Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Experimental

Materials

$NaNO_2$, NaH_2PO_4•$2H_2O$, Na_2HPO_4•$12H_2O$, KNO_3, CH_3COONH_4, $MgSO_4$, Na_2SiO_3, $ZnSO_4$, Na_2CO_3, $CaCl_2$, $K_4Fe(CN)_6$•$3H_2O$, $Zn(CH_3COO)_2$•$2H_2O$, KCl, HCl, $Na_2B_4O_7$•$10H_2O$, CH_3COOH, and ethanol ($\geq$ 99.7%) were procured from Aladdin Industrial Corp. (Shanghai, China). Glucose, $C_6H_7NO_3S$, $C_{12}H_{14}N_2$•2HCl, and $NH_2C_6H_4SO_2NH_2$ were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The mineral water and sausage samples were purchased at the local supermarket. Carbon fiber cloth (CC) with hydrophilic surfaces (WOS 1002) was purchased from the CeTech Co. Ltd. (Chinese Taipei). Other kinds of CC were purchased from the CeTech Co. Ltd. (WOS 1009, Chinese Taipei), Shang Hai Chu Xi Industrial Co. Ltd. (HCP331, Shanghai, China), and Wuxi Heshengyuan Carbon Fiber Technology Co. Ltd. (HSY-HO3P-200, Wuxi, China). Deionized (DI) water was used throughout all the experiments. 0.1 M Phosphate buffer saline (PBS, pH = 7.0) was prepared with 0.1 M NaH_2PO_4•$2H_2O$ and 0.1 M Na_2HPO_4•$12H_2O$. All chemicals of analytical reagent grade were directly used without further purification during all experiments.

Physical characterization

The crystalline structure was investigated with a powder X-ray diffractometer (XRD, Bruker D8 Advance Diffractometer System, Germany) with a Cu Kα (1.5418 Å) source. The morphology was measured with a field-emission scanning electron microscope (SEM, S-4800 Hitachi Co., Japan) operated at 10 kV. The surface chemical composition was investigated on an ESCALABMK II X-ray photoelectron spectrometer (XPS) using Mg as the exciting source (Thermo, America).

Electrode preparation

A piece of CC was firstly soaked in ethanol by sonication for 10 min in order to remove dust, insoluble grease and other impurities on the surface and rapidly infiltrate the surface of CC, then washed with DI water for several times to ensure the CC was well cleaned and wetted. After that, both the CC and unpretreated CC were inserted into the electrolytic cell (the geometric area of CC below the liquid level is 0.5 × 0.5 cm^2) to serve as the anodes for nitrite oxidation. The oxidized CC was obtained by immersing a piece of CC into the concentrated HNO_3 at 100 ^oC for 3 h.

Sausage pretreatment and determination of initial nitrite concentration

The sausage pretreatment was processed according to GB 5009.33-2016. Firstly, 5 g (accurate to 0.001 g) sausage sample was homogenized into mash and then mixed with 12.5 mL of 50 g L^{-1} saturated borax solution. Then, 150 mL of 70 °C DI water was added, and the mixture was heated at boiling point for 15 min. After the mixture was cooled to room temperature, 5 mL of potassium ferrocyanide solution (106 g L^{-1}) and 5 mL of zinc acetate solution (220 g L^{-1}) were introduced in order to precipitate the protein. Next, the mixture was diluted to 200 mL with DI water and filtered after 30 min standing in order to remove the upper fat. Finally, the resulting sample was stored at 4 °C in a refrigerator. The determinations of initial nitrite concentrations in above sample solution and mineral water were according to the Griess-saltzman (GB 5009.33-2016) and the diazo-coupled spectrophotometric (GB 8538-2016) methods, respectively.

Electrochemical measurements

Cyclic voltammetry (CV) and amperometric I-T curves were carried out on a CHI660E electrochemical workstation (CH Instruments, China). The conventional three electrode configuration was used with a piece of CC as the working electrode (0.5 × 0.5 cm^2), a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. CV tests were performed in the potential window of 0-1.2 V (*vs*. SCE). 0.1 M PBS (pH = 7) was used as the supporting electrolyte. All electrochemical experiments were conducted at room temperature.

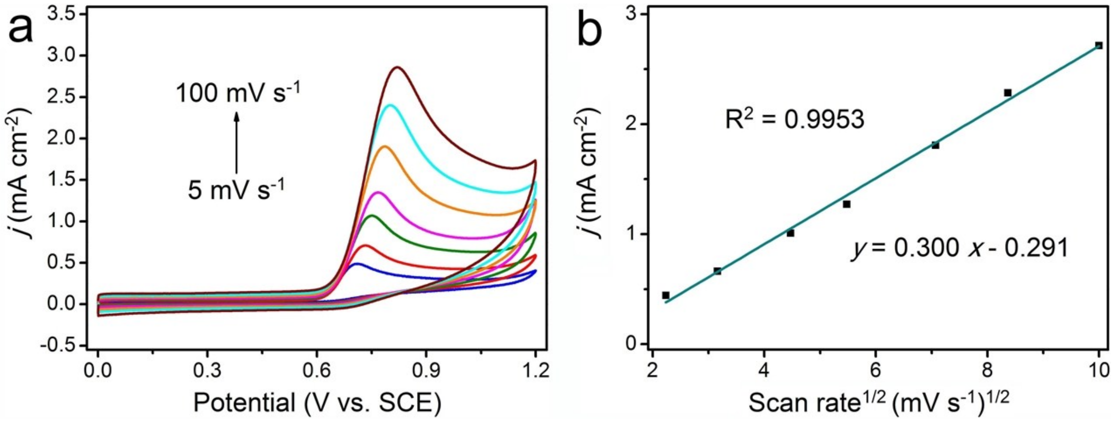

Fig. S1. (a) CVs of the CC in 0.1 M PBS with 1.0 mM nitrite at various scan rates from 5−100 mV s^{-1}. (b) Calibration curve of peak current density as a function of the square root of scan rate.

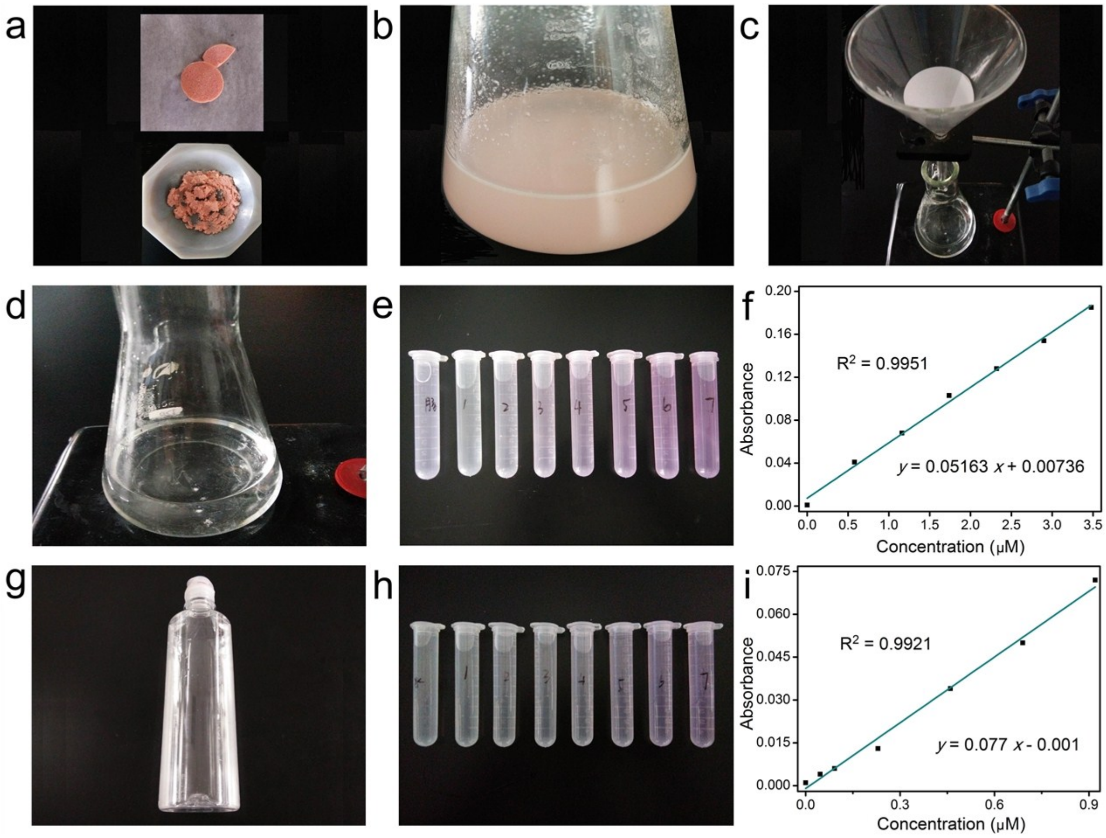

Fig. S2. (a-f) Sausage pretreatment process and calibration curve plotted by using the absorbance *vs*. nitrite concentration. (g-i) Mineral water sample preparation and calibration curve plotted by using the absorbance *vs*. nitrite concentration.

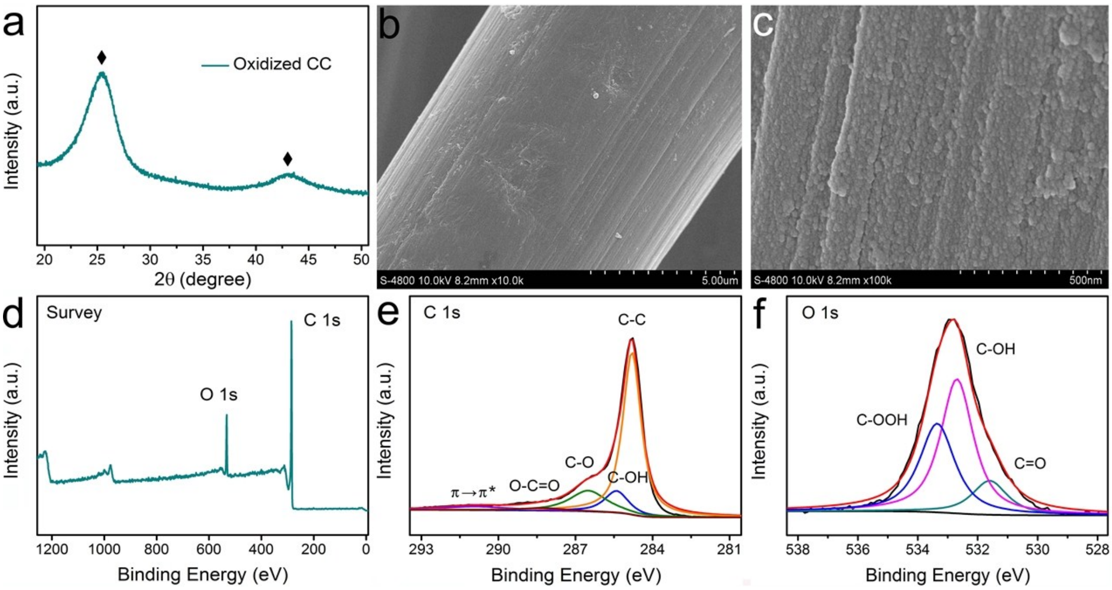

Fig. S3. (a) XRD pattern of the oxidized CC. (b) Low- and (c) high-magnification SEM images of the oxidized CC. (d) XPS survey spectrum of the oxidized CC. High-resolution XPS spectra in the (e) C 1s and (f) O 1s regions.

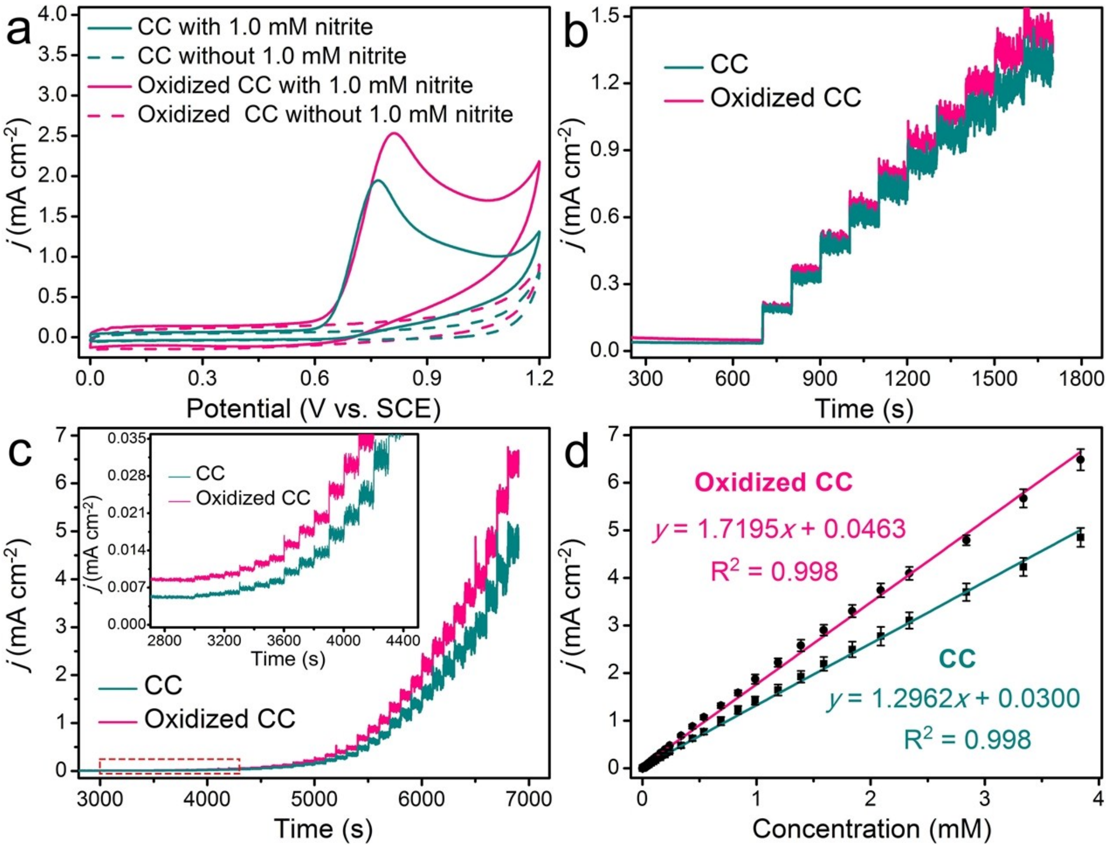

Fig. S4. (a) CVs of the CC and oxidized CC in 0.1 M PBS with and without the presence of 1.0 mM nitrite at 50 mV s^{-1}. (b) Comparison of the amperometric responses of the CC and oxidized CC to the successive addition of 0.0625 mM nitrite at 0.85 V *vs*. SCE. (c) Amperometric responses of the CC and oxidized CC to the successive addition of nitrite with the concentration from 0.25 μM to 3838.5 μM at 0.85 V *vs*. SCE (Inset: the enlarged view of amperometric responses of CC and oxidized CC towards nitrite at low concentrations. (d) Comparison of calibration curves of the amperometric response as a function of the nitrite concentration for the CC and oxidized CC.

Table S1. Performance comparison of different electrochemical nitrite sensors.

Electrode	Liner range (μM)	Electrolyte (PB/PBS)	Potential (V *vs.* Ag/AgCl)*	Determination limit (μM)	Detection limit (μM)	Sensitivity (μA mM^{-1} cm^{-2})	References
Carbon fiber cloth	**0.25-3838.5**	**0.1 M pH=7**	**0.805**	**0.25**	**0.03**	**1296.2**	**This work**
Free-standing rGO/Acr paper	0.4-3600	0.1 M pH=5	1.030	0.4	0.12	400	1
AuNPs/CP	1-30, 40-100	0.1 M pH=7	0.845	1	0.093	/	2
Au-PtNPs/PyTS-NG/GCE	0.5-1621	0.1 M pH=7	0.75	0.5	0.19	27.6	3
Cu-NDs/RGO/GCE	1.25-13000	0.1 M pH=2	-0.155	1.25	0.4	214	4
MOF-GNRs-50/ITO	100-2500	0.1 M KCl pH=7	0.895	100	0.75	93.8	5
Bare glassy carbon	2.5-10	0.1 M KCl pH=3	0.755	2.5	0.4	/	6
NiFe-LDH NSAs/CC	5-1000	0.1 M pH=7	0.945	5	0.02	803.6	7
Au/ZnO/MWCNTs/GCE	0.78-400	0.1 M pH=7	0.740	0.78	0.4	/	8
Fe_3O_4/RGO/GCE	10-2882	0.1 M pH=4	0.815	10	0.03	196	9
K-modified graphene/GCE	0.5-7800	0.1 M pH=7.4	0.705	0.5	0.2	/	10
NGE/PdNC/GCE	0.5-1510	0.1 M pH=6	0.685	0.5	0.11	342.4	11
TOSC-MoS_2/GCE	6-3140	0.1 M pH=5	0.855	6	2	/	12
a-Fe_2O_3 NAs/CF	0.5-1000	0.1 M pH=7	0.805	0.5	0.12	116.83	13
Pd/Fe_3O_4/polyDOPA/RGO/GCE	2.5-6470	0.1 M pH=7.4	0.775	2.5	0.5	/	14
Pt/Ni$(OH)_2$/MWCNTs/GCE	0.4-5670	0.1 M pH=7.4	0.705	0.4	0.13	145	15
Ag-P(MMA-*co*-AMPS)/GCE	1-100000	0.1 M pH=7	0.855	1	0.2	104.6	16
Ag/HNT/MoS_2/GCE	2-425	0.1 M pH=4	0.845	2	0.7	2900	17
a-Fe_2O_3-ZnO NRs/Ag/Glass	1-1250	0.1 M pH=7.4	0.865	1	0.015	131.2	18
Cu/MWCNTs/GC	5-1260	0.1 M pH=7	0.855	5	1.8	455.84	19
AgPs-IL-CPE	50-1000	0.1 M NaCl pH=4	0.915	50	3	/	20
Ni$(OH)_2$@PEDOT-rGO/GCE	2-7100	0.1 M NaOH	0.505	2	0.6	346	21
NGQDs@NCNFs/GCE	5-300	0.1 M pH=4.5	/	5	3	/	22

Note: *E* (SCE) = *E* (Ag/AgCl) + 45 mV.

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Table S2. Determination of nitrite in mineral water and sausage extract samples.

Samples	**Initial Con.**[*] **(μM)**	**Spiked Con. (μM)**	**Found Con. (μM)**	**Recovery (%)**
Mineral water	0.091	0.6	0.695	100.58
	0.091	1.2	1.174	90.94
	0.091	2.2	2.019	88.13
Sausage extract	0.845	5	6.498	111.17
	0.845	10	11.371	104.85
	0.845	20	18.459	88.55

[*] The Con. is the abbreviation of Concentration.