Electronic Supplementary Information

Experimental section

Materials: Condensed acetic acid (CH_3COOH), sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium sulfate (Na_2SO_4), and ethanol (C_2H_5OH) were purchased from Chengdu Kelong Chemical Reagent Factory. Manganese (II) acetate ($Mn(CH_3COO)_2$), potassium chlorate ($KClO_3$) were purchased from Aladdin Ltd. (Shanghai, China). TM purchased from Hongshan District, Wuhan Instrument Surgical Instruments business. The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

Preparation of MnO$_2$ NA/TM: MnO_2 NA/TM was prepared as follows. 5 mL CH_3COOH was diluted into 70 mL water. Then, 5 mmol $Mn(CH_3COO)_2$ and 8.75 mmol $KClO_3$ were added to the above solution. Then the solution was transferred into a Teflon-lined stainless autoclave (100 mL), and a piece of TM was immersed into the autoclave contained solution. The autoclave was sealed and maintained at 160 °C for 12 h in an electric oven. After the autoclave cooled down naturally to room temperature, the resulting MnO_2 NA/TM was taken out and washed with deionized water and C_2H_5OH several times alternatively, then dried in air at 60 °C for 6 h.

Characterizations

Powder X-ray diffraction (XRD) data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a conventional three electrode system, using MnO_2 NA/TM as working electrode, platinum wire as counter electrode and saturated Ag/AgCl as

reference electrode. All tests were carried out at room temperature.

Determination of NH$_3$

The produced NH$_3$ was detected with indophenol blue by UV-Vis absorption spectra. In detail, 4 mL electrolyte was removed from the cathodic chamber and added into 50 μL oxidizing solution containing NaClO (ρCl = 4 ~ 4.9) and NaOH (0.75 M), followed by adding 500 μL coloring solution containing 0.4 M C$_7$H$_6$O$_3$ and 0.32 M NaOH, and 50 μL catalyst solution (0.1 g Na$_2$[Fe(CN)$_5$NO]·2H$_2$O diluted to 10 mL with deionized water) in turn. Absorbance measurements were performed after 2 h at λ = 655 nm. The concentration-absorbance curve was calibrated using standard NH$_4$Cl solution with NH$_4^+$ concentrations of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 μg mL^{-1} in 0.1 M Na$_2$SO$_4$. The fitting curve (y = 0.7036x + 0.029, R^2 = 0.9996) shows good linear relation of absorbance value with NH$_3$ concentration by three times independent calibrations. NH$_3$ formation efficiency was calculated using the following equation: NH$_3$ formation efficiency = (c_{NH3} × V) / (17 × 5), where c_{NH3} is the measured NH$_3$ concentration, V is the volume of the cathodic reaction for NH$_3$ collection, 17 is the relative molecular mass of NH$_3$ and 5 is the molar mass of nitrite added.
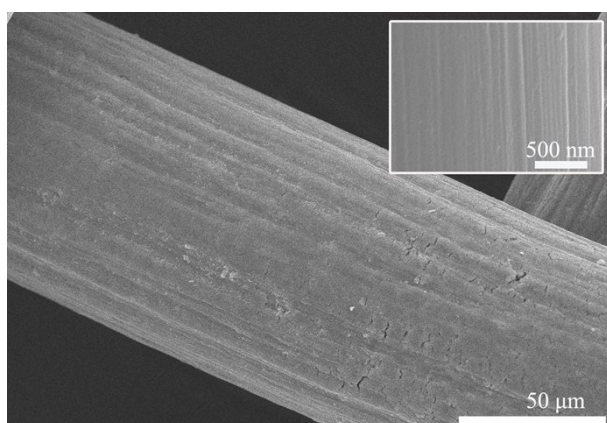
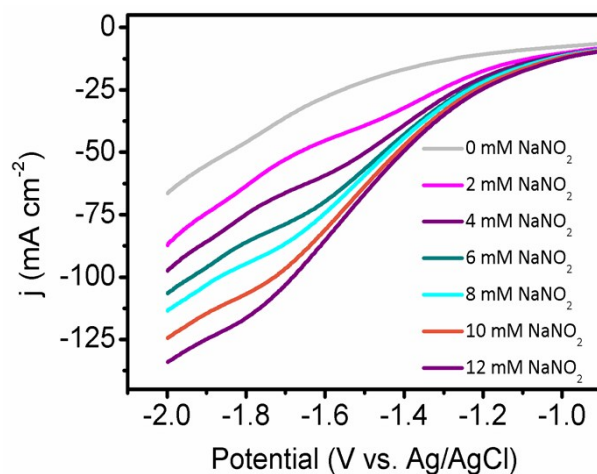**Fig. S1.** SEM images of TM.

Fig. S2. LSV curves for MnO$_2$/TM in 0.1 M NaSO$_4$ with the presence of varied NaNO$_2$ concentrations: 0, 2, 4, 6, 8, 10, and 12 mM (from inner to outer) at a scan rate of 30 mV s^{-1}, with graphite rod as counter electrode and Ag/AgCl as reference electrode.
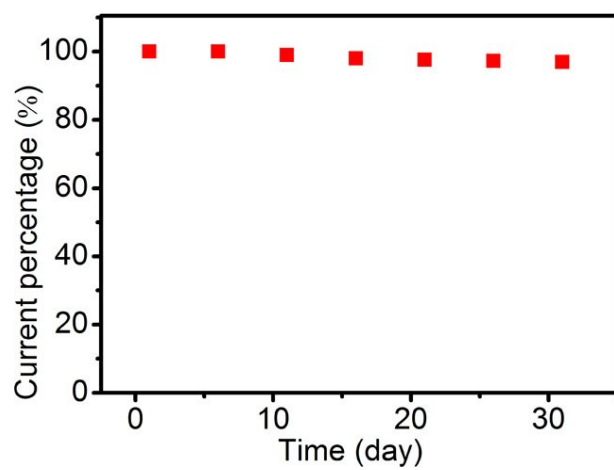
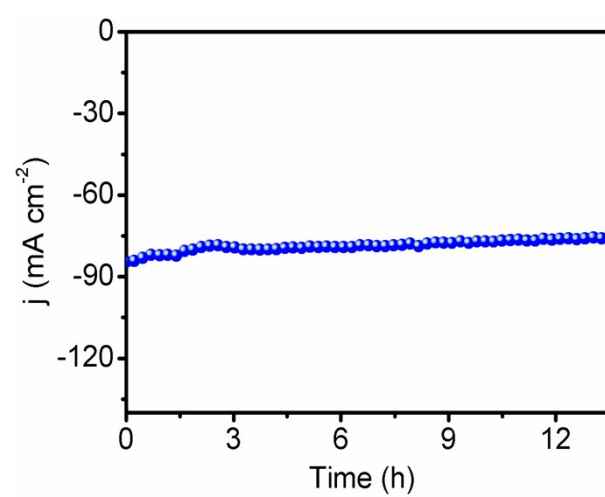**Fig. S3.** Stability of MnO$_2$ NA/TM electrode for testing 1.0 mM NaNO$_2$ in 0.1 M NaSO$_4$.

Fig. S4. Continuous stability of MnO$_2$ NA/TM electrode for testing 5.0 mM NaNO$_2$ in 0.1 M NaSO$_4$.
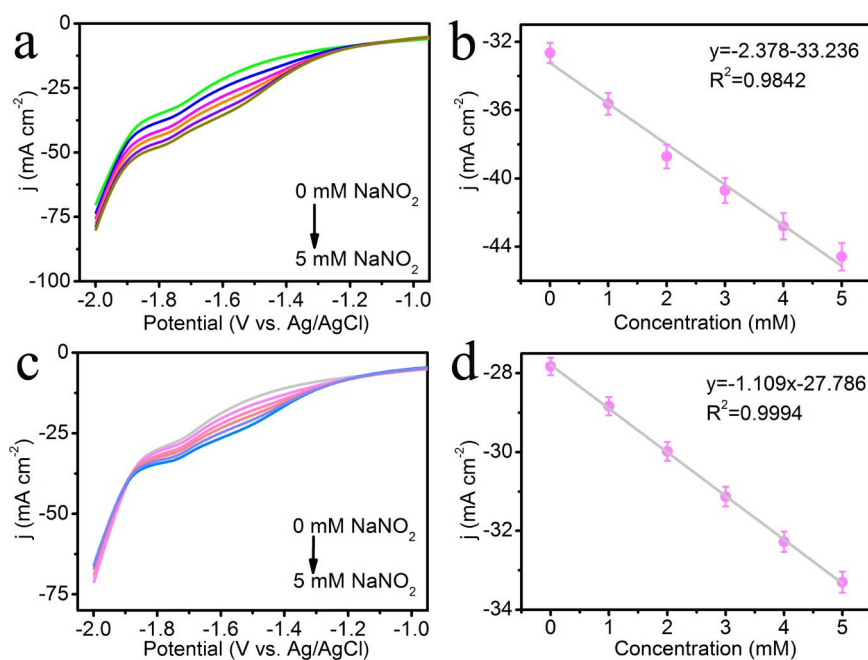
Fig. S5. (a, c) LSV curves of MnO$_2$ NA/TM in river water and tap water at −1.75 V in 0.1 M Na$_2$SO$_4$ with the presence of varied NaNO$_2$ concentration: 0, 1, 2, 3, 4, and 5 mM from inner to outer (scan rate: 30 mV s^{-1}), respectively. (b, d) Corresponding calibration curves of river water and tap water, respectively.
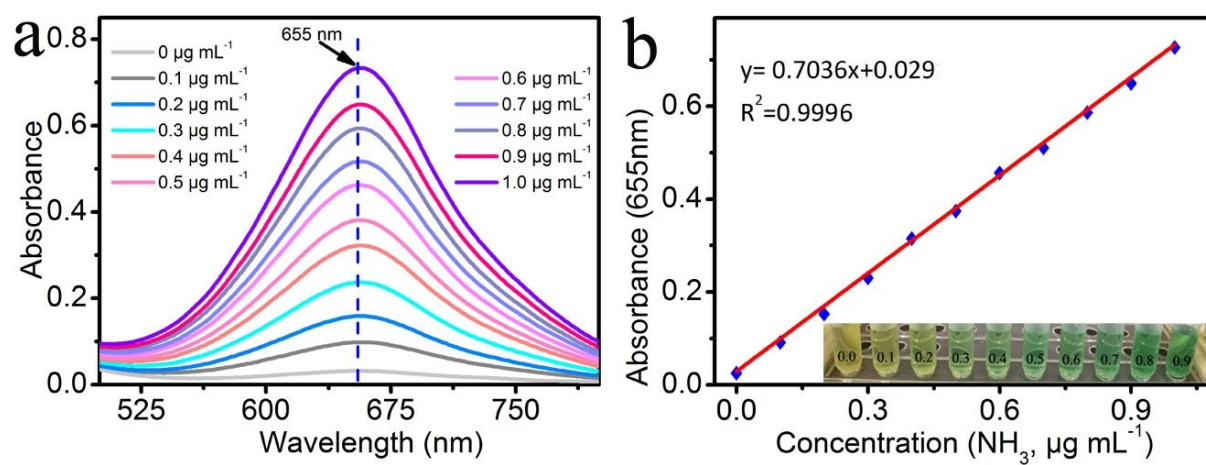
Fig. S6. (a) UV-Vis absorption spectra of indophenol assays with NH_3 after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_3.

Table S1. Comparison of the MnO_2 NA/TM performances for nitrite with reported electrocatalysts.

catalyst	sensitivity	linear range (μM)	detection limit(μM)	ref.
Pd/SWCNT	417 μA mM^{-1} cm^{-2}	2–238	0.25	1
	192 μA mM^{-1} cm^{-2}	283–1230		
Fe$_2$O$_3$/rGO	204 μA mM^{-1} cm^{-2}	0.05–780	0.015	2
Cu-NDs/RGO	214 μA mM^{-1} cm^{-2}	125–13000	0.4	3
nano-Au/Ch	0.354 μA mM^{-1}	0.4–750	0.1	4
rGO–Co$_3$O$_4$@Pt	0.026 μA mM^{-1}	10–650	1.73	5
AuNPs-ERGO	5.38 μA mM^{-1} cm^{-2}	Up to 3.38	0.133	6
f-ZnO@rFGO	/	10–8000	33	7
MnO$_2$ NA/TM	10301 μA mM^{-1} cm^{-2}	1.0–5000	0.0015	this work

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