Supplementary Information (SI) for New Journal of Chemistry.

Efficient Electrochemical Sensing of Methyl Parathion Residues Using a PEDOT:PSS/Zr(OH)$_4$/ZIF-90 Composite

Huanjing Chen, Wanqiao Bai*, Hongmei Chai and Loujun Gao*
Shaanxi Key Laboratory of Chemical Reaction Engineering, College of Chemistry and Chemical Engineering, Yan'an University, Yan'an 716000, P. R. China

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*Corresponding author. Tel.: +86 911 2650317.

*E-mail addresses: glj@yau.edu.cn (L. Gao),
baiwanqiao@yau.edu.cn (W. Bai)

1.Apparatus

XPS spectrums were conducted by a Thermo ESCALAB 250XI X-ray photoelectron spectrometer (Thermo Fisher Scientific Inc., USA); XRD patterns were analyzed by an X'Pert PRO MPD X-ray diffractometer (XRD, PANalytical B.V., Netherlands); SEM images and EDS map were characterized by a Hitachi S4800 scanning electron microscope (Hitachi Ltd., Japan); Electrochemical measurements were conducted with a CHI 760E electrochemical workstation (Chenhua Instrument Co., Ltd., Shanghai, China); TEM images and SAED patterns were obtained by a FEI Talos F200x transmission electron microscope (Thermo Fisher Scientific Inc., USA); An HT160 high-speed desktop centrifuge (Hunan Xiangyi Laboratory Instrument Development Co., Ltd., China) and a 102-2AB horizontal drying oven (Feisifu Instrument (Hebei) Co., Ltd., China) were also employed.

2.TEM characterization and SAED pattern

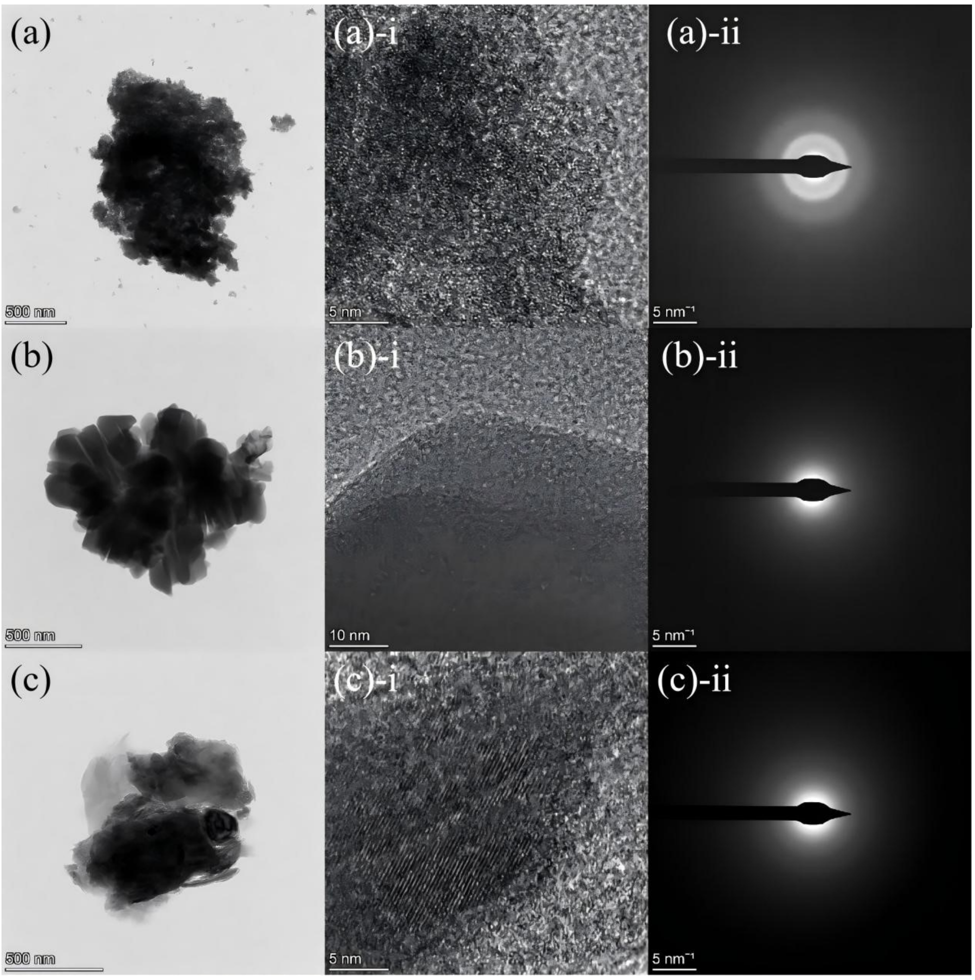

Fig. S1 TEM images, HRTEM images (i) and SAED patterns (ii) of (a) $Zr(OH)_4$, (b) ZIF-90 and (c) PEDOT:PSS/$Zr(OH)_4$/ZIF-90 composite.

3.Measurement of electrochemical active areas of the modified electrode

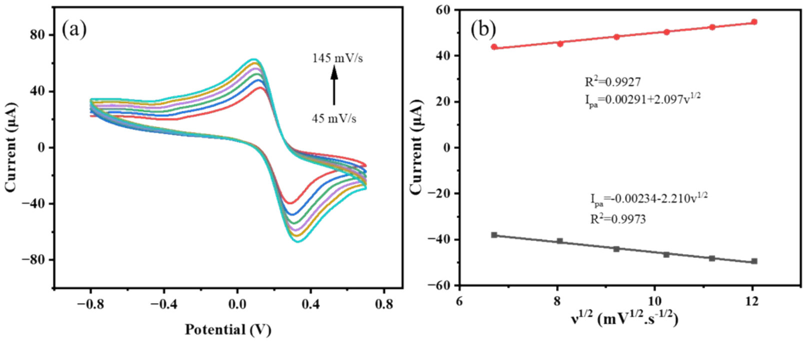

Fig. S2 (a) Cyclic voltammograms of GCE at different scan rates in a 5.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 mol/L KCl. (b) Linear fitting curve of peak current vs. square root of scan rate.

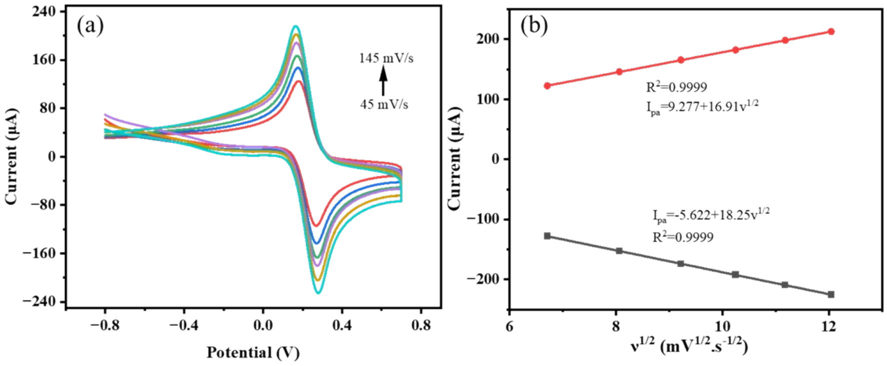

Fig. S3 (a) Cyclic voltammograms of PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE at different scan rates in a 5.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 mol/L KCl. (b) Linear fitting curve of peak current vs. square root of scan rate.

The electrochemical active areas of the bare GCE and PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE were determined by cyclic voltammetry respectively. Cyclic voltammograms were measured at different scan rates in a 5 mmol/L $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 mol/L KCl. According to the Randles-Sevcik equation: $I_p = 2.686 \times 10^5 n^{2/3} A D^{1/2} C v^{1/2}$, where: I_p (unit: A) represents the peak current of the redox reaction; n is the number of electrons transferred in the redox process of the $[Fe(CN)_6]^{3-/4-}$ couple, $n = 1$; A refers to the electrochemical active area of the sensor electrode; D and C represent the diffusion coefficient and concentration of the $[Fe(CN)_6]^{3-/4-}$ couple, respectively, $D = 1.38 \times 10^{-5}\ cm^2 \cdot s^{-1}$, $C = 5 \times 10^{-6}\ mol \cdot cm^{-3}$; v corresponds to the scan rate in the linear sweep voltammetry test (unit: $V \cdot s^{-1}$). Based on the linear relationship between the peak current I_p and the square root of the scan rate $v^{1/2}$ in the Randles-

Sevcik equation, the average electrochemical active area of each electrode can be further obtained by calculating the slope of the fitting curve between them. The measured cyclic voltammogram results and the relationship between peak current and the square root of scan rate are shown in Fig .S2 and Fig .S3. The average electrochemical active areas of the bare electrode and PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE were calculated to be 0.443 cm^2 and 3.39 cm^2, respectively. The average electrochemical active area of PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE is 7.65 times that of the bare electrode, indicating that the PEDOT:PSS/$Zr(OH)_4$/ZIF-90 composite significantly improves the electrochemical active area of the electrode.

4.Measurement of the electron rate constant and the surface coverage of methyl parathion

According to the Butler-Volmer electrode kinetics theory: $K^0=\frac{RT}{n^2F^2ARctC}$, where K^0 is the heterogeneous electron transfer rate constant ($cm \cdot s^{-1}$); R is the universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$); T is the temperature (K), assumed to be room temperature 298 K; n is the number of transferred electrons ($n = 2$); F is the Faraday constant (96485 $C \cdot mol^{-1}$); A is the geometric area of the electrode (cm^2); R_{ct} is the charge transfer resistance (Ω); C is the concentration ($mol \cdot cm^{-3}$), $C=1.5 \times 10^{-7}$ $mol \cdot cm^{-3}$. The calculated K^0 of the bare electrode is 0.00127 $cm \cdot s^{-1}$, and that of PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE is 0.00523 $cm \cdot s^{-1}$. The PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE electrode has a higher K^0 value, indicating stronger interfacial electron transfer capability.

The surface coverage was calculated using the formula $\Gamma=\frac{I_{pa}}{4RT/n^2F^2v}$, where I_{pa} is the peak current (A); n is the number of electron transfers, n=2; F is the Faraday constant (96485 $C \cdot mol^{-1}$); A is the electrochemical active area of the electrode (cm^2); Γ is the surface coverage ($mol \cdot cm^{-2}$), which is the quantity to be determined; v is the scan rate ($V \cdot s^{-1}$), $v=0.03$ $V \cdot s^{-1}$; R is the universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$); T is the temperature (K), assumed to be room temperature 298 K. The I_{pa} of the bare electrode is 2.313×10^{-7} A, and that of the PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE electrode is 2.728×10^{-6} A. The calculated surface coverage of the bare electrode is 0.0261 $mol \cdot cm^{-2}$, and that of the PEDOT:PSS/$Zr(OH)_4$/ZIF-90/GCE electrode is 0.308 $mol \cdot cm^{-2}$, which is 11.8 times that of the bare electrode, indicating that the electrode surface has more active sites and higher electrochemical activity.

5.Measurement of the coefficient of diffusion of methyl parathion

Chronoamperometric measurements were performed in PBS buffer solutions containing different concentrations of MP. The relationship between the measured current *I* and time *t* under diffusion-controlled conditions can be described by the Cottrell equation: $\mathrm{I(t)} = nFACD^{1/2}\pi^{-1/2}t^{-1/2}$, where: *I*(*t*) is the current (A); *n* is the number of electrons transferred; *F* is the Faraday constant (96,500 $\mathrm{C{\cdot}mol^{-1}}$); A is the effective surface area of the electrode ($\mathrm{cm^2}$); C is the bulk concentration ($\mathrm{mol{\cdot}cm^{-3}}$); D is the diffusion coefficient ($\mathrm{cm^2{\cdot}s^{-1}}$); *t* is the time (s). Fig. S4a shows the chronoamperograms of MP at four different concentrations (50, 100, 150, and 200 μM) on the PEDOT:PSS/$\mathrm{Zr(OH)_4}$/ZIF-90 modified electrode. It can be clearly seen that the catalytic current increases with the increase of MP concentration, which is consistent with the voltammetric results. Fig. S4b is the plot of *I* vs. the negative square root of time, showing a linear relationship, which again confirms that the electrocatalytic reaction of MP is a diffusion-controlled process. The diffusion coefficient D can be calculated by the slope in Fig. b using the Cottrell equation, and the diffusion coefficient of MP is obtained as $\mathrm{D=1.38\times10^{-5}\ cm^2{\cdot}s^{-1}}$.

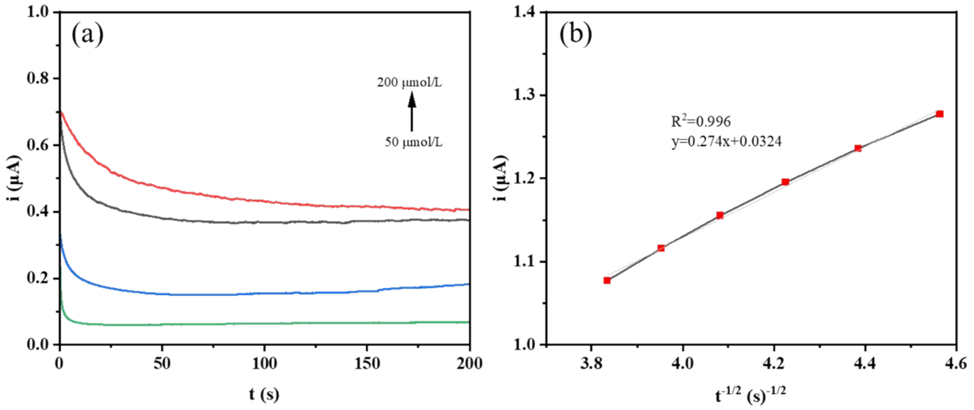

Fig. S4 (a) Chronoamperometric plots of different concentrations of MP (50, 100, 150 and 200 μmol/L) in 0.1 mol/L PBS for PEDOT:PSS/$\mathrm{Zr(OH)_4}$/ZIF-90/GCE. (b) Linear plots of $t^{-1/2}$ vs. step current at the concentrations of 150μM MP.

6.Detection result of MPs in real samples by GC method

Table S1 Detection of MPs in real samples by GC method (*n*=3)

Sample	Spiked (μmol/L)	Detected (μmol/L)	Recovery rate (%)	RSD (%)
River water	10.0	9.95	99.5	0.6
	100.0	99.2	99.2	0.4
	250.0	248.7	99.5	3.2

Apple	10.0	10.2	102.0	1.9
	100.0	102.5	102.5	2.2
	250.0	254.2	101.7	2.1