Urchin-like Covalent Organic Framework Microspheres for Electrochemical Organophosphorus Pesticide Sensing

Hongze Yao[a§], tong Lu[b§], Yu Wu[b], Fang Duan[b], Shuanglong Lu[b*], Baochun Guo[c], Mingliang Du[b*]

[a] *School of Food Science and Technology, Jiangnan University, Wuxi, 214122, P.R. China*

[b]*Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, P. R. China. Email: du@jiangnan.edu.cn, lushuanglong@jiangnan.edu.cn*

[c]*Institute of Emergent Elastomers, School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China*

Materials

1,3,5-Tris(4-aminophenyl) benzene (TB) and [3,2-b] thiophene-2,5-dicarbaldehyde (TD) were obtained from the Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. Acetonitrile (CH_3CN), acetylcholinesterase (AChE), acetylthiocholine chloride ($C_7H_{16}NOSCl$), and isopropanol (C_3H_8O) were purchased from Shanghai McLin. Methyl parathion standard solution (100 µg/mL) and Nafion solution (5 wt%) were obtained from Shanghai Aladdin.

Characterizations

Powder X-ray diffraction (PXRD) analysis was conducted using a Bruker D8 Advance diffractometer equipped with Cu Kα radiation. The Fourier transform infrared (FT-IR) spectra of the synthetic materials structures were obtained with a Nicolet iS50 spectrometer. The Brunauer–Emmett–Teller (BET) specific surface area was measured via N_2 adsorption at 77 K using an ASAP 2460 surface area analyzer. The morphology of the samples was investigated using scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, JEM-2100plus). X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific K-Alpha spectrometer. UV-vis Spectrophotometer (UV-2700i, Japan). hermogravimetric analyzer (TGA-2, Switzerland).

Synthesis of TB-TD-COF

1,3,5-Tris(4-aminophenyl) benzene (14.0576 mg, 0.04 mM) and [3,2-b] thiophene-2,5-dicarbaldehyde (11.7744 mg, 0.06 mM) were added to a 10 mL glass vial. To this, 5 mL of acetonitrile was added, and the mixture was subjected to ultrasonic treatment until complete dissolution. Subsequently, 1.67 mL of acetic acid (12 M) was introduced into the reaction system, and the mixture was vigorously stirred for 10 seconds. The resulting mixture was then left to stand at room temperature (25°C) for 3 days. Upon completion of the reaction, the sample was separated by high-speed centrifugation, followed by washing with tetrahydrofuran and acetone 3-4 times. Finally, the product was dried under vacuum at 60°C for 12 h, yielding the sea urchin-like TB-TD-COF microspheres.

Fabrication of the TB-TD-AChE biosensor

All glassy carbon electrodes (GCE) were sequentially polished using alumina slurry (0.3 and 0.05 µm) on a polishing cloth, followed by ultrasonic cleaning in deionized water and ethanol to ensure a mirror-like cleanliness of the electrode surface. The biosensor was fabricated using a layer-by-layer drop-casting method. Initially, 8 µL of a dispersion containing COF, carbon black, and Nafion (0.5%, with water as the solvent) was applied to the polished bare electrode surface. The concentrations of COF and carbon black were both 2 mg/mL, while Nafion was 20 µL/mL, with isopropanol as the solvent. After drying at room temperature, 6 µL of acetylcholinesterase (AChE) solution (2 mg/mL) was then added, followed by another drying step. Each modification step was followed by natural drying at room temperature. Prior to electrochemical testing, the prepared biosensor was immersed in phosphate-buffered saline (PBS) for 15 minutes. When not in use, the biosensor was stored in a refrigerator at 4°C.

Electrochemical Measurements

The electrochemical measurements were conducted using a Shanghai Chenhua (CHI-660E) workstation, employing a classical three-electrode system. The modified GCE served as the working electrode, Pt was used as the counter electrode, and the reference electrode was a saturated calomel electrode (SCE). For cyclic voltammetry (CV), the potential was scanned from -0.2 to 0.6 V. Electrochemical impedance spectroscopy (EIS) was performed over a frequency range of 1 Hz to 1 MHz, with an amplitude of 50 mV. Differential pulse voltammetry (DPV) was conducted in a 0.1 M PBS solution (pH = 7.0), with the following parameters: amplitude of 50 mV, pulse width of 0.05 s, and a voltage range from 0.2 to 0.9 V.

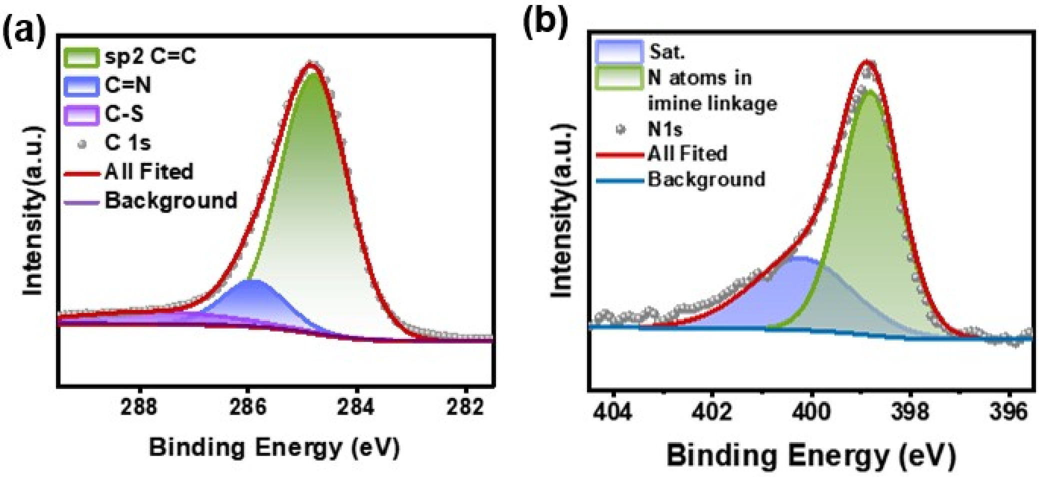

Fig. S1. (a) C 1s XPS spectrum of TB-TD-COF. (b) N 1s XPS spectrum of TB-TD-COF.

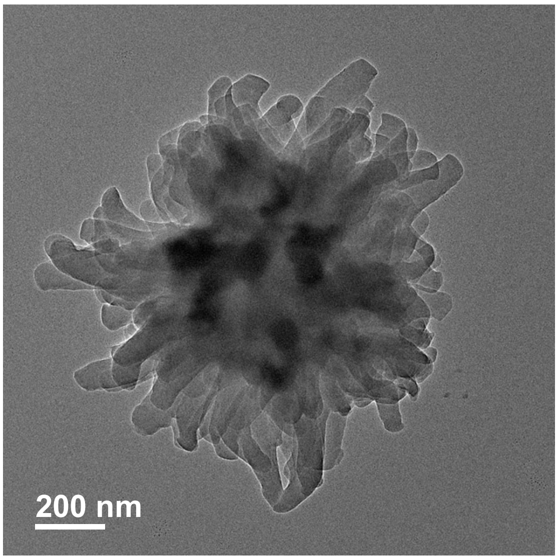

Fig. S2. TEM image of TB-TD-COF (scale bar: 200 nm).

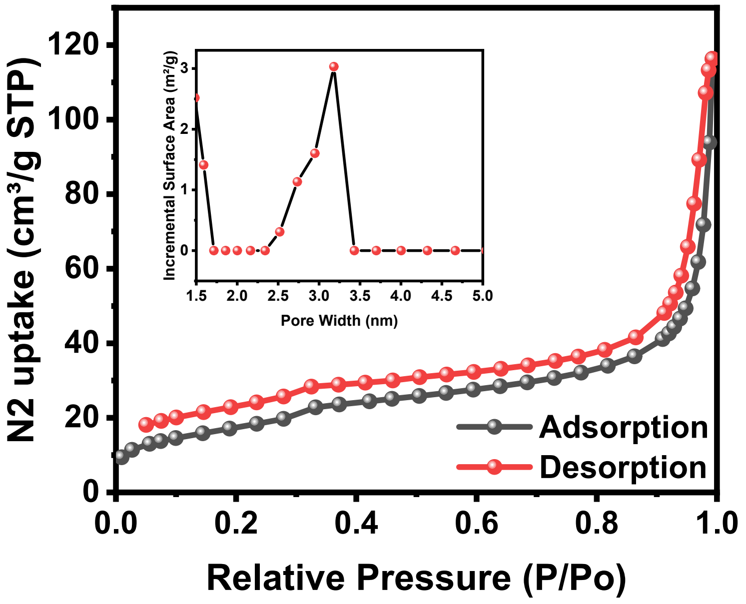

Fig. S3. N_2 adsorption-desorption isotherm and the corresponding pore size distribution.

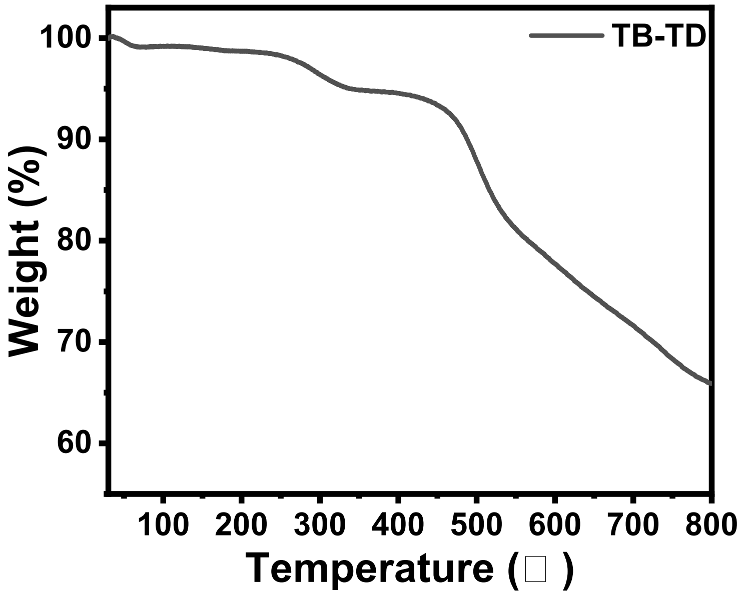

Fig. S4. The TGA curve of TB-TD-COF.

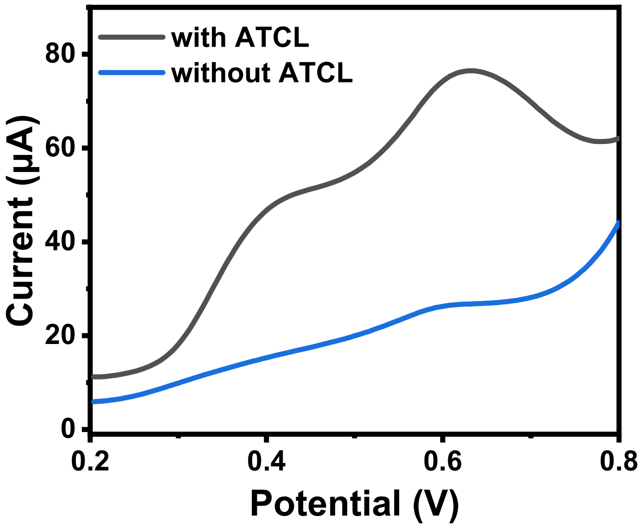

Fig. S5. DPV curves of the TB-TD-AChE electrode in the electrolyte with and without 1.5 mM ATCl.

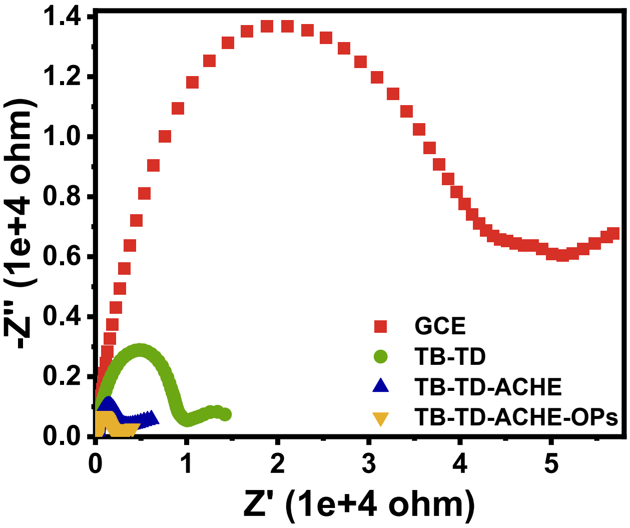

Fig. S6. EIS spectra of different modified electrodes.

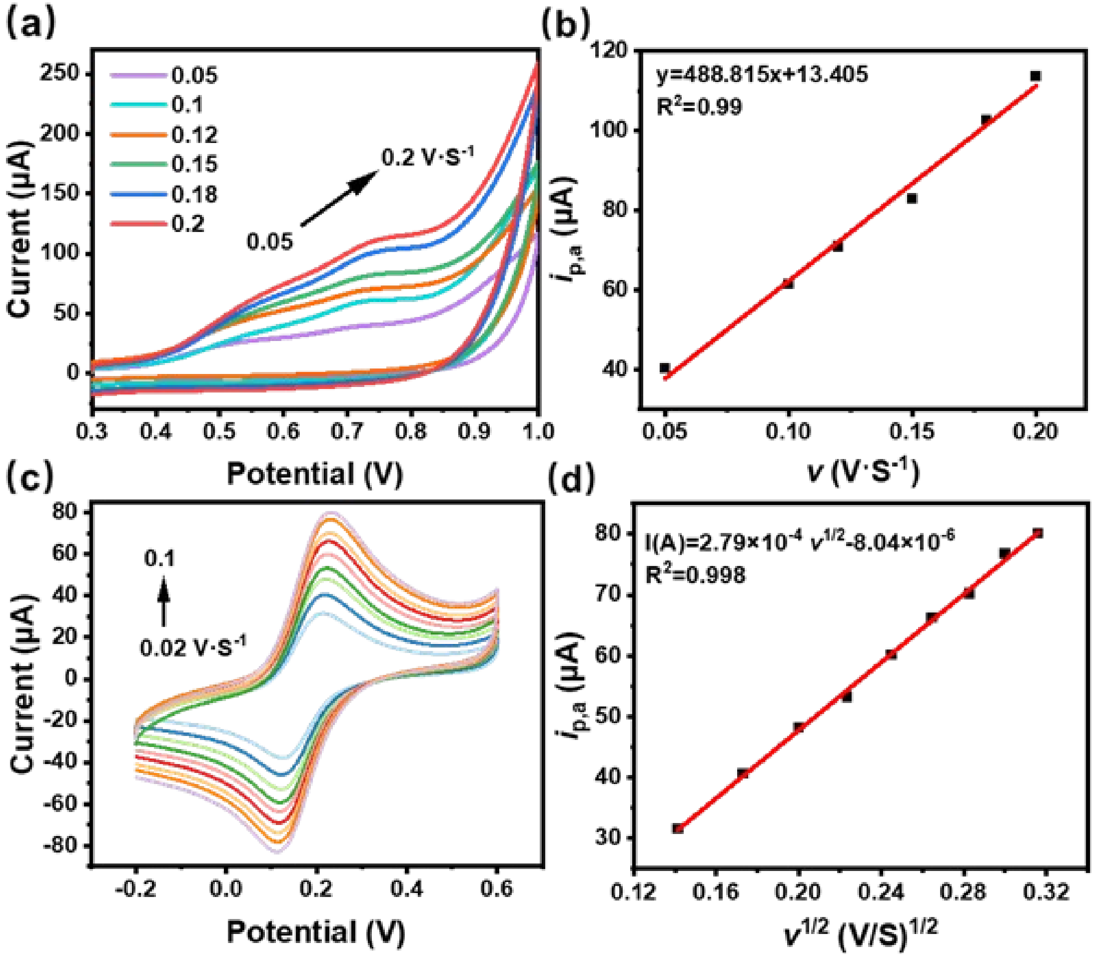

Fig. S7. CV curves of TB-TD-AChE in 0.1 M PBS containing 1.5 mM ATCL at various scan rates from 0.05 to 0.2 V s^{-1}. (b) Linear fitting plot of the anodic peak current Ip, a versus the scan rate. (c) CV curves of TB-TD-AChE in 5.0 mM [Fe (CN)$_6$]$^{3-}$/$^{4-}$ solution containing 0.1 M KCl at various scan rates. (d) Corresponding linear relationship between the anodic peak current and the square root of the scan rate.

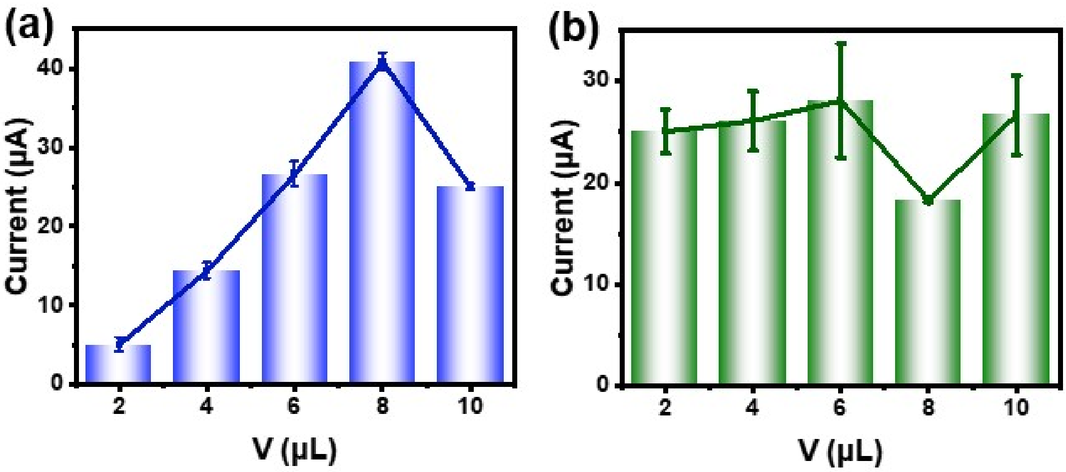

Fig. S8. (a) Effect of TB-TD-COF dosage on the response current. (b) Effect of AChE amount on the response current.

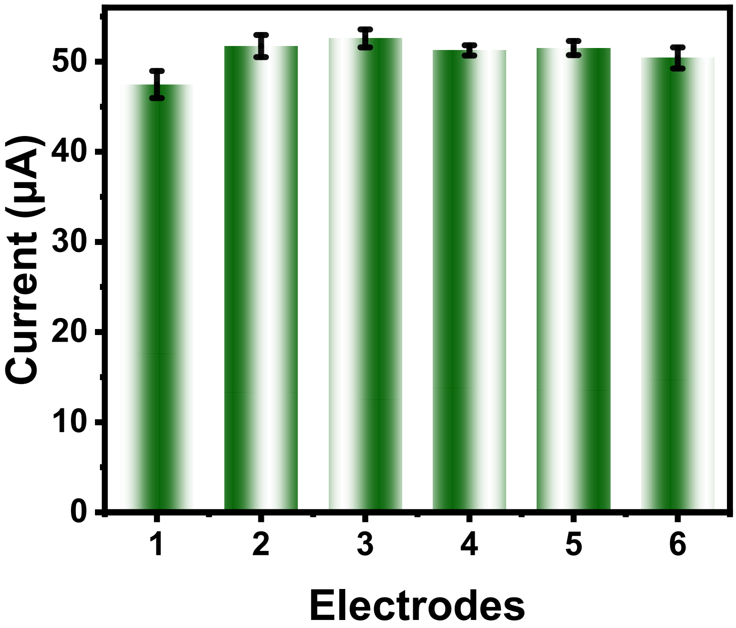

Fig. S9. Reproducibility of the biosensor: Histogram of the current responses of six electrodes.

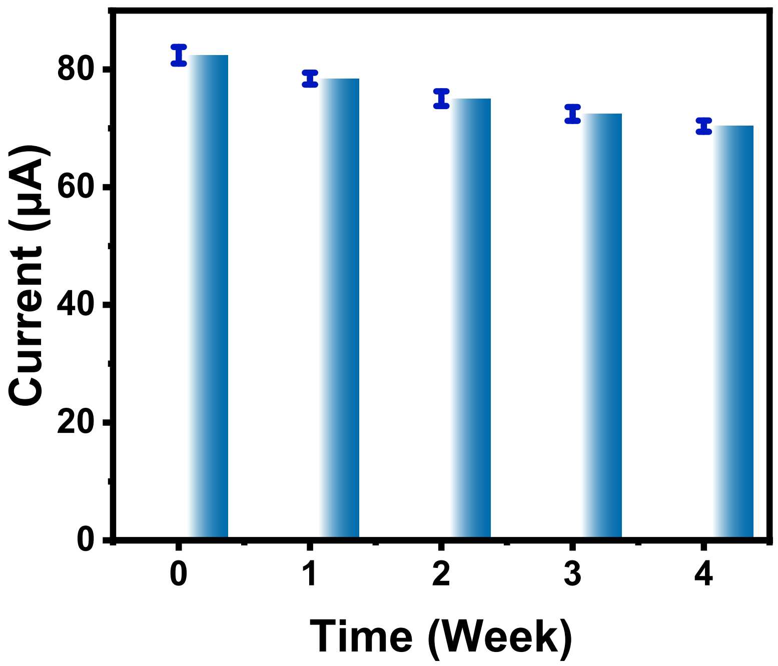

Fig. S10. Stability: Change in the electrical signal of TB-TD-AChE stored for 4 weeks.

Table S1 Comparisons of the reported biosensors for detection OPs.

Sensing platform	Target pesticide	Linear range	LOD	Ref
TB-TD-AChE	**Methyl parathion**	**1.0×10^{-10}–1.0×10^{-6} g mL^{-1}**	**2.13×10^{-13} g mL^{-1}**	**This work**
GC/COF1/AChE	Paraoxon	10–1000 ng mL^{-1}	1.4×10^{-9} g mL^{-1}	[1]
AChE/COF-Bta-NSs/CPE	Methyl parathion	5.0×10^{-13}–1.0×10^{-6} g mL^{-1}	2.04×10^{-13} g mL^{-1}	[2]
NF/AChE/NF-[Fe-MOF-NH$_2$] N$_2$/CPE	Methyl parathion	3.8×10^{-6}–0.038 μM	3.1×10^{-13} g mL^{-1}	[3]
NF/AChE/NF-[Zr-MOF-NH$_2$] N$_2$/CPE	Methyl parathion	1.9×10^{-6}–0.019 μM	1.8×10^{-12} g mL^{-1}	[3]
NF/AChE/NF-[La-MOF-NH$_2$] N$_2$/CPE	Methyl parathion	3.8×10^{-6}–0.019 μM	0.5×10^{-13} g mL^{-1}	[3]
MXene/CNHs/PPy/AChE sensor	Methyl parathion	0.002–346 ng mL^{-1}	0.00021 ng mL^{-1}	[4]

References

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