

High-performance electrochemical sensor for sensitive detection of tetracycline based on Zr-UiO- 66/MWCNTs/AuNPs composite electrode

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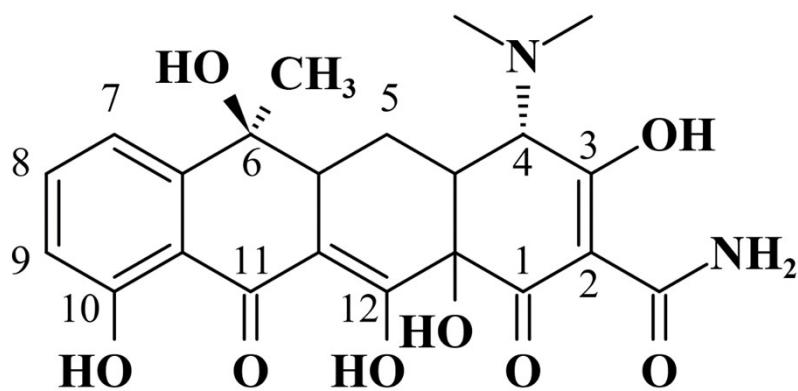


Fig. S1. The structure of tetracycline.

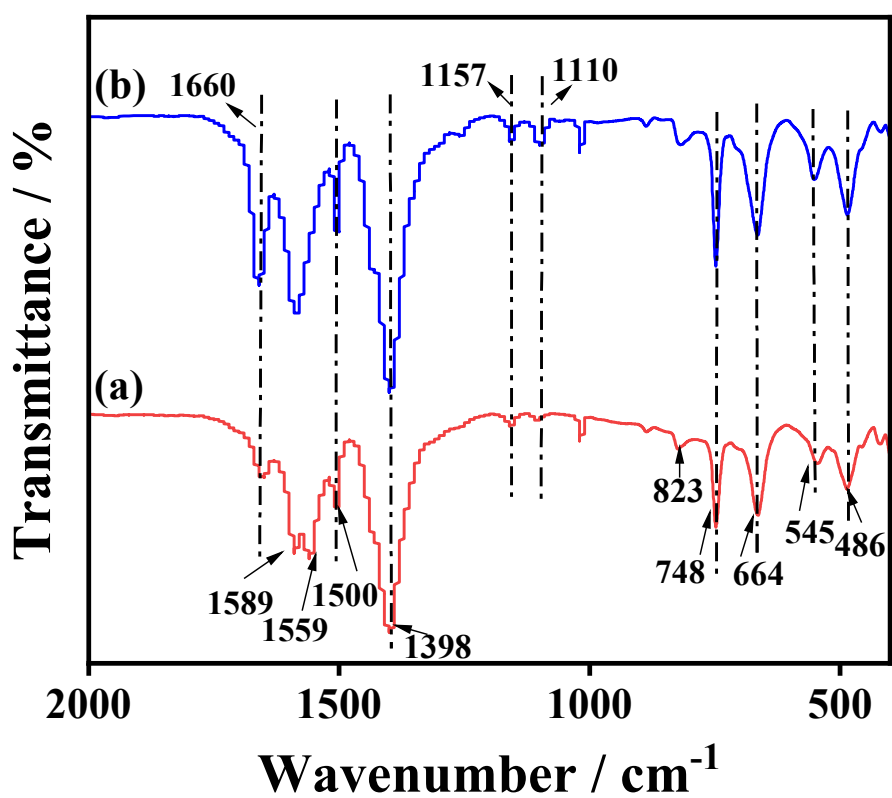


Fig. S2. The FTIR spectra of (a) Zr-Uio-66 and (b) Zr-Uio-66/MWCNTs composites.

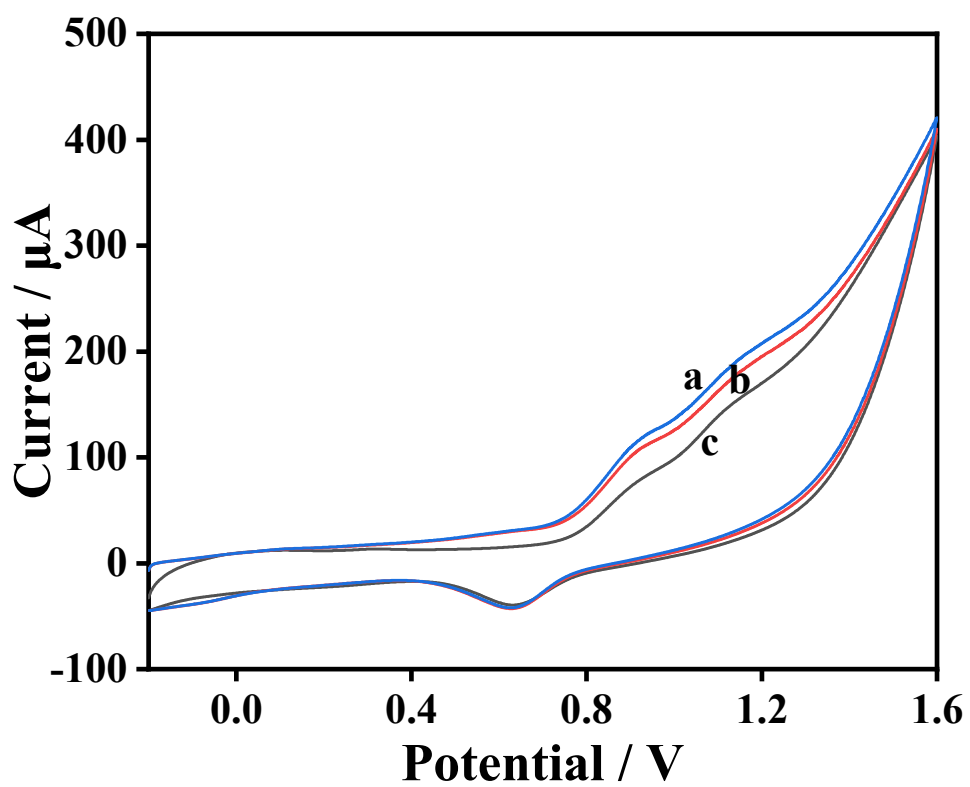


Fig. S3. The detection of tetracycline at Zr-UiO-66/MWCNTs/AuNPs/GCE in (a) phosphate buffer, (b) citric acid-sodium citrate buffer, (c) acetic acid-ammonium acetate buffer

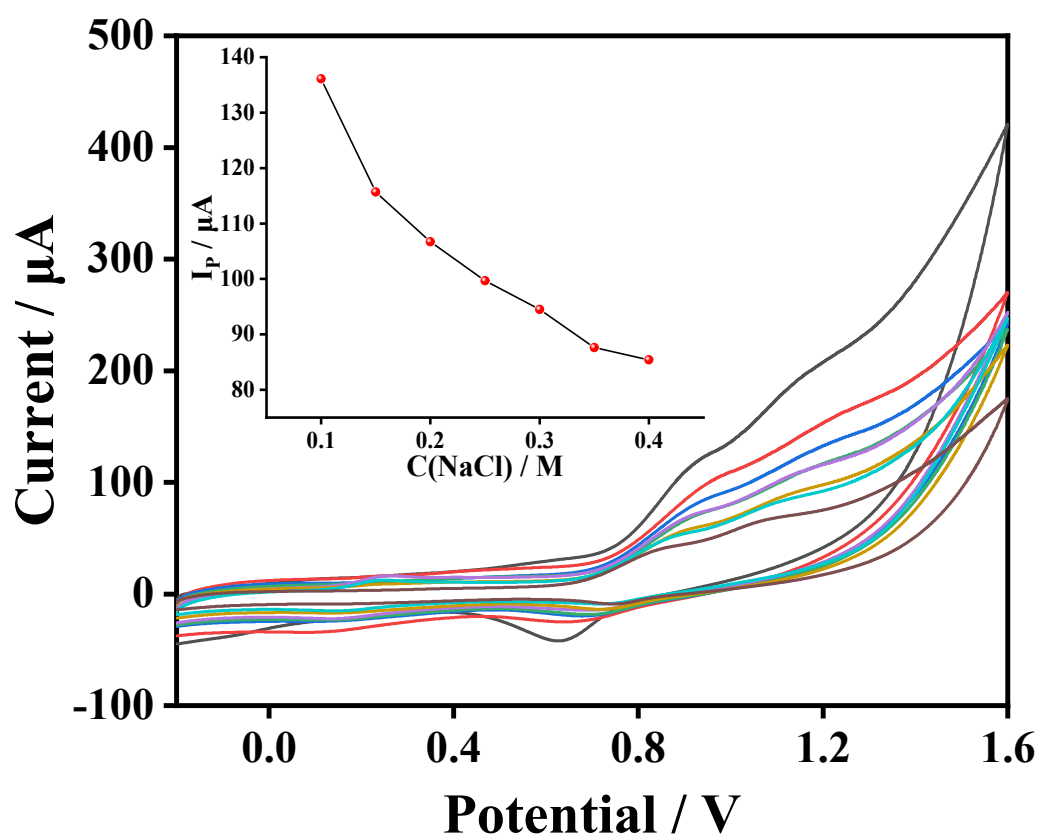


Fig. S4. Effect of ionic strength on the peak current of 2 mM tetracycline at the Zr-UiO-66/MWCNTs/AuNPs/GCE in the 0.1 M PBS (pH = 7) buffer solution; (Inset: The effect of different NaCl concentrations on peak current of tetracycline).

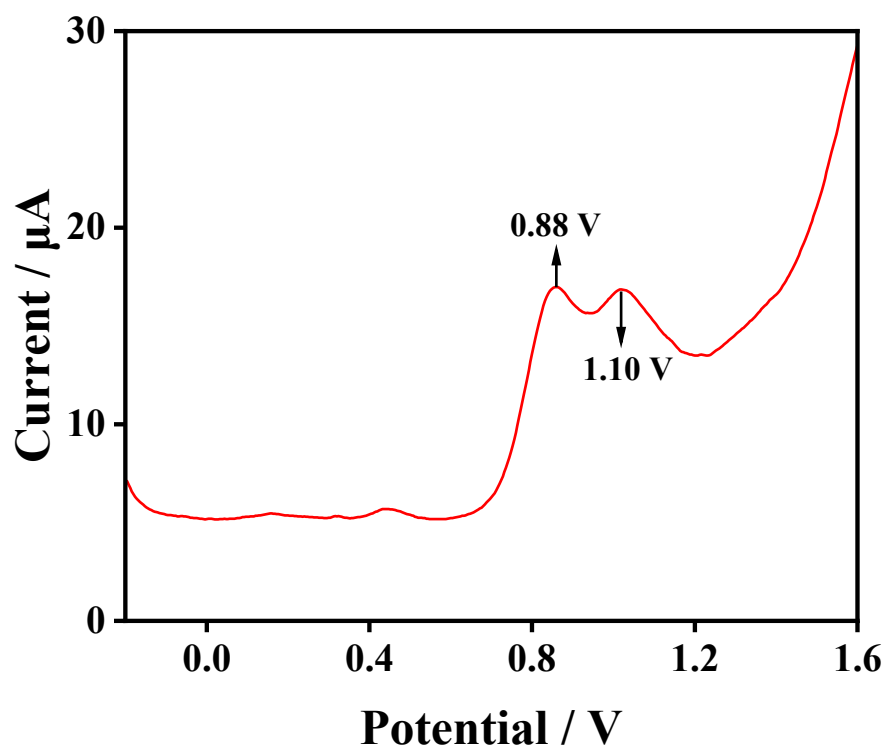


Fig. S5. The DPV test of Zr-UiO-66/MWCNTs/AuNPs/GCE in the detection of 2 mM tetracycline in 0.1 M PBS solution.

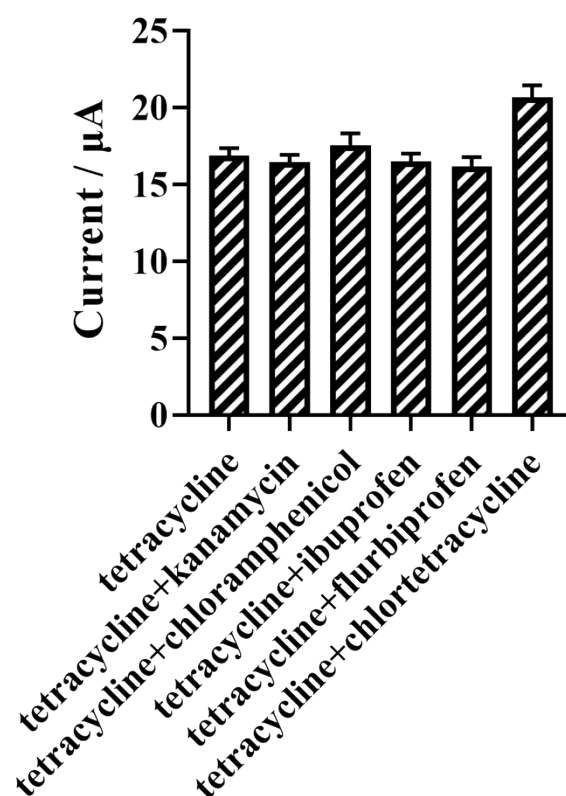


Fig. S6. Comparison of the current response of Zr-UiO-66/MWCNTs/AuNPs composites with 3.5×10^{-5} M tetracycline in the absence or presence of other antibiotics kanamycin, chloramphenicol, ibuprofen, flurbiprofen and chlortetracycline.

Table S1. Comparison of several typical electrochemical methods for tetracycline detection.

Modified Materials	Technique	Linear Range	Limit Detection	Ref.
^a NIOPPy-AuNP/SPCE	DPV	1 ~ 20 μ M	0.65 μ M	1
^b p-Mel@ERGO	DPV	5 ~ 225 μ M	2.2 μ M	2
^c PtNPs/C	CV	9.99 ~ 44.01 μ M	4.28 μ M	3
Graphite/polyurethane	DPV	3.8 ~ 38 μ M	2.6 μ M	4
^d GPUE/MIP	DPV	4 ~ 60 μ M	0.55 μ M	5
^e ERGO/SPE	DPV	20 ~ 80 μ M	12 μ M	6
rGO/AuNPs/MWCNTs	DPV	0.12 ~ 12 μ M	0.042 μ M	7
CNT-COOHs/ZnO	ECL	0.01 ~ 100 μ M	0.0067 μ M	8
^h IL/CNTPE	DPV	0.50 ~ 300 μ M	0.2 μ M	9
Zr-Uio-66/MWCNTs/AuNPs	Amperometry	0.5 ~ 225 μ M	0.167 μ M	This work

^a Molecularly imprinted overoxidized polypyrrole-gold nanoparticles/screen-printed carbon electrode.

^b Polymelamine@electrochemically reduced graphene oxide composites.

^c Platinum nanoparticles/carbon electrode.

^d Graphite-polyurethane composite/molecularly imprinted polymer electrode.

^e Electrochemical reduced graphene oxide/ screen-printed carbon electrode.

^h Ionic liquid-modified carbon nanotubes paste electrode.

Table S2. Comparison of several typical electrochemical methods for tetracycline detection in real samples.

Modified Materials	Recovery	Ref.
NIOPPy-AuNP/SPCE	92.2 ~ 105.0%	1
p-Mel@ERGO	99.0 ~ 99.8%	2
PtNPs/C	102.6%	3
Graphite/polyurethane	96 ~ 100%	4
GPUE/MIP	97 ~ 105%	10
ERGO/SPE	85 ~ 123%	11
rGO/AuNPs/MWCNTs	97.50 ~ 103.0%	12
CNT-COOHs/ZnO	97 ~ 97.6%	13
Zr-UiO-66/MWCNTs/AuNPs	99.0 ~ 100.7%	This work

References

1. L. Devkota, L. T. Nguyen, T. T. Vu and B. Piro, *Electrochimica Acta*, 2018, **270**, 535-542.
2. S. Kesavan, D. R. Kumar, Y. R. Lee and J.-J. Shim, *Sensors and Actuators B: Chemical*, 2017, **241**, 455-465.
3. R. T. Kushikawa, M. R. Silva, A. C. D. Angelo and M. F. S. Teixeira, *Sensors and Actuators, B: Chemical*, 2016, **228**, 207-213.
4. C. M. F. Calixto and É. T. G. Cavaleiro, *Analytical Letters*, 2015, **48**, 1454-1464.
5. E. Laviron, *Journal of Electroanalytical Chemistry*, 1974, **52**, 355-393.
6. M. E. Parolo, M. C. Savini, J. M. Vallés, M. T. Baschini and M. J. Avena, *Applied Clay Science*, 2008, **40**, 179-186.
7. P.-H. Chang, Z. Li, T.-L. Yu, S. Munkhbayer, T.-H. Kuo, Y.-C. Hung, J.-S. Jean and K.-H. Lin, *Journal of Hazardous Materials*, 2009, **165**, 148-155.
8. A. J. Brad and L. R. Faulkner, *Electrochemical Methods, Fundamentals and*

Applications, New York: Weley, 2001, 2nded.

9. D. A. Borisova, M. Vedenyapina and I. K. J. R. C. Bulletin, *Russian Chemical Bulletin*, 2013, **62**, 2590-2594.
10. J. E. S. Clarindo, R. B. Viana, P. Cervini, A. B. F. Silva and E. T. G. Cavaleiro, *Analytical Letters*, 2020, 1-24.
11. A. S. Lorenzetti, T. Sierra, C. E. Domini, A. G. Lista, A. G. Crevillen and A. Escarpa, *Sensors*, 2020, **20**.
12. N. Dou and J. Qu, *Analytical and Bioanalytical Chemistry*, 2021, **413**, 813-820.
13. X. Shan, Y. Pan, F. Dai, X. Chen, W. Wang and Z. Chen, *Microchemical Journal*, 2020, **155**, 104708.