### Supplementary material for

# Carbon-doped bimetallic oxide nanoflakes for simultaneous electrochemical analysis of ascorbic acid, uric acid, and acetaminophen in sweat

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#### **1.** Materials and methods

#### **1.1 Reagents and apparatus**

NaCl, K<sub>2</sub>SO<sub>4</sub>, acetic acid, ascorbic acid (AA), acetaminophen (AC), glucose (Glu), glutathione (GSH) and glycine (Gly) were bought from Sigma-Aldrich. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Graphite, pyruvic acid, glutamic acid and urea were purchased from Sinopharm Chemical Reagent Co., Ltd. H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, KMnO<sub>4</sub>, NH<sub>4</sub>Cl and lactate (LA) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. H<sub>2</sub>O<sub>2</sub> (30%, v/v) and isopropanol were obtained from Aladdin Industrial Inc. Homocysteine (Hcy) and glutamic acid (Glx) were

bought from Selleck, and uric acid (UA) was bought from Zhonghe Chemical Co., Ltd. HCl and glycerol were purchased from Shanghai Taitan Scientific Co., Ltd. Polyimide film (PI film, 50 μm) used to fabricate flexible electrode was purchased from Suzhou Mckess Plastic Products Co., Ltd, and ultrapure water (18.2 M cm) used in experiments was obtained by Millipore Milli-Q purification system.

The surface morphology of modified electrode was characterized by a scanning electron microscope (SEM, 3.0/S-3400N, Hitachi, Japan), and the structure and morphology of materials was observed by a transmission electron microscope (TEM, JEM-1400, JEOL, Japan). The elemental composition and energy dispersive spectrometer (EDS) spectrum were revealed by a field emission scanning electron microcopy (FESEM, GeminiSEM 500, Germany). The composition and crystal structure of synthesized materials was analyzed by a rotating anode X-ray powder diffractometer (XRD, D/max2550, Rigaku, Japan). The elemental valance and chemical state were obtained by an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, ThermoFisher, USA), and the molecular structure and vibrational modes of chemical bonds were measured by a laser micro-Raman spectrometer (Raman, invia reflex, Renishaw, UK).

#### 1.2 Synthesis of GO

GO was prepared by the improved Hummer's method with some modifications [1]. Briefly, 1.5 g graphite was immersed in 130 mL HNO<sub>3</sub> and 20 mL H<sub>2</sub>SO<sub>4</sub>. Then, 9 g KMnO<sub>4</sub> was added slowly to the mixture. The reaction solution was further stirred for 12 h at 50 °C, and then poured into 450 mL water. Excess KMnO<sub>4</sub> was removed by adding 1.5 mL H<sub>2</sub>O<sub>2</sub> to obtain a golden GO solution. After sedimentation and centrifugation, GO was washed by 3 M HCl and water, and finally freeze-dried.

Subsequently, the synthesis of  $C-Fe_xCo_yO_4$  was achieved through solvothermal method [2] and calcination.

#### **1.3 Preparation of artificial perspiration**

The artificial perspiration containing common ions and biomolecules was prepared by Tugba's method with some modifications [3]. In detail, 2.0 g NaCl, 1.75 g NH<sub>4</sub>Cl, 1.5 g lactate (LA), 0.5 g acetic acid, 60 mg urea, 180  $\mu$ M pyruvic acid, 10  $\mu$ M AA, 200  $\mu$ M glucose (Glu) and 370  $\mu$ M glutamic acid (Glx) was ultrasonically dissolved in 100 mL water, and the pH of solution was further adjusted to 5.5 by adding 10 mM HCl.

#### **1.4 Electrochemical measurements**

Screen-printed carbon electrodes (SPCEs) were prepared on PI film by a home-made semiautomatic screen printer [4], and 10  $\mu$ L suspension of C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub> was dropped on the sensing area of SPCE to fabricate modified electrode (noted as C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub>/SPCE), which acted as the work electrode. All electrochemical measurements were conducted on a CHI850D workstation (Chenhua, China) with a three-electrodes system, using an Ag/AgCl electrode and a Pt wire as reference electrode and counter electrode, respectively. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were two main technologies used in electrochemical analysis. In CV tests, the scan window was set in -0.3 ~ 0.6 V with a scan rate of 100 mV/s. In DPV tests, the scan range was in -0.3 ~ 0.8 V with a pulse width of 0.05 s and pulse period of 0.5 s. The conductivity of modified electrodes were evaluated by CV and electrochemical impedance spectroscopy (EIS) by an Autolab M204 workstation (Metrohm, Switzerland) in 5 mM  $[Fe(CN)_6]^{3-/4-}$  (containing 0.1 M KCl), where the scan window of CV was set in  $-0.2 \sim 0.6$  V and the frequency of EIS was set from 100k Hz to 0.01 Hz. Besides, the artificial perspiration was diluted 5 times and sweat was diluted 100 times by 0.1 M PBS before adding standard solutions in recovery tests.

#### 2 Electrochemical detection of AA, UA, and AC

DPV testing was conducted in optimized conditions to comprehensively evaluate the detection performance of proposed sensor to AA, UA, and AC. As shown in Fig. S9A, the peak current around 0.2 V steadily increased as the addition of AA referring to the good electrochemical response of C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub> to AA. The oxidation peak current presented a two-segment linear dependence on the concentration of AA in a pretty wide range of 0.004-11.5 mM (Fig. S9B). The detection sensitivity in 0.004-4 mM and 1-11.5 mM were 72.08 µA mM<sup>-1</sup> cm<sup>-2</sup> and 34.11µA mM<sup>-1</sup> cm<sup>-2</sup>, respectively. The wide detection range exhibited by proposed sensor was suitable in many situations, and was capable to detect AA in various biofluids such as blood (28.5-85.2 µM) [5], tears (0.02-1.2 mM) [6] and sweat (10-30 µM) [7]. Also, the sensor based on C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub>/SPCE displayed good current responses to UA and AC. The oxidation peak current around 0.3 V rise with the addition of UA, as well as the oxidation peak current around 0.4 V rise with the addition of AC (Fig. S9C, S9E), and they both exhibited a two-segment linear correlation. In the detection of UA, fabricated sensor presented a high sensitivity of 4360  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> in the concentration range of 0.6-69.6  $\mu$ M and a sensitivity of 1330 µA mM<sup>-1</sup> cm<sup>-2</sup> in the concentration range of 69.6-333.6 µM. For AC detection, a pretty high sensitivity of 6350 µA mM<sup>-1</sup> cm<sup>-2</sup> was obtained by proposed sensor within 0.1-52  $\mu$ M, and a sensitivity of 1640  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> was obtained within 52-232  $\mu$ M.

## **3** Figures and caption



Fig. S1. TEM images of (A) GO, (B)  $Fe_xCo_yO_4$  precursors, (C) C-Co<sub>3</sub>O<sub>4</sub>, and (D)  $Fe_xCo_yO_4$ .



Fig. S2. FESEM image of C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub>.



Fig. S3. CV and DPV response of C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub>/SPCE to (A, D) 6 mM AA, (B, E) 150  $\mu$ M UA, and (C, F) 50  $\mu$ M AC.



**Fig. S4**. CV and DPV response of bare SPCE to **(A, D)** 6 mM AA, **(B, E)** 150 μM UA, and **(C, F)** 50 μM AC.



Fig. S5. The liner regression of current (I)-v in oxidation of (A) AA, (C) UA, and (E) AC; the liner regression of  $I-v^{1/2}$  in oxidation of (B) AA, (D) UA, and (F) AC, according to the CV curves of C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub>/SPCE at different scan rates in 0.1 M PBS with addition of AA, UA, and AC.



Fig. S6. DPV curves of (A) AA, (B) UA, and (C) AC detection in different pH; and corresponding bar graphs of (D) AA, (E) UA, and (F) AC; line charts of (G) AA, (H) UA, and (I) AC detection with different loading amount of C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub>.



Fig. S7. Oxidation mechanisms of AA, UA, and AC.



Fig. S8. The bar graphs of current response of different modified electrodes to (A) AA, (B) UA, and (C) AC.



Fig. S9. The electrochemical detection of (A) AA, (C) UA, and (E) AC by proposed sensor based on C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub>/SPCE; and the corresponding linear regression of (B) AA, (D) UA, and (F) AC.



Fig. S10. The reproductivity detection of (A) AA, (C) UA, and (E) AC; the stability detection of (B) AA, (D) UA, and (F) AC.



Fig. S11. Variation of performance retention with deformation times for C-Fe<sub>1.33</sub>Co<sub>1.67</sub>O<sub>4</sub> /SPCE to (A) AA, (B) UA, and (C) AC detection.

## 4 Tables and caption

Materials	<b>Detection Range</b>	Sensitivity	LOD	Ref.
	(µM)	(µA mM <sup>-1</sup> )	(µM)	
Co-L/GO	AA: 2-15	AA: 20	AA: 1.94	[8]
	UA: 0.2-3	UA: 100	UA: 0.57	
FeS/RGO/GCE	AC: 5-300	AC: 38.6	AC: 0.18	[9]
GO/MWNT	AA: 5.0-300	AA: 81.9	AA: 1.0	[10]
	UA: 3.0-60	UA: 523.5	UA: 1.0	
Fe-NC	AC: 0-100	AC: 270	AC: 0.026	[11]
ITO-rGO-	AA: 20-150	AA: 118	AA: 9.4	[12]
AuNPs	UA: 10-100	UA: 310	UA: 10.9	
ZIF-67-OMC	AC: 0.05-100	AC: 193.1	AC: 0.02	[13]
MXene/MoS <sub>2</sub>	AA: 10-5000	AA: 54.6	AA: 4.2	[14]
BHA/GO	UA: 20-160	UA: 241	/	[15]
	AC: 20-160	AC: 89		
Fe <sub>3</sub> O <sub>4</sub> @Au-S-	AA: 6-350	AA: 30	AA: 5	[16]
Fc/GS-chitosan	UA: 1-90	UA: 150	UA: 0.1	
	AC: 0.4-32	AC: 400	AC: 0.01	
Fc-S-Au/C	AA: 8-2556	AA: 5.5	AA: 1.00	[17]
NC/graphene	UA: 0.6-273	UA: 110.5	UA: 0.12	
	AC: 0.5-275	AC: 39.1	AC: 0.10	
SWCNTs-CHIT-	AA: 50-1800	AA: 36.8	AA: 1.03	[18]
RTIL	UA: 10-380	UA: 81.2	UA: 0.46	
	AC: 10-360	AC: 149.3	AC: 0.25	
CeO <sub>2</sub> /CNT/GCE	AA: 10-120	AA: 18.1	/	[19]
	UA: 50-61	UA: 29.8		
	AC: 10-42	AC: 70.6		
C-Fe <sub>1.33</sub> Co <sub>1.67</sub> O <sub>4</sub>	AA: 4.0-11500	AA: 4.2	AA: 1.69	This
	UA: 0.6-333	UA: 304.5	UA: 0.23	work
	AC: 0.1-232	AC: 404.1	AC: 0.07	

Table S1. Detection performance of other electrochemical sensors for AA, UA, and AC analysis.

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