

Electronic support information (ESI) for Nanoscale

Nano-ZnS decorated hierarchically porous carbon electrocatalyst with multiple enzyme-like activities as nanozyme sensing platform for simultaneous detection of dopamine, uric acid, guanine, and adenine

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1. XRD of different material

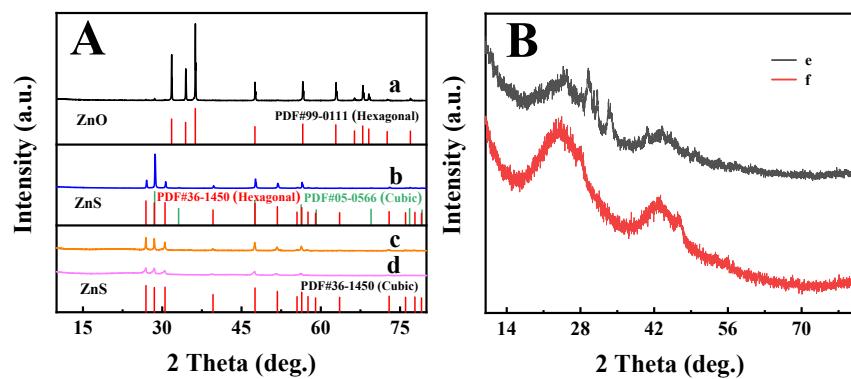


Figure S1 Wide-angle XRD patterns of unetched ZS (a), ZS (b), unetched ZSHPC (c), ZSHPC (d), unetched PC (e) and PC (f).

2. TEM of different materials

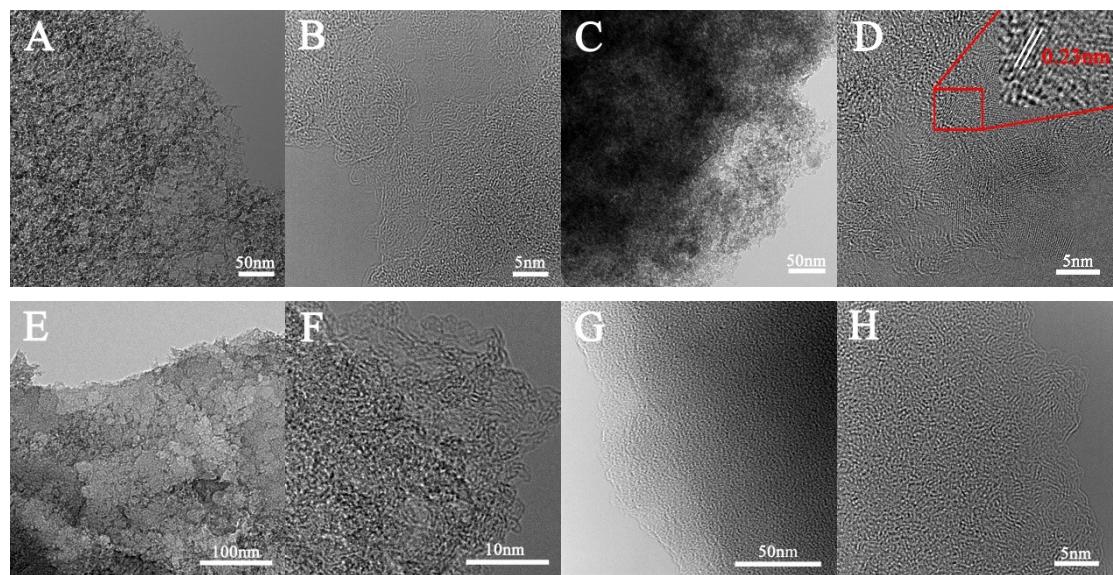


Figure S2 TEM images of ZHPC (A and B), ZSPC (D and E), SHPC (E and F), and PC (G and H).

3. EIS and CVs of different materials

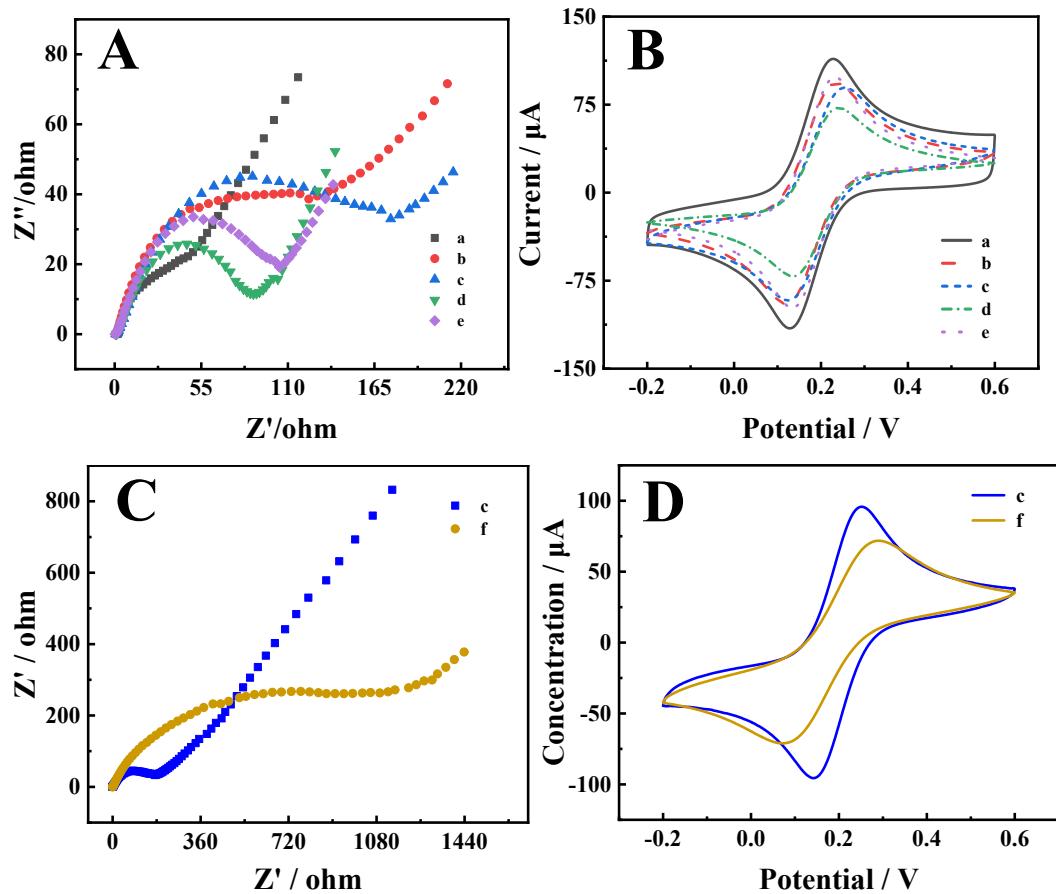


Figure S3 Nyquist plots (A and C) and CVs (B and D) of HPC/GCE (a), SPC/GCE (b), PC/GCE (c), ZS/GCE (d), bare GCE (e) and unetched PC/GCE (f).

4. CVs of DA, UA, G and A

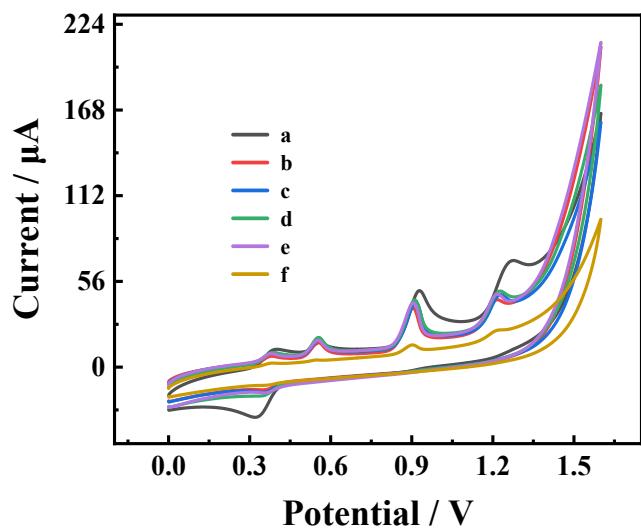


Figure S4 CVs of 60 μM DA, UA, G and A at ZSHPC/GCE (a), ZHPC/GCE (b), ZSPC/GCE (c), SHPC/GCE (d), PC/GCE (e) and bare GCE (f) in 0.1 M PBS ($\text{pH} = 3.0$).

5. Peroxidase and oxidase activity of different materials

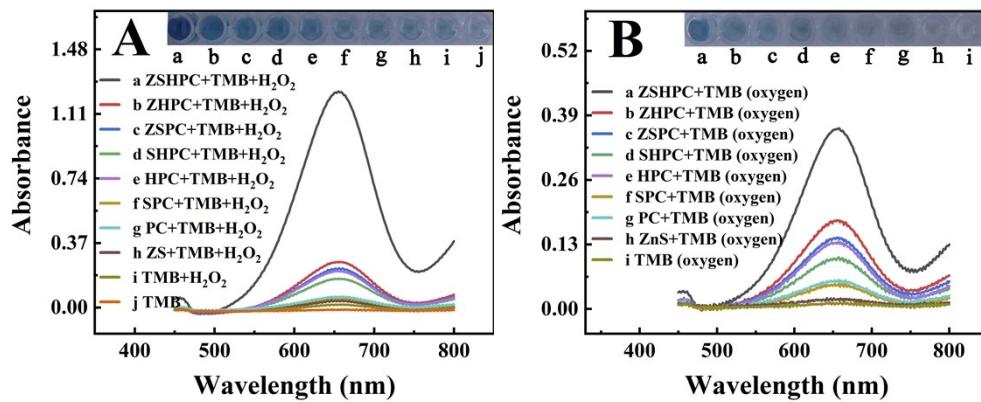


Figure S5 UV-vis absorption spectra of TMB + different materials system in the presence of H₂O₂

(A) and different materials system in the presence of TMB (B). Insets are corresponding photographs of above.

6. Simultaneous detection of DA, UA, G and A

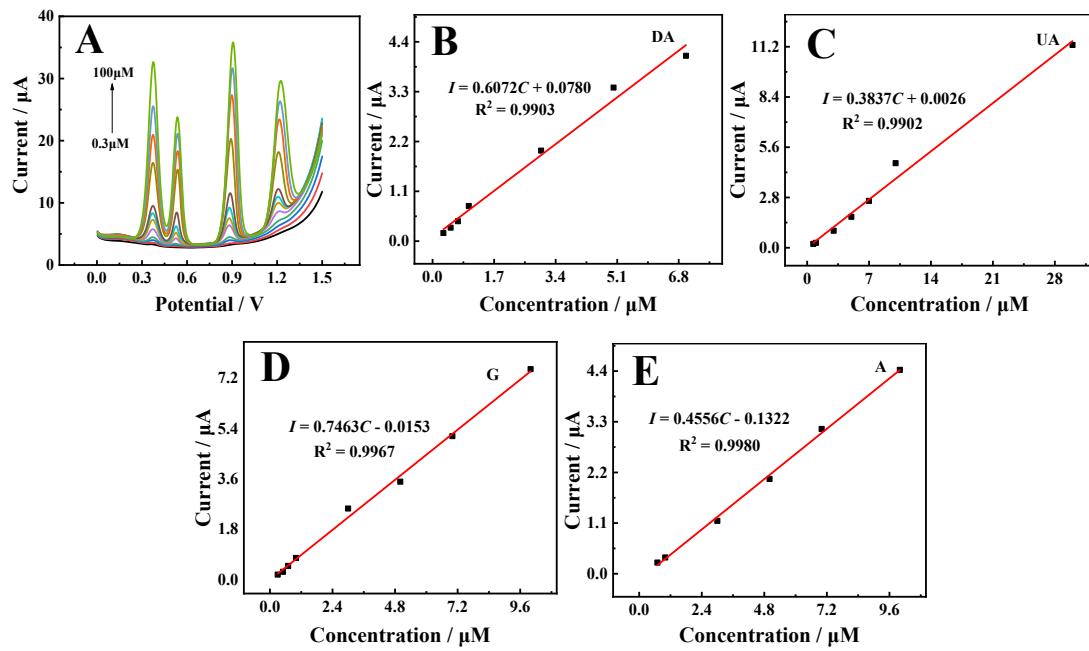


Figure S6. DPVs obtained for the simultaneous addition of DA, UA, G and A in the concentration range of 0.3 to 100 μM each at ZSHPC/GCE in 0.1 M PBS (pH = 3.0), and the relationship between concentration and $I_{p,a}$ at low concentrations of DA (B), UA (C), G (D) and A (E).

7. Interference, repeatability and reproducibility

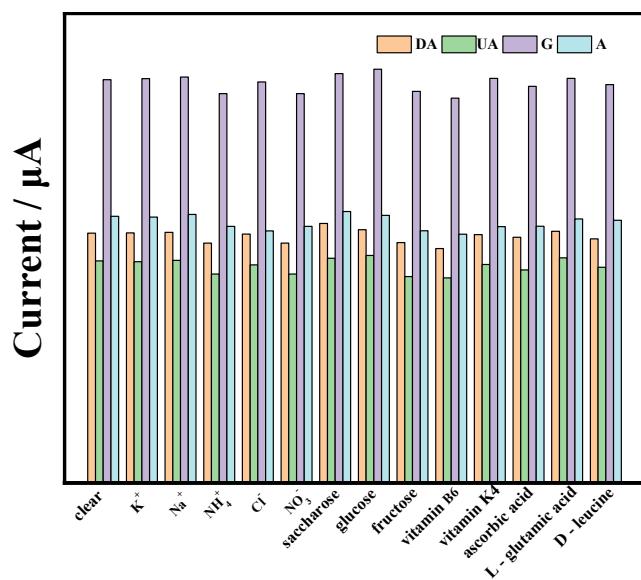


Figure S7 Influence of coexisting substances on the current response of DA, UA, G and A for ZSHPC/GCE in 0.1 M PBS (pH = 3.0) containing 60 μM DA, UA, G and A and several interferences.

8. Repeatability and reproducibility

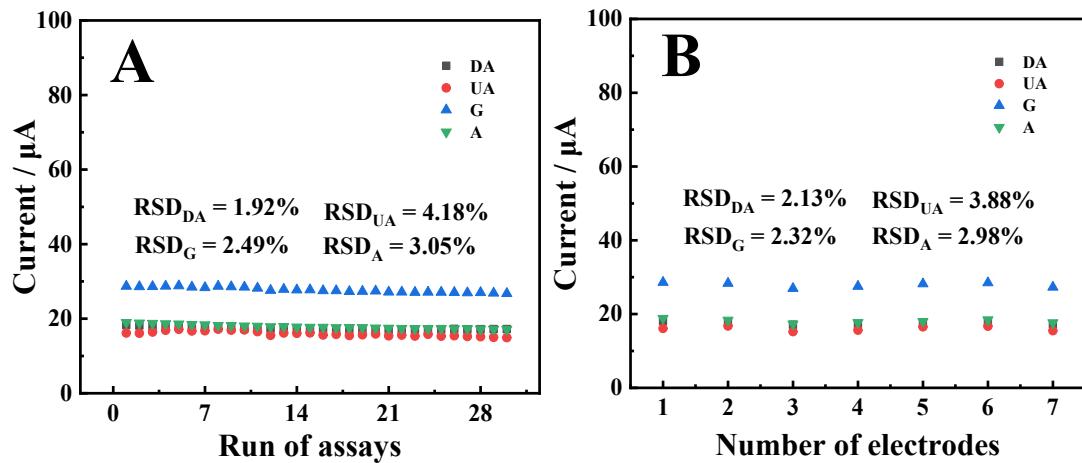


Figure S8 The repeatability (A) and reproducibility (B) of ZSHPC/GCE for voltametric responses

of DA, UA, G and A.

9. Comparative analysis of synthetic methods of zinc sulfide-carbon composites in recent years

Table S1 Comparative analysis of synthetic methods of zinc sulfide-carbon composites in recent years.

zinc source	sulfur source	carbon source	process	Ref
zinc acetate	sodium sulfide	multiwalled carbon nanotube	step 1 synthesis of negatively charged zinc sulfide step 2 synthesis of positively charged multiwalled carbon nanotube step 3 synthesis of zinc sulfide-carbon composite by heteroaggregation	1,2
Zinc nitrate	sodium sulfide	multiwalled carbon nanotube	step 1 synthesis of $\text{SiO}_2@$ carbon nanotube step 2 synthesis of $\text{SiO}_2/\text{ZnSilicate}@$ carbon nanotube step 3 synthesis of zinc sulfide@ carbon nanotube by hydrothermal treatment	3
zinc acetate	thiocarbamide	PVA/PTFE nanofiber	step 1 synthesis of preoxidized PVA/PTFE nanofiber by spinning process step 2 synthesis of zinc sulfide-carbon composite by solvothermal treatment	4
zinc sulfate	sodium sulfide	graphene	step 1 synthesis zinc sulfide step 2 synthesis of zinc sulfide-graphene composite by hydrothermal treatment	5
zinc acetate	chicken feather	chicken feather	one pot hydrothermal treatment of aqueous solution of zinc acetate and chicken feather	6
zinc acetate	pig bristle	pig bristle	one pot reflux of zinc acetate and pig bristle in potassium hydroxide aqueous solution	7
zinc chloride	sulfuric acid	leave of camphor tree	one pot hydrothermal treatment of zinc chloride and leave of camphor tree in sulfuric acid aqueous solution	This work

10. I_D / I_G values of Raman spectra of different materials.

Table S2 I_D / I_G values of Raman spectra of different materials.

Different carbon materials	I_D / I_G
ZSHPC	1.0527
ZHPC	1.0103
ZSPC	1.0632
SHPC	1.0476
PC	1.0466

11. Elemental composition of different materials from XPS analysis

Table S3 Elemental composition of different materials from XPS analysis.

Sample	% Carbon (C1s)	% Zinc (Zn2p)	% Sulfur (S2p)	% Oxygen (Os1)
ZSHPC	91.46	0.51	1.76	3.84
ZHPC	88.92	/	0.38	6.97
ZSPC	83.95	3.08	3.43	6.37
SHPC	94.28	/	0.78	4.93
PC	85.33	/	/	11.59

12. Textural properties of different materials

Table S4 Textural properties of different materials.

Textural property	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Micropore-H-K (nm)	Mesoporous-DFT (nm)	Macropore-DFT (nm)
ZSHPC	1116.59	2.11	0.63	22.65	48.69
ZHPC	911.83	1.38	0.54	22.65	45.90
ZSPC	728.89	0.57	0.59	/	48.69
SHPC	541.44	0.48	0.66	22.65	48.69
PC	198.43	0.12	/	/	/
unetched PC	13.61	/	/	/	/

13. Comparative analysis of DA, UA, G and A with different electrodes in recent years

Table S5 Comparison and analysis of DA, UA, G and A with different electrodes in recent years.

Electrode	Linear range (μM)				Detection limit (μM)				Ref
	DA	UA	G	A	DA	UA	G	A	
p-GLY/GO/GCE	0.2-62	0.10-105	0.15-48	0.090-103	0.63	0.59	0.48	1.28	8
Au/HG	0.4-20	0.6-40	6-500	0.6-40	0.02	0.57	2.5	0.42	9
Ag@Cu ₂ O@GO/GCE	0.001-0.5	0.05-6	0.002-1	0.02-6	0.1	6.0	0.2	3.0	10
PImox-GO/GCE	12-278	3.6-249.6	3.3-103.3	9.6-215	18	0.63	6.48	1.28	11
PAE/GCE	2.5-75	10-750	7.5-75	—	0.075	0.35	0.025	—	12
Nano-Au/DNA/nano-Au/ Poly (SFR)/GCE	0.008-1.1	0.09-12	0.009-5.0	0.06-0.8	0.2	8.0	0.5	4.0	13
FeTe ₂ /GP	5-120	3-120	1-160	3-100	0.028	0.042	0.034	0.026	14
ZSHPC/GCE	0.3-500	0.7-500	0.3-500	0.5-500	0.116	0.262	0.07	0.075	This work

References

1. L. K. Sarpong, M. Bredol, M. Schönhoff, *Carbon*, 2017, **125**, 480-491.
2. L. K. Sarpong, M. Bredol, M. Schönhoff, A. Wegrzynowicz, K. Jenewein, H. Uphoff, *Optical Materials*, 2018, **86**, 398-407.
3. X. Y. Hou, T. Peng, J. B. Cheng, Q. H. Yu, R. J. Luo, Y. Lu, X. M. Liu, J. K. Kim, J. He, Y. S. Luo, *Nano Res.*, 2017, **10**, 2570-2583.
4. L. Y. Wang, J. G. Ju, N. P. Deng, G. Wang, B. W. Cheng, W. M. Kang, *Electrochem. Commun.*, 2018, **96**, 1-5.
5. A. Hassan, R. Liaquat, N. Iqbal, G. Ali, X. Fan, Z. L. Hu, M. Anwar, A. Ahmad, *J. Electroanal. Chem.*, 2021, **889**, 115223.
6. V. M. Rangaraj, A. A. Edathil, P. Kadirvelayutham, F. Banat, *Mater. Chem. Phys.*, 2020, **248**, 122953.
7. C. M. Cova, A. Zuliani, M. J. Muñoz-Batista, R. Luque, *ACS Sustainable Chem. Eng.*, 2019, **7**, 1300-1307.
8. S. Y. He, P. He, X. Q. Zhang, X. J. Zhang, K. L. Liu, L. P. Jia, F. Q. Dong, *Anal. Chim. Acta*, 2018, **1031**, 75-82.
9. S. H. Gao, H. J. Li, M. J. Li, C. P. Li, L. R. Qian, B. H. Yang, *J. Solid State Electrochem.*, 2018, **22**, 3245-3254.
10. T. Gan, Z. K. Wang, Z. X. Shi, D. Y. Zheng, J. Y. Sun, Y. M. Liu, *Biosens. Bioelectron.*, 2018, **112**, 23-30.
11. X. F. Liu, L. Zhang, S. P. Wei, S. H. Chen, X. Ou, Q. Y. Lu, *Biosens. Bioelectron.*, 2014, **57**, 232-238.
12. H. Y. Li, X. L. Wang and Z. X. Wang, *Anal. Sci.*, 2015, **31**, 1225-1231.
13. L. M. Niu, K. Q. Lian, H. M. Shi, Y. B. Wu, W. J. Kang, S. Y. Bi, *Sens. Actuators, B*, 2013, **178**, 10-18.
14. S. Pradhan, S. Pramanik, D. K. Das, R. Bhar, R. Bandyopadhyay, P. Millner, P. Pramanik, *New J. Chem.*, 2019, **43**, 10590-10600.