Supporting information

Effects of additives on performance of a laser-induced graphene sensor modified with ZrO2 particle for OP detection

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Supporting Equations

Equation S1

Randles-Sevcik:[1]

$$I_p = 2.69\times10^5 n^{\frac{3}{2}} A D_0^{\frac{1}{2}} v^{\frac{1}{2}} C \,; \qquad (1\text{-}1)$$

Where I_p is the peak current (A), n is the number of electrons transferred during the redox process, A is the electroactive area of the electrode (cm^2), D_0 is the diffusion coefficient (6.73×10^{-6} cm^2 s^{-1}), and C is the concentration of the probe in solution (5×10^{-6} cm^3). From this equation the surface active area is calculated to a bare LIG electrode of 0.100 cm^2 and the surface active area of 0.0286 cm^2 for a bare GCE electrode.

Equations S2

Nicholson's:[2]

The kinetic parameter (Ψ) of infinite order can be calculated using the following equation, whose value depends on the peak potential separation $\triangle E_p$.

$$\Psi = k^0 \left(\frac{D_0}{D_r}\right)^{\frac{\alpha}{2}} \left(\frac{RT}{nFD_0 v\pi}\right)^{\frac{1}{2}} \,; \qquad (1\text{-}2)$$

where D_0/D_r is the ratio of diffusion coefficient of oxidation and reduction forms of electroactive substances, α is the transfer coefficient, R is the molar gas constant (8.314 J K^{-1} mol^{-1}), T is the temperature, n is the number of electrons transferred in the electrochemical reaction, v is the scanning rate (V s^{-1}), F is the Faraday constant (96489 C mol^{-1}). Here, D_0/D_r can be simplified as:

$$\Psi = k^0 \left(\frac{RT}{FDv\pi}\right)^{\frac{1}{2}} ; \qquad (1\text{-}3)$$

Since the reaction is a one-electron transfer process, Ψ depends on ΔE_p and can be caculated by the following formula where X is equal to ΔE_p*n.

$$\Psi = \frac{-0.6288 + 0.0021X}{1 - 0.017X} ; \qquad (1\text{-}4)$$

Calculated from the above equations, k^0=0.000825 cm^2 s^{-1}.

Equations S3

Laviron:[3]

The CV curve also conveys the determination of the apparent electron transfer coefficient α that can be calculated from the Laviron equation for quasi-reversible reactions.

$$E = k + \frac{RT \ln v}{\alpha n F} \text{ ;} \tag{1-5}$$

where R is the molar gas constant of 8.314 J K^{-1}, T was 298 K, F is the Faraday's constant of 96485 C mol^{-1}, k is a constant and n is the number of electrons transferred. The apparent electron transfer rate constant k_s can be calculated from the following equation.

$$\lg k_s = \alpha \lg(1-\alpha) + (1-\alpha)\lg\alpha - \lg\frac{RT}{nFv} - (1-\alpha)\alpha\frac{nF\Delta E}{2.303RT} \text{ ;} \tag{1-6}$$

Supporting Figures

Fig. S1 Bare LIG electrode.

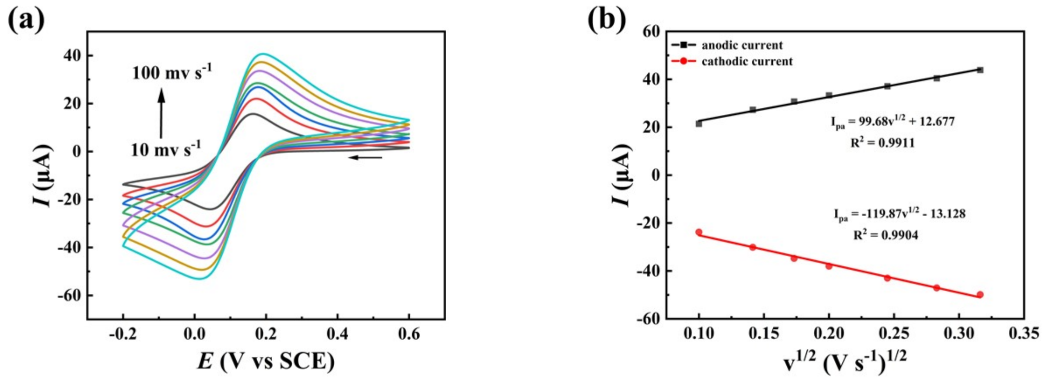

Fig. S2 CVs of the GCE varying scan rate from 10 to 100 mV s^{-1} in 0.1 M KCI containing 5 mM $K_3[Fe(CN)_6]$ (a); Linear relationship between I_p and $v^{1/2}$ for GCE (b).

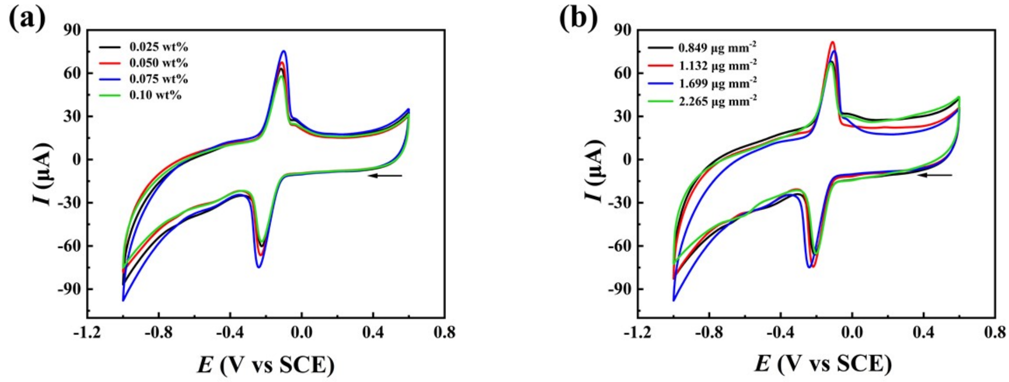

Fig. S3 CVs of varying concentrations of CS (a); CVs of varying loadings of ZrO_2NPs with CS as binder (b) in 0.1 M PBS (pH=7.4) containing 2.5 μg ml^{-1} MP at the scan rate of 0.1 V s^{-1}.

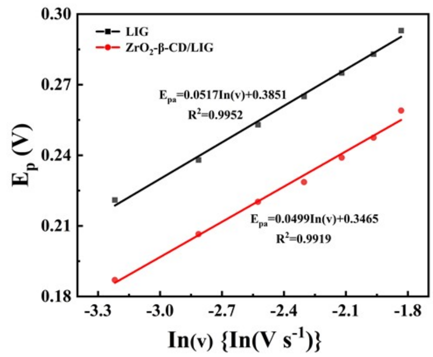

Fig. S4 Linear relationship between E_p and In(v) for LIG and ZrO_2-β-CD/LIG.

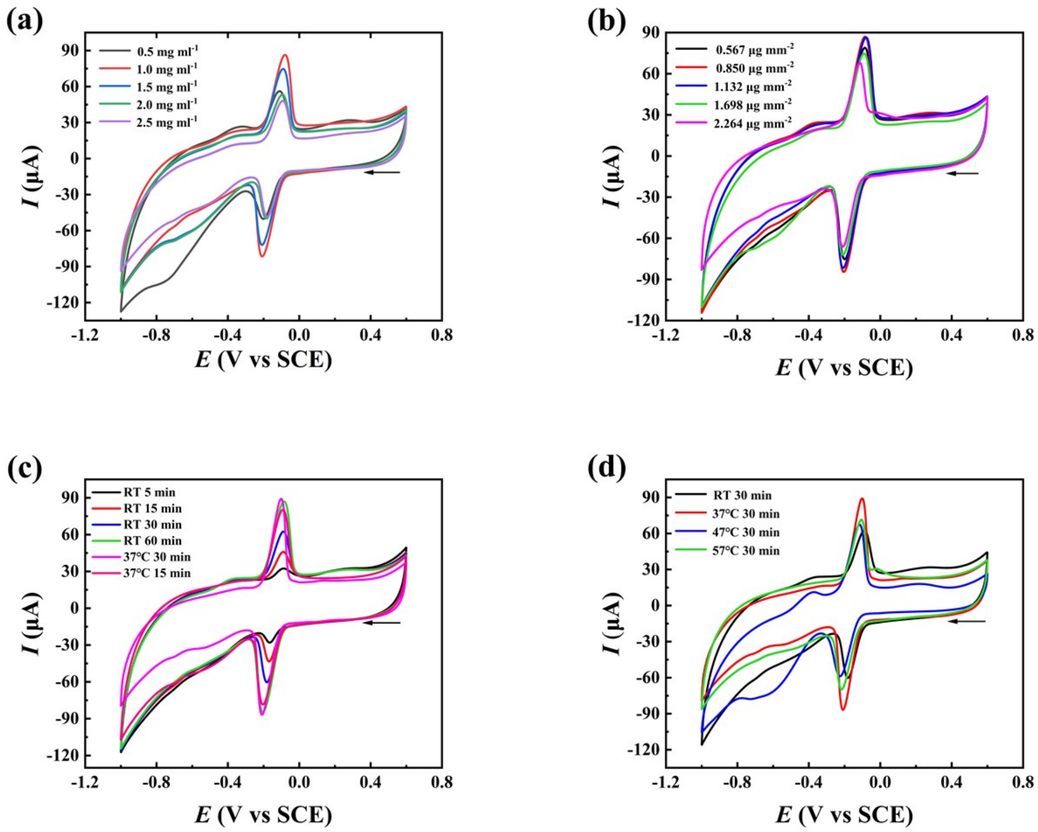

Fig. S5 CVs of ZrO_2-β-CD/LIG modified by different β-CD concentrations (a); CVs of ZrO_2-β-CD/LIG modified with different loading amounts of ZrO_2 (b); CVs of ZrO_2-β-CD/LIG at various times of adsorption (c); CVs of ZrO_2-β-CD/LIG at various temperatures in 0.1 M PBS (pH=7.4) containing 2.5 μg ml^{-1} MP at the scan rate of 0.1 V s^{-1} (d).

References

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3. S. Sain, S. Roy, A. Mathur, V. M. Rajesh, D. Banerjee, B. Sarkar and S. S. Roy, *ACS Applied Nano Materials*, 2022, **5**, 17516-17525.