Supplementary Material

Electrochemical Sensor Formed from a Poly(3,4-ethylenedioxyselenophene) and Nitrogen-doped Graphene Composite for Dopamine Detection

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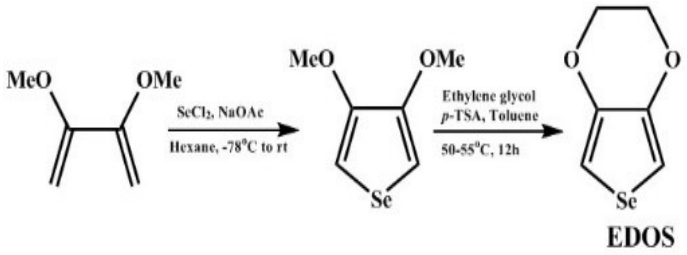
1. Synthesis of EDOS

2,3-dimethoxy-1,3-butadiene was synthesized according to a previously reported method [23].

EDOS was synthesized according to a previously reported method [16]. First prepared $SeCl_2$, SO_2Cl_2 and selenium powder were as reactants, and n-hexane as solvent. A solution of freshly-prepared $SeCl_2$ in hexanes was added to a well-stirred mixture of 2,3-dimethoxy-1,3-butadiene (24.0 g, 210 mmol) and CH_3COONa (8.2 g, 100 mmol) (as the buffering agent) in hexanes (250 mL) (as the solvent) at –78 °C (dry ice/acetone bath) under an inert atmosphere. The resulting yellowish solution was further stirred for 1 h at -78 °C and the reaction mixture was warmed to room temperature stirred for another 4 h. The reaction mixture was filtered and washed with n-hexane. The residue was concentrated to provide a brown oil that was purified by recrystallization in hexanes at low temperature to furnish a white crystalline solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.55 (s, 2H), 3.85 (s, 6H).

A solution of 3,4-dimethoxyselenophene (1 g, 5.24 mmol), with 6 equivalents of ethylene glycol (2 g, 32.41 mmol) and a *p*-toluene sulfonic acid (160 mg) (as catalytic agent) in dry toluene (150 mL) was stirred for 12 h at 50 – 55 °C. Toluene was removed under reduced pressure, and the residue was diluted with water (100 mL). The mixture was extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with dilute NaCl solution and brine and then Spinning solvent to concentrated. Purification of the crude residue by silica gel chromatography gave 3,4-ethylenedioxyselenophene as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm)

= 6.79 (s, 2H), 4.17 (s, 4H).



Scheme S 1. The synthetic route of EDOS monomers

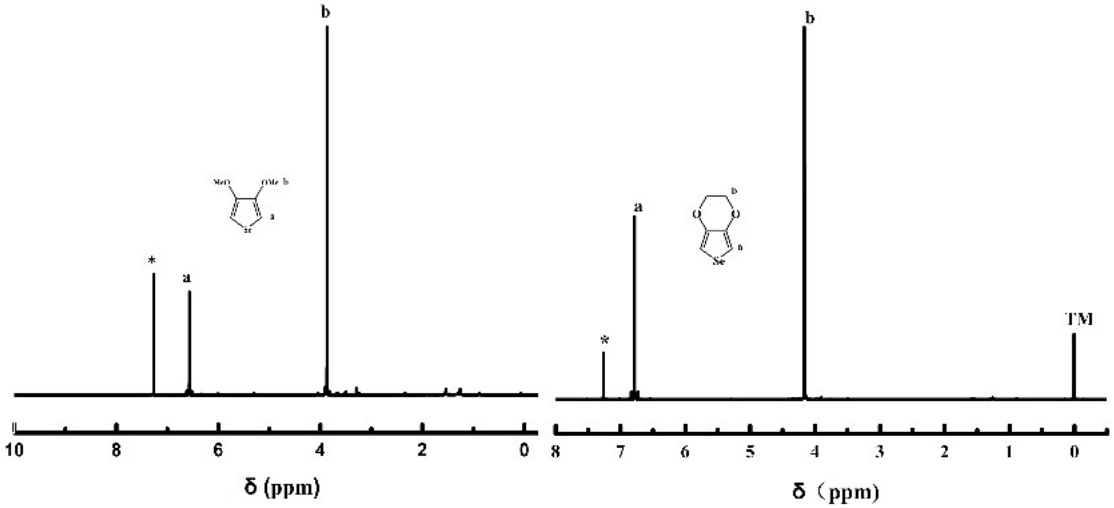


Fig. S 1 1H-NMR spectra of 3,4-dimethoxyselenophene and EDOS in $CDCl_3$

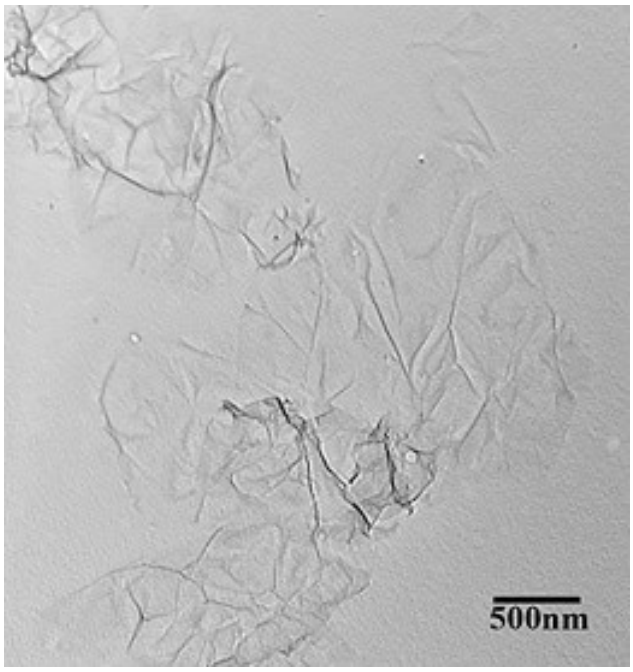


Fig. S 2 TEM of N-Gr

Table S1 C, O, N and Se atomic concentrations of N-Gr, PEDOS and PEDOS/N-Gr

Sample	C1s (%)	O1s (%)	N1s (%)	Se3d (%)
N-Gr	84.30	12.11	3.56	-
PEDOS	73.75	19.90	-	6.35
PEDOS/N-Gr	61.87	19.53	2.66	6.50

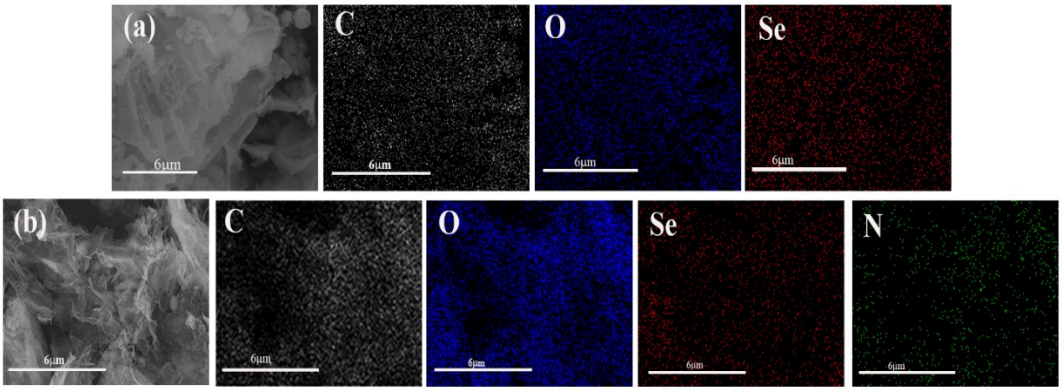


Fig. S 3 Mapping images of (a) PEDOS (b)PEDOS/N-Gr

Table S 2 Detection performances of modified GCEs

Sample	Linear response range (mM)	Linear regression equation	R^2	Limit of detection (mM)	Sensitivity ($mAmM^{-1}cm^{-2}$)
PEDOS/N-Gr	0.008-80	y=39.68+10.9x y=78.9+0.43x	0.996 0.996	0.0066	28.9
PEDOT/N-Gr	0.04-70	y=50.35+2.3x y=71.15+0.4x	0.997 0.992	0.018	18.3

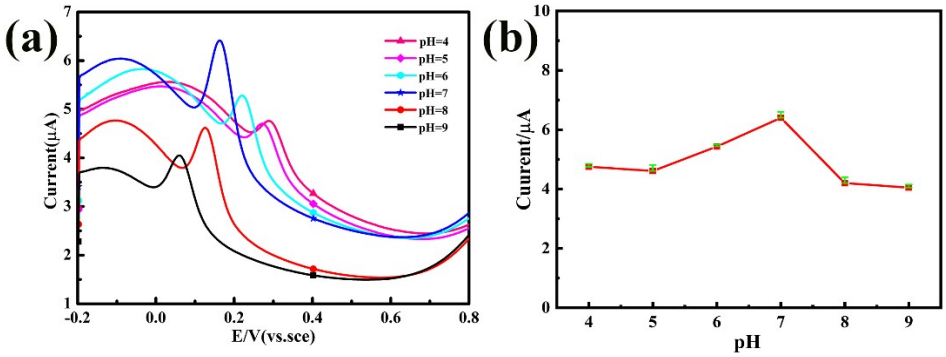


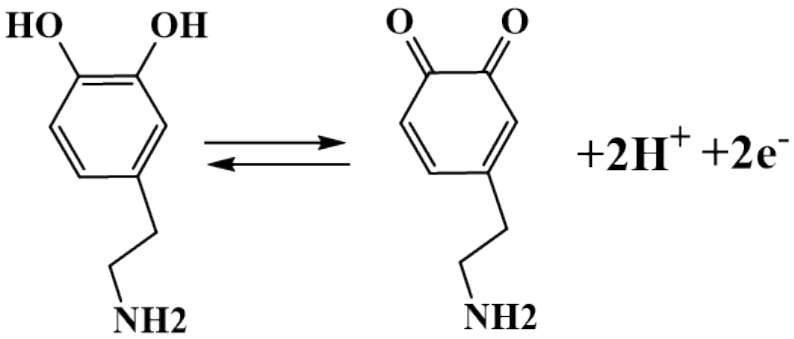
Fig. S 4 Effects of a pH values on the high value currents of DA at N-Gr/PEDOS/GCE (in 0.1 M PBS containing 5 μM DA); b shows their linear relationship.

Calculation of the effective electrode surface area

To evaluate the importance of the modified electrode surface toward the electrochemical oxidation of $[Fe(CN)_6]^{3-/4-}$, we have calculated the effective electrode surface area values of bare GCE and for the modified electrodes, the Randles–Sevcik equation was used[56]. The corresponding linear plots between $\nu^{1/2}$ and I_{pa} indicated the diffusion-controlled processes. The Randles–Sevcik equation is as following:

$$I_{pa} = 2.69 \times 10^5 n^{3/2} A D^{1/2} \nu^{1/2} C$$

Where I_{pa} is the anodic peak current, A shows the effective electrode surface area, D is the diffusion coefficient of the $K_3Fe(CN)_6$ ($D=6.5 \times 10^5$), n is the electron transfer number of the electrode reaction ($n = 1$), ν is the sweep speed, C is the concentration of the $K_3Fe(CN)_6$ ($C = 0.5 mol/cm^3$) and the other symbols have their usual meaning. The effective electrode surface area values for bare GCE, PEDOT/N-Gr/GCE and PEDOT/N-Gr/GCE were found to be 0.132, 0.29, and 0.37 cm^2, respectively.



Scheme S2. Mechanisms for electrooxidation of dopamine.

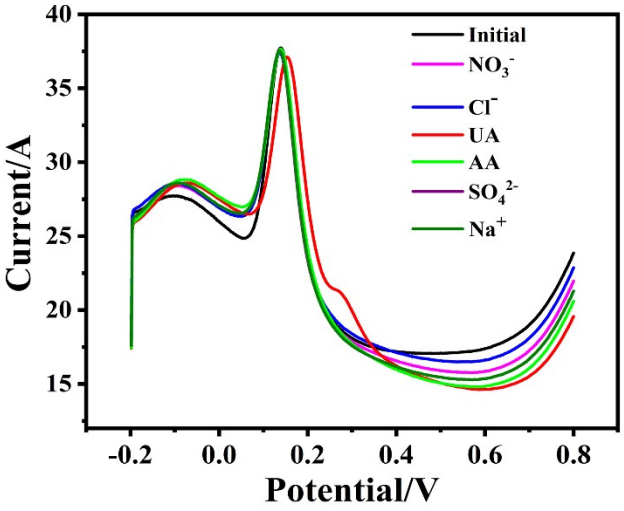


Fig. S 5 Interference test of PEDOS/N-Gr/GCE real DPV data

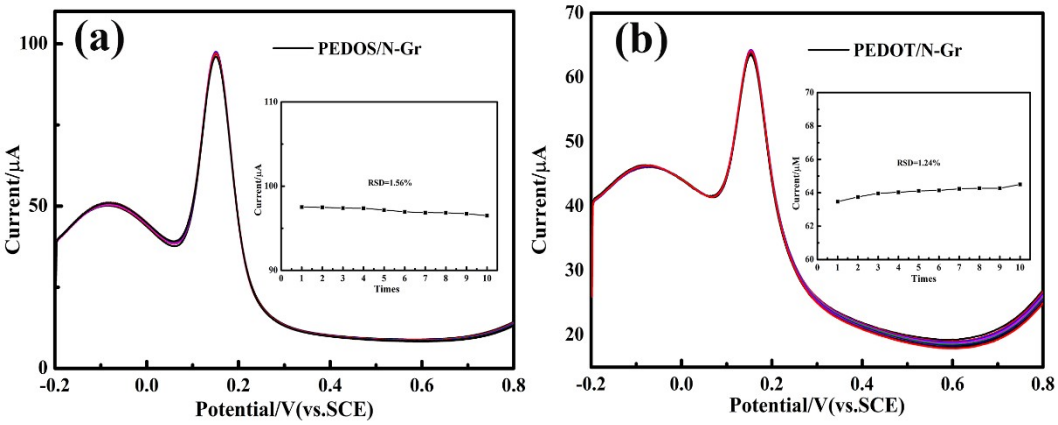


Fig. S 6 (a) DPV response of 5mM DA with the prepared sensors for ten times PEDOS/N-Gr/GCE, (b) DPV response of 5mM DA with the prepared sensors for ten times PEDOT/N-Gr/GCE

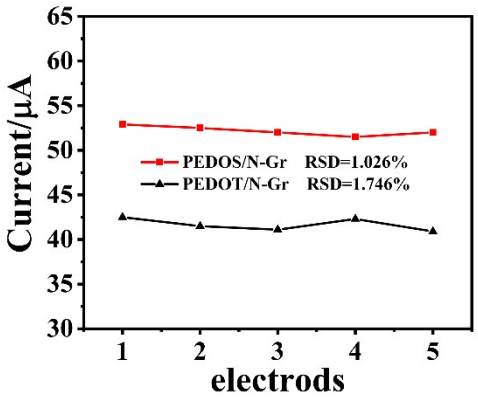


Fig. S 7 Reproducibility of composites modified GCEs