Supporting information

A high-energy-state biomimetic enzyme of oxygen-deficient $MnTiO_3$ nanodiscs for sensitive electrochemical sensing of superoxide anion

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Part 1: Experimental methods

Reagents and apparatus. Tetrabutyl titanate and ethylene diamine were purchased from Adamas. Ethylene glycol (EG), manganese (II) chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$) were purchased from Aladdin. Potassium chloride (KCl) was purchased from Shanghai Aibi Chemistry. Other chemicals including dopamine (DA), uric acid (UA), potassium superoxide (KO_2), phosphate buffer (PBS, 0.01 M, pH=7.4) and Nafion (5 wt.%) were purchased from Sigma-Aldrich. Deionized (DI) water was used for all aqueous solutions.

Morphology and structure of the materials were checked using transmission electron microscope (TEM, FEI Titan G2 60-300). Crystal structure was characterized via X-ray diffraction (XRD, Bruker D8 Advance). X-ray photoelectron spectroscopy (XPS, Escalab 250xi, Thermo Scientific) was utilized to analyze valence states of elements.

Preparation of S-OD $MnTiO_3$ nanodiscs and sensing platform. The precursor of $MnTiO_3$ nanodiscs were prepared as followings. 0.425 mL tetrabutyl titanate was dropped into 16 mL EG with stirring to form solution A. 247.8 mg $MnCl_2{\cdot}4H_2O$ was dissolved in 4 mL ethylene diamine with stirring to form solution B. Then, solution A and B were added to a 50 mL a Teflon-lined stainless-steel autoclave, and added 5 mL DI water drop by drop under stirring. The autoclave was heated at 200 °C for 24 h, and the solid product was collected by centrifugation, followed by washing with ethanol and water. The solid product was dried and heated under air to obtain $MnTiO_3$ nanodiscs. Finally, S-

OD $MnTiO_3$ nanodiscs were prepared after heating at different temperatures under Ar/H_2 (95:5). The optimized heating treatment temperature to reach the best performance was 200 °C.

Glassy carbon electrodes (GCE, d = 3 mm) were polished by 0.3 and 0.05 μm alumina slurry and rinsed thoroughly with absolute ethyl alcohol and DI water followed by ultrasonically cleaning in absolute ethyl alcohol and DI water for 30 s to a shining surface, respectively. 4 μL of 2 mg mL^{-1} S-OD $MnTiO_3$ based ink were casted on GCE surface, and fixed with 4 μL of 0.25% Nafion solution. The modified electrodes were used in subsequent experiments. Electrochemical measurements were performed on a CHI 660E electrochemical workstation with a three-electrode system that composed of a GCE working electrode, a platinum wire auxiliary electrode and a saturated calomel (SCE) reference electrode.

Electrochemical measurement conditions of the S-OD $MnTiO_3$-based $O_2^{\bullet-}$ sensor. All electrochemical measurements were performed at 25 °C in 0.01M pH=7.4 PBS solution. To achieve the best detection limit, the potential for amperometric measurement was optimized. The current-time response of S-OD $MnTiO_3$ to $O_2^{\bullet-}$ were recorded every 50s by successive addition of same concentration of $O_2^{\bullet-}$ at 0.5, 0.6, 0.7 V, respectively. The maximum amperometric response was achieved at a potential of 0.6 V. For real-time detection of $O_2^{\bullet-}$, amperometric measurements were conducted in 0.01M pH=7.4 PBS solution by successive adding $O_2^{\bullet-}$ every 50s at an applied potential of 0.6 V. Selectivity tests were performed at the same conditions , where the concentration of $O_2^{\bullet-}$ was 115 nM and the concentration of interference species (K^+, Cl^-, DA, AA, H_2O_2, UA and NO) was 1 μM. Stability test was conducted by adding 1.15 μM $O_2^{\bullet-}$ for 1000s under an applied potential of 0.6 V.

Part 2: Additional figures

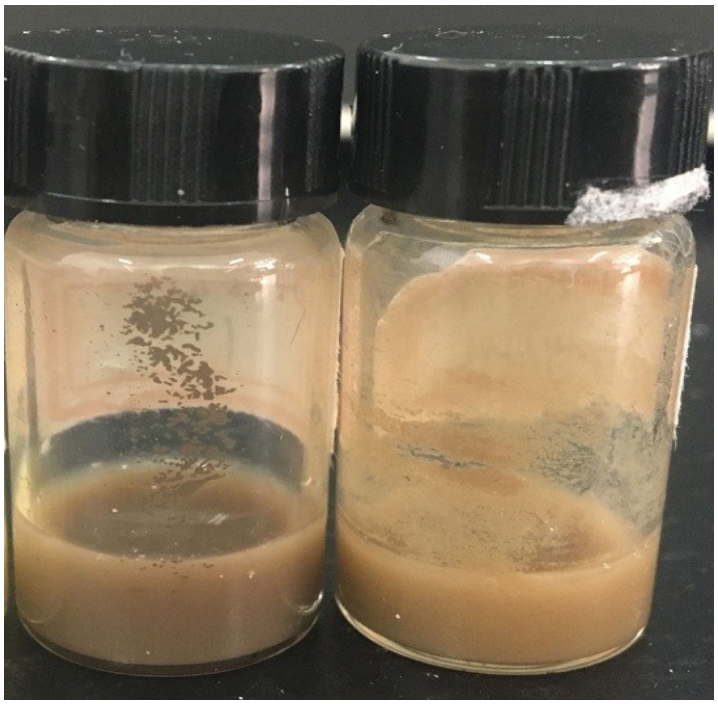

Fig. S1. Pictures showing plain $MnTiO_3$ nanodiscs (left) and oxygen deficient $MnTiO_3$ nanodiscs (right) aqueous solutions.

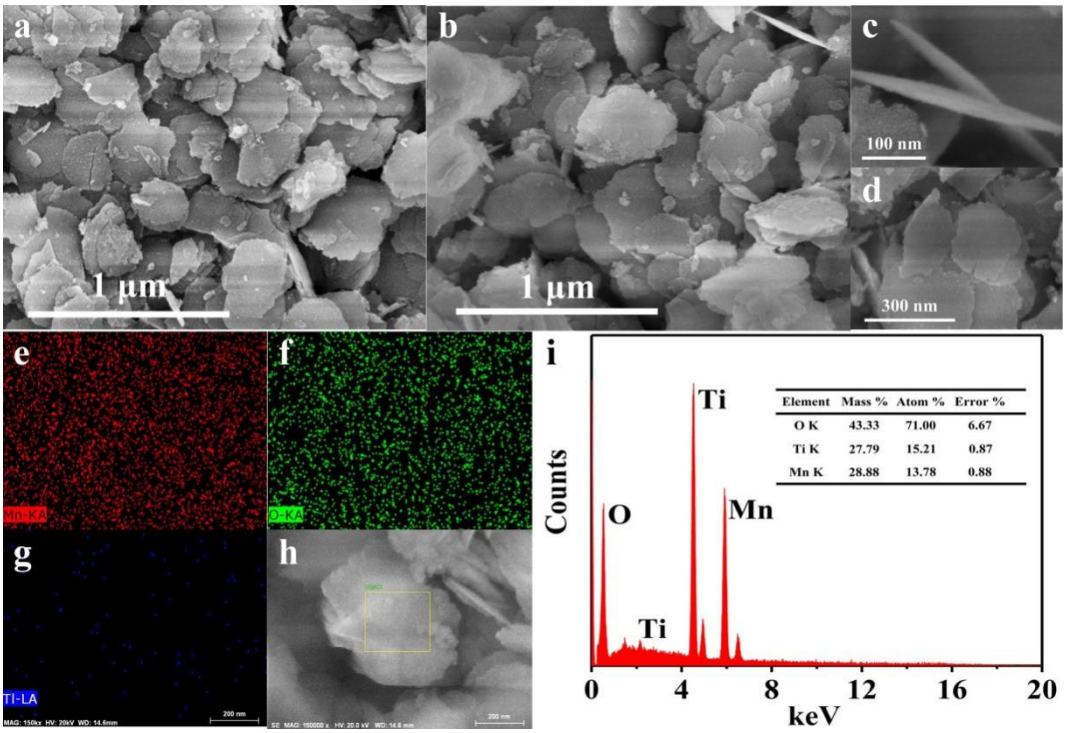

Fig. S2. (a) FESEM image of plain $MnTiO_3$ nanodiscs. (b-d) FESEM images of surface oxygen deficient (S-OD) $MnTiO_3$ nanodiscs. (e-h) EDS mappings of S-OD $MnTiO_3$ nanodiscs. (I) Elemental analysis of S-OD $MnTiO_3$ nanodiscs.

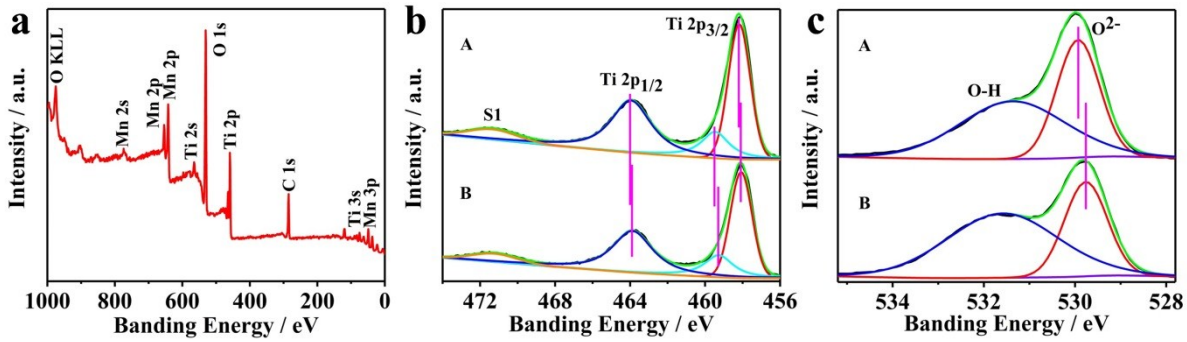

Fig. S3. (a) XPS survey spectra of S-OD $MnTiO_3$ nanodiscs. (b) Ti 2p and (c) O 1s spectra of plain and S-OD $MnTiO_3$ nanodiscs (Curve A for S-OD $MnTiO_3$ nanodiscs; curve B for plain $MnTiO_3$ nanodiscs).

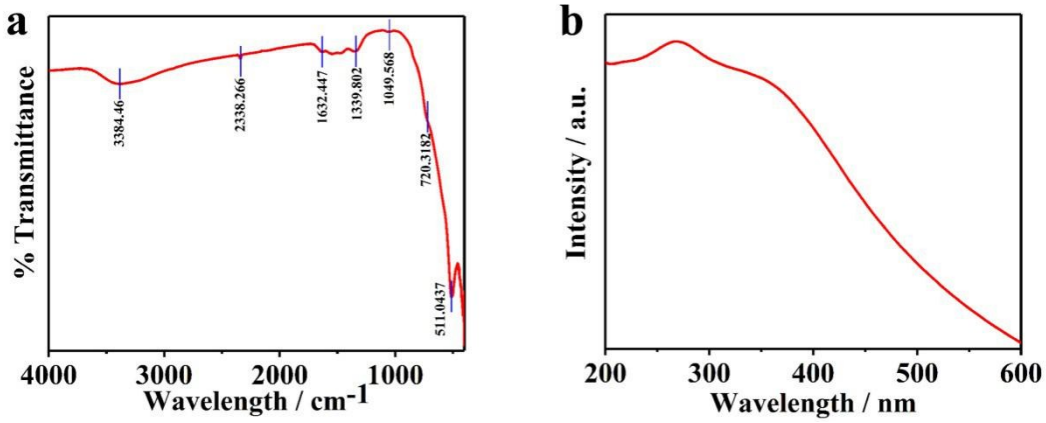

Fig. S4. (a) FTIR image and (b) UV-Vis spectrum of S-OD $MnTiO_3$ nanodiscs.

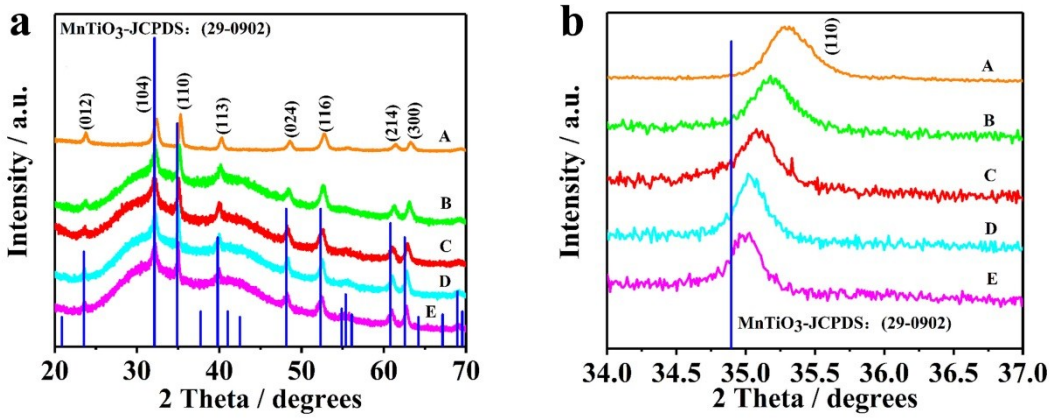

Fig. S5. (a) XRD patterns of $MnTiO_3$ nanodiscs treated with Ar/H_2 to induce oxygen defects at different temperatures. (b) XRD patterns of S-OD $MnTiO_3$ nanodiscs at a narrow range from 34° to 37°. Curves A for plain $MnTiO_3$ nanodiscs; curve B for 150 °C; curve C for 200 °C; curve D for 250 °C; and curve E for 300 °C.

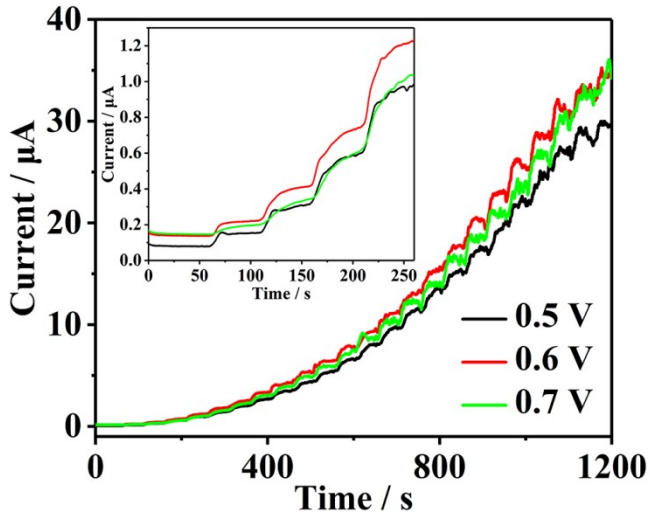

Fig. S6. Chronoamperometry curves of S-OD $MnTiO_3$ nanodiscs towards $O_2^{\bullet-}$ at different potentials, (Inset is narrow range of 0-250 s, electrolyte of PBS solution: 0.01 M, pH = 7.4).

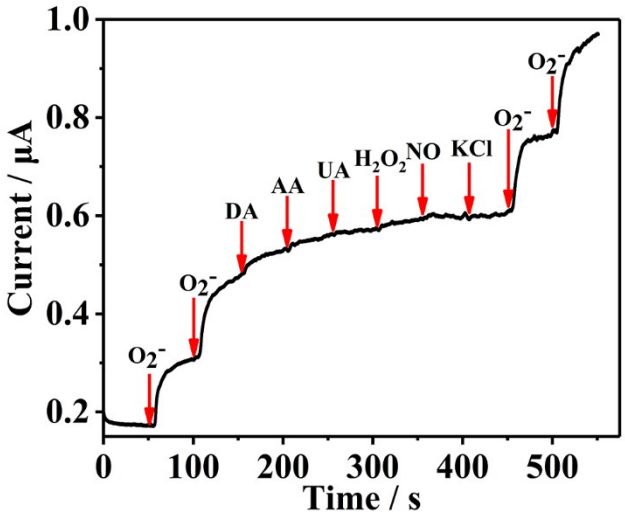

Fig. S7. Chronoamperometry curve of S-OD $MnTiO_3$ nanodiscs for selectivity testing at 0.6 V (electrolyte of PBS solution: 0.01 M, pH = 7.4).