

# Supporting information

## Ultrasensitive stimulation effect of fluoride ions on a novel nanozyme-SERS system

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**Containing: 8 pages, 5 Figures and 2 Tables**

### **Additional images and data:**

**Figure S1.** UV-vis spectra of oxTMB catalyzed by the R-MnCo<sub>2</sub>O<sub>4</sub>/Au (a) without F<sup>-</sup>; (b) with F<sup>-</sup>.

**Figure S2.** UV-vis absorption spectrum of oxidized TMB catalyzed by (a) R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes without the addition of F<sup>-</sup>. (b) UV-vis absorption spectrum of oxidized TMB catalyzed by R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes with the addition of F<sup>-</sup>. (c) Comparison of the catalytic activity of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes without and with the addition of F<sup>-</sup>.

**Figure S3.** EPR spectrum of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes (red) and DMPO (black).

**Figure S4.** XPS spectrum of R-MnCo<sub>2</sub>O<sub>4</sub>/Au-F after washing with water for many

times: (a) Mn 2p, (b) Co 2p, (c) O 1s, (d) Au 4f and (e) F 1s regions.

**Figure S5.** SERS spectra of oxTMB molecules on R-MnCo<sub>2</sub>O<sub>4</sub>/Au substrate (a) before and (b) after two weeks. (c) The comparison of SERS intensities of oxTMB molecules at 1191, 1337 and 1611 cm<sup>-1</sup> on R-MnCo<sub>2</sub>O<sub>4</sub>/Au substrate before and after two weeks.

## Experimental section

### Chemicals

Poly(vinyl pyrrolidone) (PVP, Mw = 1,300,000 g·mol<sup>-1</sup>) and sodium borohydride (NaBH<sub>4</sub>) were purchased from Sigma-Aldrich. 3,3,5,5-tetramethylbenzidine (TMB) and manganese chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O) and 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) were obtained from Aladdin (Shanghai, China). Cytochrome (Cyt C) was purchased from Sigma. Dimethyl sulfoxide (DMSO) was bought from Sinopham Chemical Reagent Co. Cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and sodium acetate anhydrous were acquired from Xilong Chemical Industry Co. Ltd. Acetic acid, ethanol, and N,N-dimethylformamide (DMF) were commercially purchased from Beijing Chemical Works. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was bought from Beijing Chemical Works. Tetrachloroauric(III) acid tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O) was acquired from Chinese Medicines Group Chemical Reagent Co. Ltd.

### Characterization

Transmission microscope (TEM, JEM-2100F) was used to characterize the morphologies of the as-prepared samples at 200 kV. The X-Ray photoelectron spectroscopy (XPS) data were taken from a Thermo ESCALAB 250 photoelectron spectrometer with Al as the excitation source. UV-vis spectra were obtained from PerkinElmer (Lambda 365). The electron paramagnetic resonance (EPR) data were taken from BRUKER E500 EPR spectrometer at room temperature. SERS spectra of CV<sup>+</sup> and the catalytic reaction of Raman spectra were measured with a LabRAM

ARAMIS Smart Raman Spectrometer with a HeNe lasers as the excitation line of 633 nm. Data acquisition time was 10 s accumulation for one measurement. The Raman band of a Si wafer at  $520.7\text{ cm}^{-1}$  was used to calibrate the spectrometer.

### **Synthesis of R-MnCo<sub>2</sub>O<sub>4</sub> nanotubes**

MnCo<sub>2</sub>O<sub>4</sub> nanotubes were synthesized through an electrospinning and calcination process.<sup>1</sup> To prepare R-MnCo<sub>2</sub>O<sub>4</sub> nanotubes, 1 mg of MnCo<sub>2</sub>O<sub>4</sub> nanotubes and 0.08 g NaBH<sub>4</sub> were added into an agate mortar, after gently grinding at room temperature for 10 min and standing for 6 h. Then, 1 ml of water was added under ultrasound for 1 min and then left at room temperature for further 12 h. Finally, the prepared R-MnCo<sub>2</sub>O<sub>4</sub> nanotubes were collected with centrifugation and washed with water for several times.

### **Facbrication R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes through a self-reduction process**

For the preparation of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes, R-MnCo<sub>2</sub>O<sub>4</sub> nanotubes after washing many times were dispersed into 5 ml water under ultrasound for 1 min, then 0.5 ml of HAuCl<sub>4</sub> aqueous solution (4 mM) was added into the above solution with syringe. After stirring for 0.5 h, the obtained samples were washed for several times with water, and finally dispersed into water for further studies.

### **Electron paramagnetic resonance (EPR) measurement**

DMPO was used as a spin trap for the hydroxyl radical and the secondary radicals generated by the action of HO•, O<sub>2</sub><sup>•-</sup>/•OOH, <sup>1</sup>O<sub>2</sub>. R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes (70 μL, 0.3 mg/mL), H<sub>2</sub>O<sub>2</sub> (70 μL, 10<sup>-3</sup> M), DMPO (33 μL) and acetate buffer (67 μL, 0.1 M, pH=4) were mixed evenly, and then the mixed solution was subjected to EPR measurement.

### **SERS properties of CV<sup>+</sup> on the surface of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes**

CV<sup>+</sup> molecules were used as Raman probes to detect the SERS sensitivity of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes. In a typical procedure, 5 μL of of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes suspension (3 mg/mL) was mixed with 45 μL of CV<sup>+</sup> solution with different concentrations from 0.1-1 μM for 2 h to study the detection sensitivity. SERS spectra were collected directly from the mixing solution containing

R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes and CV<sup>+</sup>. Before SERS detection, the mixed solution was under ultrasound for about 1 min.

### **In situ monitoring of peroxidase-like catalytic activity of the R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes via SERS and UV-vis spectroscopy**

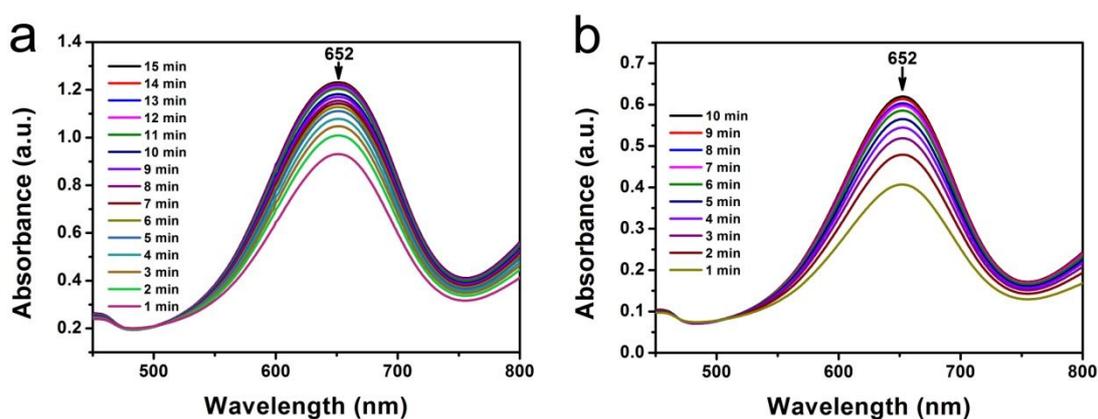
In a typical procedure, TMB solution (30  $\mu$ L, 15 mM in DMSO), H<sub>2</sub>O<sub>2</sub> solution (30  $\mu$ L, 1 mM) and R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes dispersion (30  $\mu$ L, 3 mg/mL) were mixed in an acetate buffer (2.91 ml, 0.1 M, pH=4). Finally, the above mixed solution was subjected to UV-vis spectroscopy measurements.

TMB (20  $\mu$ L, 0.45 mM), H<sub>2</sub>O<sub>2</sub> (20  $\mu$ L, 10<sup>-3</sup> M) and R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes dispersion (20  $\mu$ L, 0.3 mg/mL) were mixed and the SERS measurement was started at the same time.

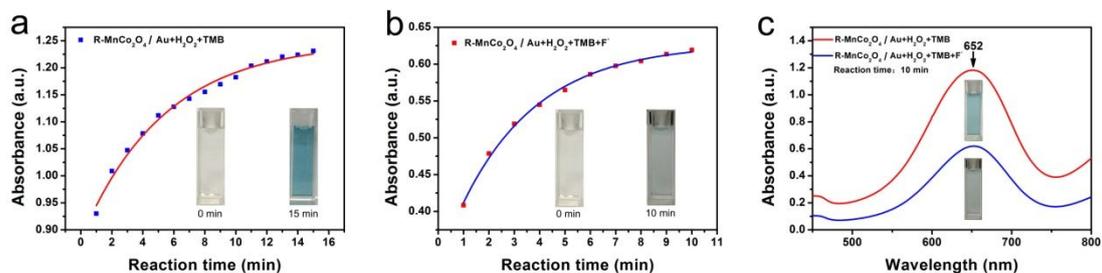
### **Detection of F<sup>-</sup> via SERS spectra**

15  $\mu$ L of different concentrations of F<sup>-</sup> (0.1-100 nM) was added to the fully mixed solution containing TMB (15  $\mu$ L, 0.45 mM), H<sub>2</sub>O<sub>2</sub> (15  $\mu$ L, 10<sup>-3</sup> M) R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes (15  $\mu$ L, 0.3 mg/mL) for 15 min. SERS measurement was performed under continuous 633 nm laser excitation at the same reaction time.

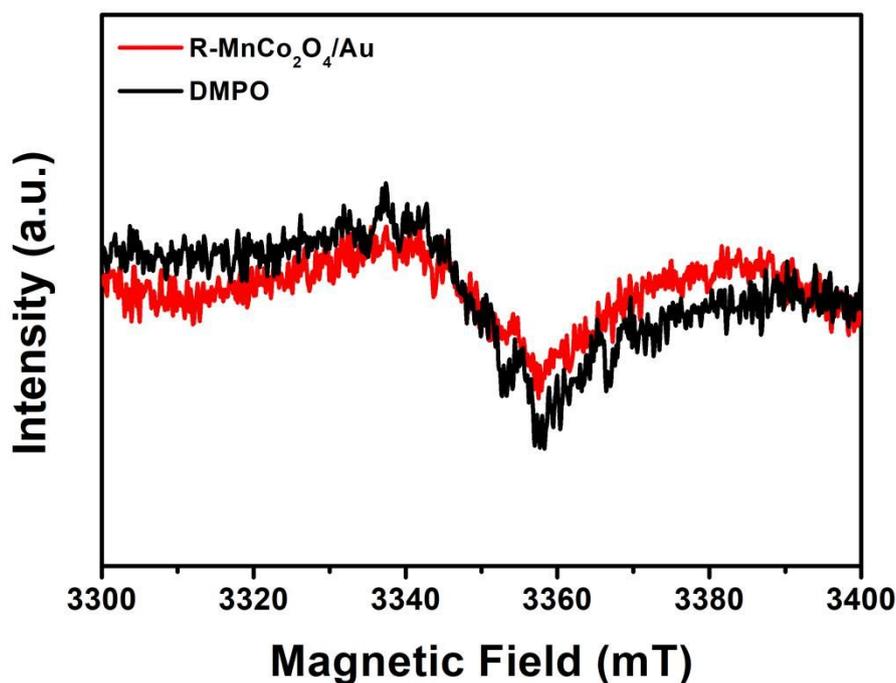
### **Supporting Figure**



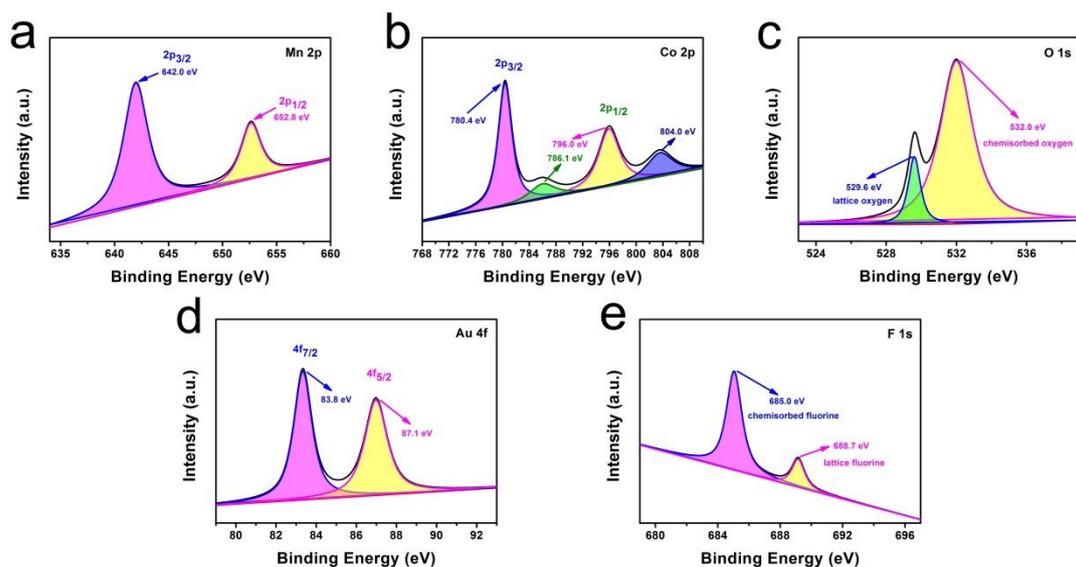
**Figure S1.** UV-vis spectra of oxTMB catalyzed by the R-MnCo<sub>2</sub>O<sub>4</sub> /Au (a) without F<sup>-</sup>; (b) with F<sup>-</sup>.



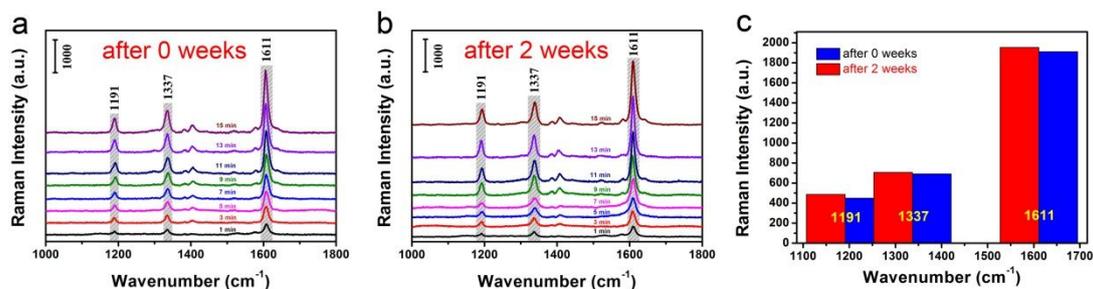
**Figure S2.** Time-dependent absorption curves of oxidized TMB catalyzed by (a) R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes without the addition of F<sup>-</sup>. (b) UV-vis absorption spectrum of oxidized TMB catalyzed by R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes with the addition of F<sup>-</sup>. (c) Comparison of the catalytic activity of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes without and with the addition of F<sup>-</sup>.



**Figure S3.** EPR spectrum of R-MnCo<sub>2</sub>O<sub>4</sub>/Au nanotubes (red) and DMPO (black).



**Figure S4.** XPS spectrum of R-MnCo<sub>2</sub>O<sub>4</sub>/Au-F after washing with water for many times: (a) Mn 2p, (b) Co 2p, (c) O 1s, (d) Au 4f and (e) F 1s regions.



**Figure S5.** SERS spectra of oxTMB molecules on R-MnCo<sub>2</sub>O<sub>4</sub>/Au substrate (a) before and (b) after two weeks. (c) The comparison of SERS intensities of oxTMB molecules at 1191, 1337 and 1611 cm<sup>-1</sup> on R-MnCo<sub>2</sub>O<sub>4</sub>/Au substrate before and after two weeks.

**Table S1** Observed Raman peaks of CV<sup>+</sup> and assignments.

$\nu_{\text{SERS}}$ (cm <sup>-1</sup> )	Band Assignment
1615	$\nu$ (C-C) <sub>ring</sub>
1584	$\nu$ (C-C) <sub>ring</sub>
1380	$\nu$ (C <sub>center</sub> -C)/ $\nu$ (phenyl-N)
1173	$\delta$ (C-C) <sub>  ,ring</sub>
915	$\delta$ (C-C <sub>center</sub> -C)
810	$\delta$ (C-H) <sub>⊥,ring</sub>
441	$\delta$ (CNC)

⊥ and || indicate out-of-plane and in-plane vibrations,  $\delta$  and  $\nu$  indicate bending and stretching.

As shown in the Table S1, the band at 441 cm<sup>-1</sup> is assigned to planar bending vibration of C-N-C in CV<sup>+</sup>.<sup>2</sup> The spectral bands at 810 and 1173 cm<sup>-1</sup> are ascribed to bending vibration of benzene ring in-plane. The band at 915 cm<sup>-1</sup> is assigned to bending vibration of C-C<sub>center</sub>-C, and 1380 cm<sup>-1</sup> is assigned to C<sub>center</sub>-C stretching. The spectral bands at 1584 and 1615 cm<sup>-1</sup> are assigned to C-C stretching vibration in ring.<sup>2</sup>

**Table S2** Observed Raman peaks of the TMB<sup>2+</sup> complex and assignments.

$\nu_{\text{SERS}}$ (cm <sup>-1</sup> )	Band assignment
1191	$\delta$ (CH <sub>3</sub> )
1337	$\nu$ (C-C) <sub>  ,ring</sub>
1611	$\nu$ (C-C) <sub>ring</sub> and $\delta$ (C-H) <sub>⊥,ring</sub>

⊥ and || indicate out-of-plane and in-plane vibrations,  $\delta$  and  $\nu$  indicate bending and stretching.

The formula for calculating the enhancement factor(EF) is as follows:

$$EF = \frac{I_{\text{surf}}}{I_{\text{bulk}}} \times \frac{N_{\text{bulk}}}{N_{\text{surf}}} \quad (\text{S1})$$

$$N_{\text{surf}} = C_{\text{surf}} \times S_{\text{laser}} \times h \times N_A \quad (\text{S2})$$

$I_{\text{surf}}$  and  $I_{\text{bulk}}$  are respectively the SERS strength of CV adsorbed on R-MnCo<sub>2</sub>O<sub>4</sub>/Au substrate and the SERS strength of bulk solution. In this manuscript,

the peak at  $1615\text{ cm}^{-1}$  is selected to calculate.  $N_{\text{surf}}$  and  $N_{\text{bulk}}$  are the number of probe molecules effectively excited by laser in substrate solution and bulk solution, respectively.

## REFERENCES

- (1) Gao, M.; Lu, X. F.; Chi, M. Q.; Chen, S. H.; Wang, C. Fabrication of Oxidase-Like Hollow  $\text{MnCo}_2\text{O}_4$  Nanofibers and Their Sensitive Colorimetric Detection of Sulfite and L-Cysteine. *Inorg. Chem. Front.* **2017**, *4*, 1862-1869, DOI: 10.1039/c7qi00458c
- (2) Canameres, M. V.; Chenal, C.; Brike, R. L.; Lombardi, J. R. DFT, SERS, and Single-Molecule SERS of Crystal Violet. *J. Phys. Chem. C.* **2008**, *112*, 20395-20300, DOI: 10.1021/jp807807j