Electronic Supplementary Information

for

Three-dimensional nitrogen-doped graphene-based metal-free electrochemical sensors for simultaneous determination of ascorbic acid, dopamine, uric acid, and acetaminophen

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Experimental section

Chemicals

Graphite powder, sodium tetraborate decahydrate, AA, and AP were bought from Sinopharm Chemical Reagent Co., Ltd. (China). DA and ethylenediamine (EDA) were purchased from Aladdin Biochemical Technology Co., Ltd. (China). Urea and N,N-dimethylformamide (DMF) were bought from Shanghai Macklin Biochemical Co., Ltd. (China). UA was purchased from Alfa Aesar. All aqueous solutions were prepared using ultrapure water from the Milli-Q water purification system with a resistivity of 18.2 MΩ·cm (Millipore, USA). Prior to use, different concentrations of AA, DA, UA, and AP solutions were freshly obtained in phosphate buffered salines (PBS, 0.1 M) containing 0.15 M NaCl. All other chemicals in our experiments were of analytical purity and used without any additional treatment.

Instruments and measurements

Wide-angle X-ray diffraction (XRD) patterns were recorded on a D8 advance superspeed powder diffractometer (Bruker, Germany) with a Cu-Kα radiation source in the angular range between 5 and 80°. Morphological representations of the obtained 3D-NG were carried out using a Supra 55 scanning electron microscope (SEM, Zeiss, Germany). Room-temperature Raman spectra were acquired on a Renishaw InVia Raman spectrometer (UK) using a 50× objective lens at a laser excitation of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements for analyzing surface properties were performed by an ESCALAB 250Xi spectrometer system (Thermo Fisher Scientific, USA) equipped with a monochromatized Al Kα radiation as the

excitation source. All electrochemical experiments including cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) analyses were performed on a CHI 660C electrochemical workstation (Chenhua Instruments Co., China). A standard three-electrode system was composed of a modified glassy carbon electrode (GCE, ϕ = 3 mm) as the working electrode, a Pt wire electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Prior to measurement, a continuous flow of high purity nitrogen was bubbled for deoxygenating the electrolyte solutions and a stable nitrogen atmosphere was maintained during the whole experiments.

Table S1 Peak positions of D and G bands, and intensity ratios between D peak and G peak for graphite, GO, and 3D-NG.

Sample	D band (cm^{-1})	G band (cm^{-1})	I_D/I_G
Graphite	1352	1581	0.12
GO	1354	1590	0.84
3D-NG	1346	1591	0.92

Table S2 Atomic concentrations of C, N, and O of GO and 3D-NG.

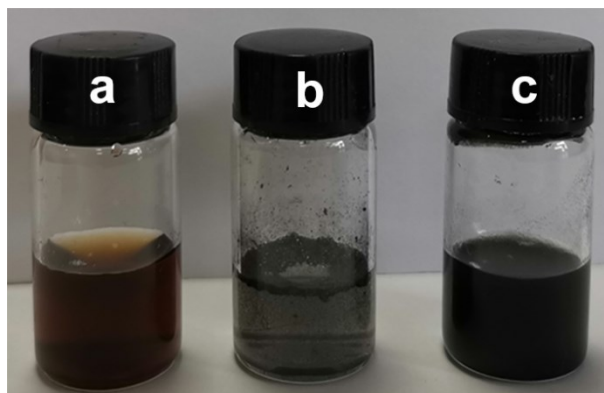| Sample	C 1s (at. %)	N 1s (at. %)	O 1s (at. %)
GO	62.8	−	37.2
3D-NG	82.6	9.5	7.9

Fig. S1 Photographs of (a) GO and (b) 3D-NG in aqueous solution, and (c) 3D-NG in DMF.
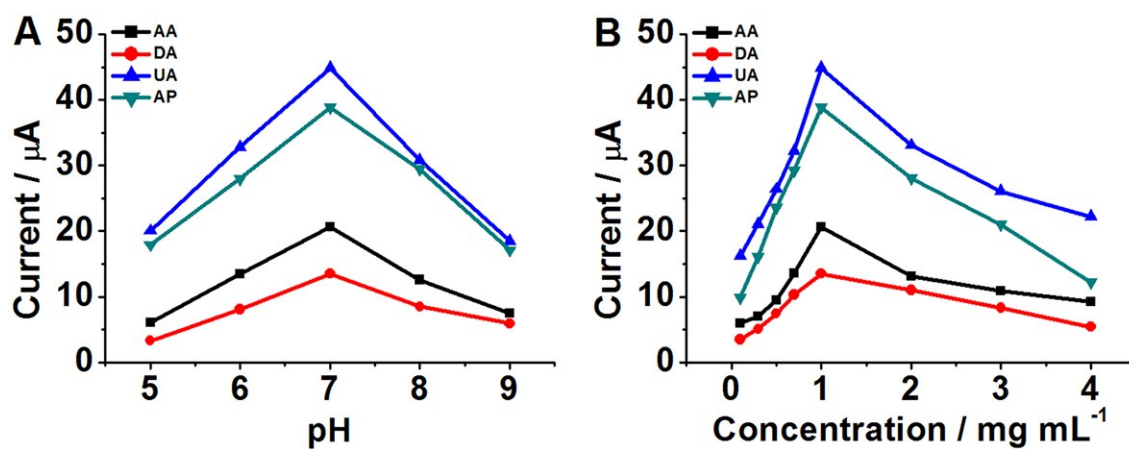

Fig. S2 Influence of (A) pH and (B) the concentration of 3D-NG for the detection of 3 mM AA, 200 μM DA, 400 μM UA, and 200 μM AP by the DPV method.
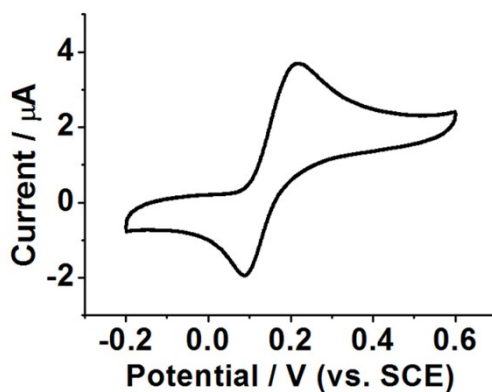

Fig. S3 The magnified CV curve of 0.2 mM DA on GCE in 0.1 M PBS solutions (pH 7.0): scan rate, 0.1 V s^{-1}.

Table S3 Comparison between the proposed sensor with other reported modified electrodes for electrochemical determination of AA, DA, and UA.

Electrode	Linear range (μM)			Detection limit (μM)			Reference
	AA	DA	UA	AA	DA	UA	
3D-MoS$_2$/RGO/Au@GCE	2−5400	0.3−198.3	5−2215	0.93	0.11	0.74	S1
ERGO/CFE	8−2016.45	1.5−224.82	6−899.3	4.5	0.77	2.23	S2
RGO-ZnO/GCE	50−2350	1−70	3−330	3.71	0.33	1.08	S3
Trp-GR/GCE	200−12900	0.5−110	10−1000	10.09	0.29	1.24	S4
ZnCl$_2$-CF/GCE	0.05−200	2−2000	1−2500	0.02	0.16	0.11	S5
[Ni(phen)$_2$]$^{2+}$/SWCNTs/GCE	30−1547	1−780	1−1407	12	1.0	0.76	S6
3D-NG/DMF/GCE	20−10000	1−1000	0.5−1000	3.91	0.26	0.12	this work

RGO, reduced graphene oxide

ERGO, electrochemically reduced graphene oxide

CFE, carbon fiber electrode

Trp-GR, tryptophan-functionalized graphene nanocomposite

CF, microporous carbon

SWCNTs, single-walled carbon nanotubes

Table S4 Summary of recently reported electrochemical sensors for AP.

Electrode	Linear range (μM)	Detection limit (μM)	R^2	Reference
P-RGO/GCE	1.5−120	0.36	0.9965	S7
ERG/GCE	5−800	1.2	0.996	S8
Co,N-MoO$_2$/MoC/GCE	0.05−200	0.015	0.998	S9
RGO-TiN/GCE	0.06−660	0.02	0.9997	S10
PCA@Zn/Ni-ZIF-8-800/GCE	0.08−1000	0.029	0.994	S11
Co/Co$_3$O$_4$@HNCP/PVDF/GCE	0.025−50	0.0083	0.998	S12
Au/Co-NCNHP/GCE	0.1−250	0.05	0.9909	S13
3D-NG/DMF/GCE	0.1−600	0.02	0.9933	this work

P-RGO, phosphorus-doped graphene

ERG, electrochemically reduced graphene

RGO-TiN, reduced graphene oxide-titanium nitride nanohybrid

PCA, poly caffeic acid

HNCP, hollow nanoporous carbon polyhedrons

PVDF, poly(vinylidene fluoride)

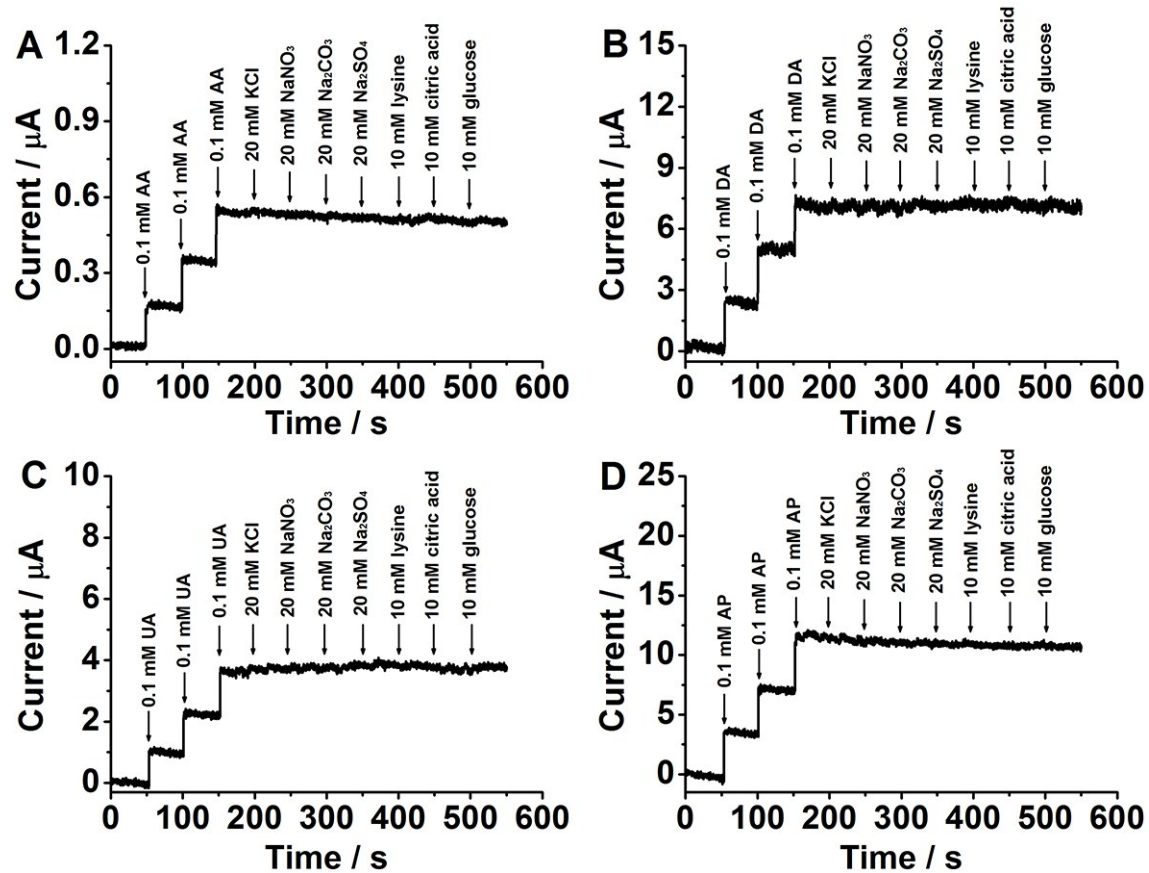Co-NCNHP, cobalt-nitrogen co-doped carbon nanotube hollow polyhedron

Fig. S4 Amperometric responses of 3D-NG/DMF/GCE upon successive addition of (A) 0.1 mM AA, (B) 0.1 mM DA, (C) 0.1 mM UA, (D) 0.1 mM AP, and other chemicals to 0.1 M PBS solutions (pH 7.0).

Table S5 Results for determination of AA, DA, UA, and AP in human urine samples.

Sample	Analyte	Detected (μM)	Added (μM)	Found (μM)	Recovery (%, n = 5)	RSD (%, n = 5)
Urine 1	AA	−	200	197.8	98.9	2.2
	DA	−	20	20.3	101.5	1.4
	UA	10.4	40	49.4	98.0	1.5
	AP	−	40	38.7	96.8	1.7
Urine 2	AA	−	300	298.2	99.4	2.0
	DA	−	40	40.3	100.7	1.3
	UA	31.5	20	50.8	98.6	1.1
	AP	−	60	59.2	98.7	1.5
Urine 3	AA	−	400	398.9	99.7	1.9
	DA	−	30	29.8	99.3	1.3
	UA	21.2	50	70.7	99.3	1.4
	AP	−	50	49.7	99.4	1.2

References

S1 Y. A. Zhao, J. Zhou, Z. M. Jia, D. Q. Huo, Q. Y. Liu, D. Q. Zhong, Y. Hu, M. Yang, M. H. Bian and C. J. Hou, *Microchim. Acta*, 2019, **186**, 92.

S2 B. B. Yang, H. W. Wang, J. Du, Y. Z. Fu, P. Yang and Y. K. Du, *Colloid. Surface. A*, 2014, **456**, 146−152.

S3 X. Zhang, Y. C. Zhang and L. X. Ma, *Sens. Actuators B*, 2016, **227**, 488−496.

S4 Q. W. Lian, Z. F. He, Q. He, A. Luo, K. W. Yan, D. X. Zhang, X. Q. Lu and X. B. Zhou, *Anal. Chim. Acta*, 2014, **823**, 32−39.

S5 W. J. Zhang, L. Liu, Y. G. Li, D. Y. Wang, H. Ma, H. L. Ren, Y. L. Shi, Y. J. Han and B. C. Ye, *Biosens. Bioelectron.*, 2018, **121**, 96−103.

S6 S. L. Yan, X. Li, Y. Xiong, M. M. Wang, L. L. Yang, X. Liu, X. Y. Li, L. A. M. Alshahrani, P. Liu and C. C. Zhang, *Microchim. Acta*, 2016, **183**, 1401−1408.

S7 X. Zhang, K. P. Wang, L. N. Zhang, Y. C. Zhang and L. Shen, *Anal. Chim. Acta*, 2018, **1036**, 26−32.

S8 B. R. Adhikari, M. Govindhan and A. C. Chen, *Electrochim. Acta*, 2015, **162**, 198−204.

S9 Y. Y. Dong, M. Zhou and L. Zhang, *Electrochim. Acta*, 2019, **302**, 56−64.

S10 F. Y. Kong, S. X. Gu, J. Y. Wang, H. L. Fang and W. Wang, *Sens. Actuators B*, 2015, **213**, 397−403.

S11 W. Q. Zhang, L. K. Zong, S. Q. Liu, S. Pei, Y. S. Zhang, X. M. Ding, B. Jiang and Y. P. Zhang, *Biosens. Bioelectron.*, 2019, **131**, 200−206.

S12 K. D. Wang, C. Wu, F. Wang, N. Jing and G. Q. Jiang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 18582−18592.

S13 Y. F. Jin, X. B. Li, C. Y. Ge, J. J. Ma, Y. C. Li, E. Q. Zhao, S. W. Yao, G. R. Xu and D. H. Li, *Microchim. Acta*, 2020, **187**, 6.