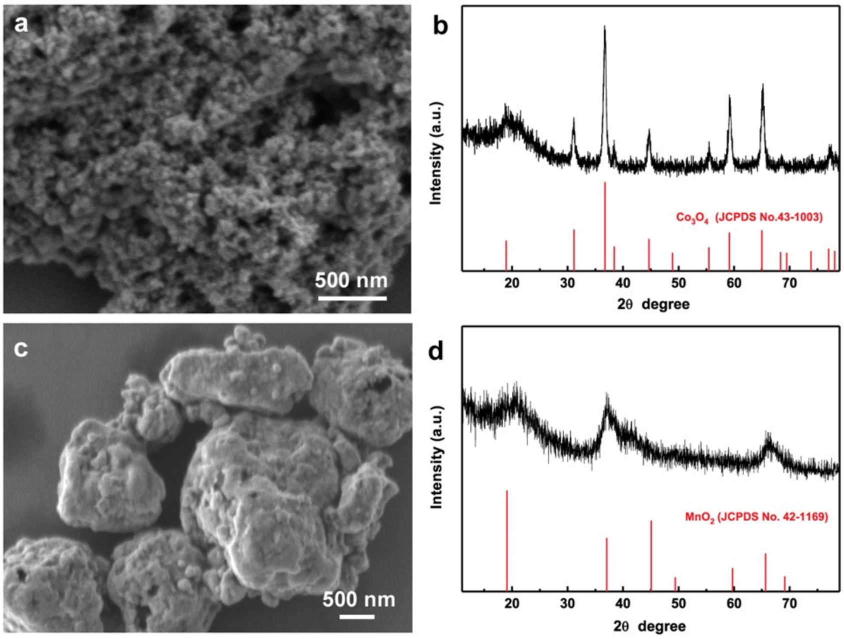


Fig. S3. (a, b) SEM images and XRD patterns of Co_3O_4. (c, d) SEM images and XRD patterns of MnO_2.

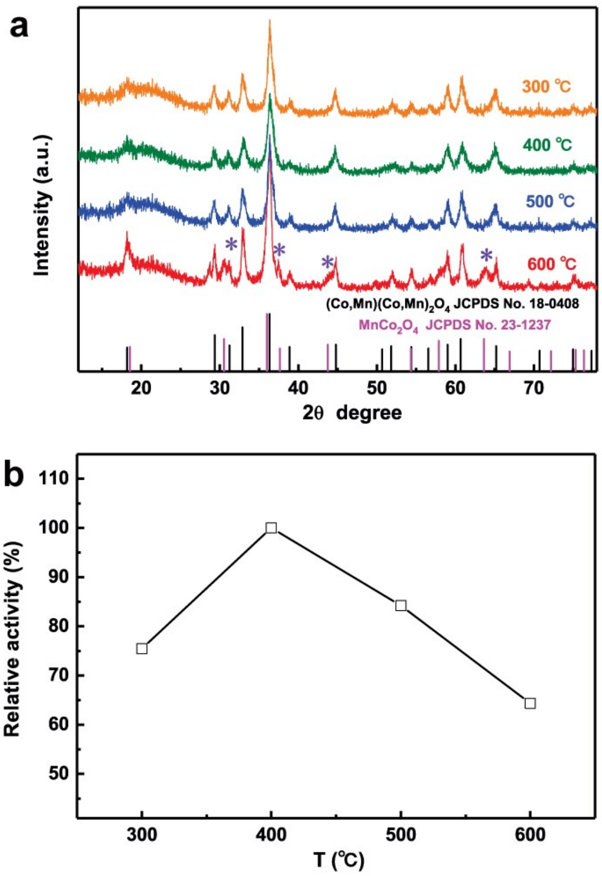


Fig. S4. (a) XRD patterns and (b) The relative oxidase-like activity of Mn-Co oxide obtained at different pyrolysis temperature.

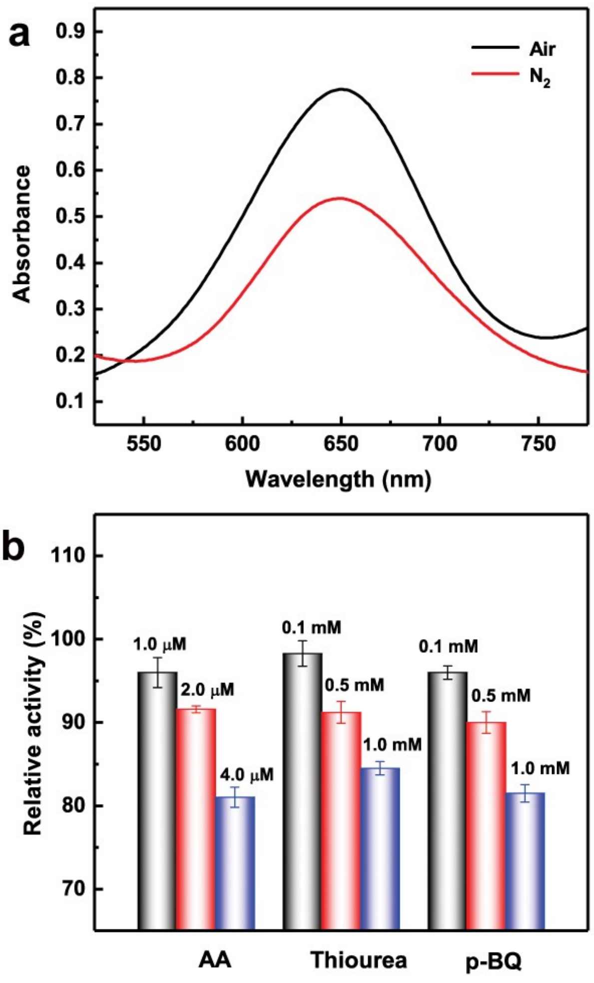


Fig. S5. (a) N_2 purging and (b) radical scavenging experiment. (AA concentration: 1, 2, and 4 μM; Thiourea and p-BQ concentration: 0.1, 0.5 and 1.0 mM.)

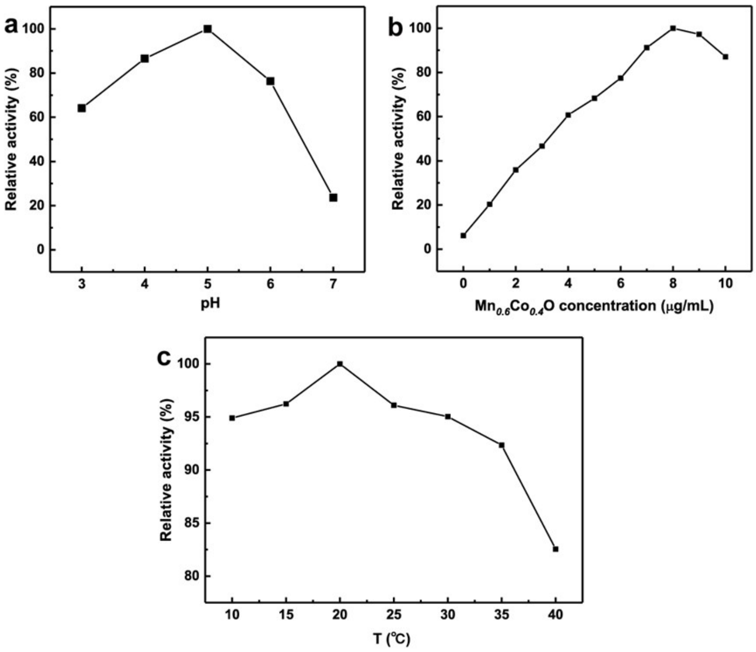


Fig. S6. Dependency of $Mn_{0.6}Co_{0.4}O$ oxidase mimicking activity on (a) pH, Reaction condition: 50 μM TMB, 8 μg/mL $Mn_{0.6}Co_{0.4}O$, 0.2 M HAc-NaAc buffer (pH 5), (b) $Mn_{0.6}Co_{0.4}O$ concentration, Reaction condition: 50 μM TMB, 0.2 M HAc-NaAc buffer (pH 5), and (c) incubation temperature, Reaction condition: 50 μM TMB, 8 μg/mL $Mn_{0.6}Co_{0.4}O$, 0.2 M HAc-NaAc buffer (pH 5).

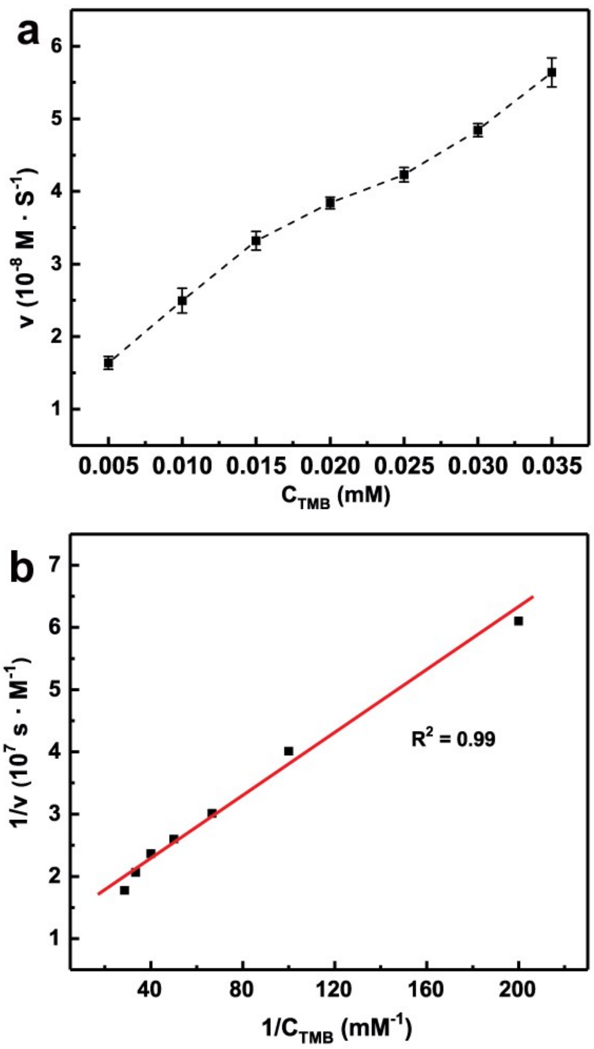


Fig. S7. (a) Steady-state kinetic assays of $Mn_{0.6}Co_{0.4}O$. (b) Corresponding double reciprocal plots of the Michiaelis-Menten equation. Reaction conditions: 8 mg/mL $Mn_{0.6}Co_{0.4}O$, 0.2 M HAc-NaAc buffer (pH 5), 20 °C.

Table S1. The dosages of raw materials for the preparation of Mn-Co PBA with different Mn/Co ratios.

Sample	$MnSO_4 \cdot H_2O$ (mmol)	$K_3[Co(CN)_6]$ (mmol)	citrate (mmol)
$Mn_{0.2}Co_{0.8}O$	0.2	0.8	0.9
$Mn_{0.4}Co_{0.6}O$	0.4	0.6	0.9
$Mn_{0.6}Co_{0.4}O$	0.6	0.4	0.9
$Mn_{0.8}Co_{0.2}O$	0.8	0.2	0.9

Table S2. Comparison of the as-prepared $Mn_{0.6}Co_{0.4}O$ nanoenzyme with previous colorimetric methods for S^{2-} detection in tap water.

Material	Detection methods	Linear range	Detection limit	Reference
Cu NCs	Colorimetric	0.5-20 μM	0.5 μM	26
Ag NPs	Photometric	0.8-6.4 μM	0.35μM	27
Au NPs	Colorimetric	2-9 μM	2 μM	28
$Mn_{0.6}Co_{0.4}O$	Colorimetric	0-25 μM	0.1 μM	This work

Table S3. Recovery experiments for S^{2-} detection in tap water.

Sample	Spiked (μM)	Measured (μM, n = 3)	recovery (%)
Tap water	5	5.04 ± 0.22	100.8
	10	10.33 ± 0.34	103.3
	15	15.44 ± 0.11	102.9