Supporting information for:

Highly sensitive and selective dopamine biosensor based on a phenylethynyl ferrocene/graphene nanocomposite modified electrode

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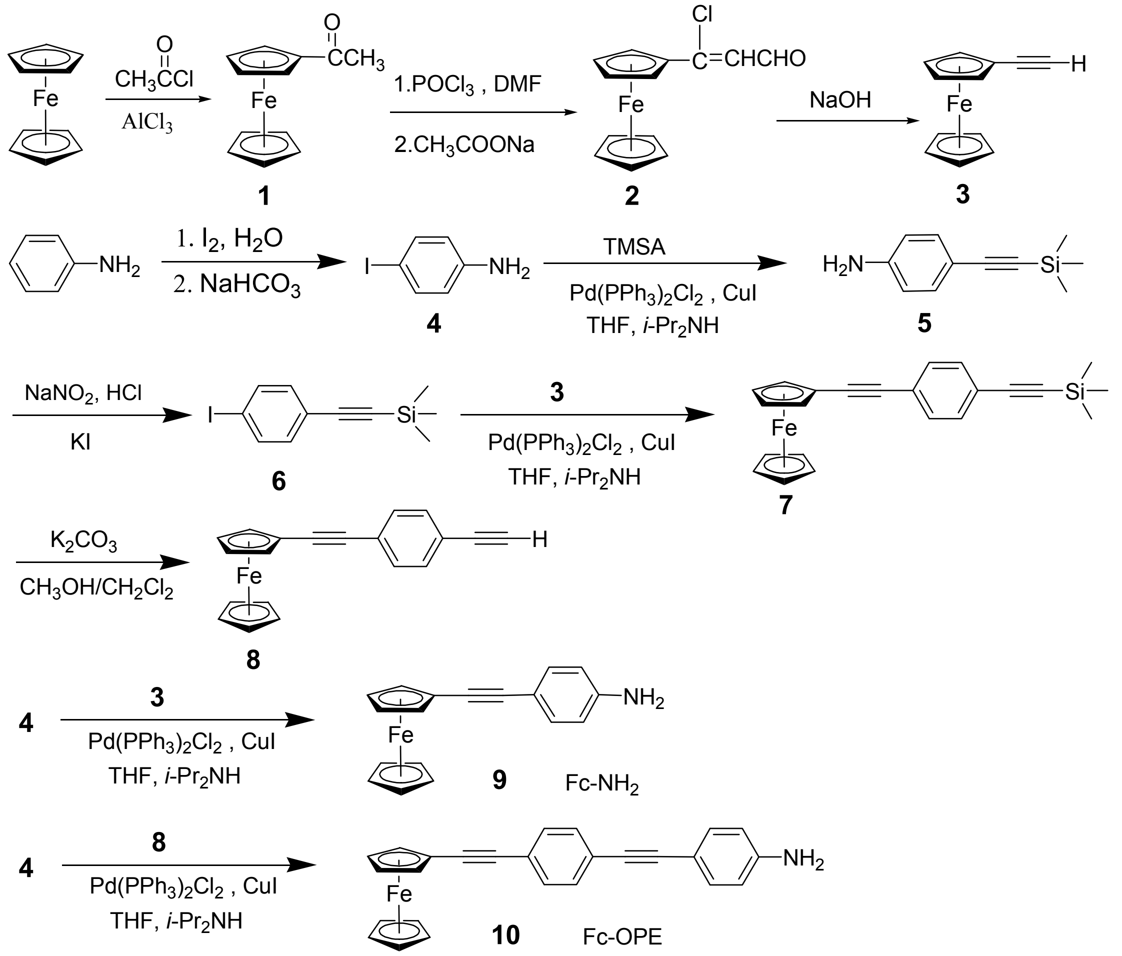
The synthesis and charechrization procedure of Fc-NH$_2$ and Fc-OPE

Compounds **1**-**3** were synthesized as reported[1]. The synthesis of 1-[(4-amino) phenylethynyl] ferrocene (Fc-NH$_2$) was shown in Scheme 1. Simply, a 100 mL of one-necked flask was charged with 252 mg (1.33 mmol) ferrocenylacetylene, 262 mg (1.33 mmol) 4-Iodoaniline, 93 mg Pd (PPh$_3$)$_2$ Cl$_2$, 40 mg CuI . The flask was then sealed with a serum cap, evacuated and backfilled with nitrogen several times. Dry THF (24 mL) and diisopropylanmine (24 mL) were added via a syringe through the serum cap. After being stirred at 55 ºC for reflux and the system was orange-red and the reaction was trapped with TLC. The reaction was stopped and the solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography the solvent was removed by vacuum, and the remains was dissolved in dichloromethane and was separated and purified with 200-300-meshed chromatography column(petroleum ether : ethyl acetate) =10:1 as extract) to give the compound Fc-NH$_2$ (318 mg, 88 %) as orange solid. ^{1}H NMR (CDCl$_3$) δ: 4.23 (s, 2H, C$_5$H$_4$), 4.25 (s, 5H, C$_5$H$_5$), 4.50 (s, 2H, C$_5$H$_4$), 6.55 (s, 2H, NH$_2$), 7.39 (d, 2H, *J*=8.5 Hz, C$_6$H$_4$), 7.60 (d, 2H, *J*=8.5 Hz, C$_6$H$_4$); ^{13}C NMR (CDCl$_3$) δ: 68.53 (Fc), 69.91 (Fc), 70.17 (Fc), 71.22 (Fc), 85.93 (C≡C), 86.44 (C≡C), 112.65 (Ph), 114.96 (Ph), 132.75 (Ph), 146.77 (NH$_2$); IR (cm^{-1}): 3440, 3358, 2924, 2853, 2197, 1701, 1622, 1604, 1519, 1408, 1289, 1102,1027, 823. MS: m/e: 301(M$^+$,100%); UV(272 nm, 308 nm, in C$_2$H$_5$OH).



Scheme S1 The synthesis route of Fc-NH_2 and Fc-OPE.

Compounds **4**, **5**, **6**, **7**, **8** were synthesized as reported [2,3]. The synthesis of ferrocenyl phenylene-ethynylene aniline (Fc-OPE) was shown in Scheme 1. Simply, a 100 mL one-necked flask was charged with 200 mg (0.65 mmol) compound **8**, 142 mg (0.60 mmol) 4-Iodoaniline, 70 mg Pd $(PPh_3)_2Cl_2$, 40 mg CuI . The flask was then sealed with a serum cap, evacuated and backfilled with nitrogen several times. Dry THF (12 mL) and diisopropylanmine (12 mL) were added via a syringe through the serum cap. After being stirred at 55 ºC for reflux and the system was orange-red and the reaction was trapped with TLC. The reaction was stopped and the solvent was evaporated *in vacuo*, and the residue was purified by flash chromatography. The solvent was removed by vacuum, the remains was dissolved in dichloromethane and was separated and purified with 200-300-meshed chromatography column (petroleum ether : ethyl acetate) =3:1 as extract) to give the object compound Fc-OPE (220 mg, 85 %) as orange solid. ^1H NMR ($CDCl_3$) δ: 4.22 (s, 7H, C_5H_4), 4.47 (s, 2H, C_5H_4), 6.58 (s, 2H, NH_2), 7.28 (d, 2H, $J = 8.0$ Hz, C_6H_4), 7.39 (dd, 4H, $J = 16$ Hz, C_6H_4); ^{13}C NMR ($CDCl_3$) δ: 65.2 (Fc), 69.1 (Fc), 70.1 (Fc), 71.6 (Fc), 85.8 (C≡C), 87.5 (C≡C), 90.3 (Ph), 91.9 (Ph), 112.6 (Ph), 114.9 (Ph), 123.2 (Ph), 131.3 (Ph), 133.1(Ph), 146.8 (Ph); IR(cm^{-1}): 3449, 3383, 2922, 2852, 2202, 1619, 1520, 1289, 1104, 832； MS m/e: 401 (M^+, 100 %).

The synthesis of graphene

Graphite oxide (GO) prepared from natural graphite flakes by a modified Hummer's method[4-6]. Briefly, 500 mg of natural graphite was mixed with 20 mL concentrated H_2SO_4 in a flask, followed by the addition of 1.75 g $KMnO_4$ over a 15 minute period; during addition of $KMnO_4$, the mixture was stirred while residing in the water bath at room temperature. After addition of $KMnO_4$, the mixture was heated at 35 ^oC and stirred for another 2 hours. An ice bath was then used to cool down the solution to 3-4 ^oC and 23 mL of deionized water was slowly added into the flask under stirring to minimize heating. The temperature in the ice bath was monitored and controlled to be no higher than 7 ^oC. Once the temperature was stabilized, 270 mL deionized water was added to further dilute the suspension. The suspension was stirred at 300 rpm throughout. H_2O_2 solution was added drop-wise to remove excess $KMnO_4$. The final suspension was filtered and washed with HCl (10% in water), and dried in air. Further drying was done in vacuum at room temperature for one day. After filtering and washing with water using a 0.2 μm Nylon Millipore filter, the partially reduced graphene oxide could be redispersed in 75 mL water via mild sonication. In the final reduction step, 2 g hydrazine in 5 mL water was added into the dispersion and the reaction mixture was kept at 100 ^oC for 24 h under constant stirring. After filtering and washing with water thoroughly, the graphene thus prepared, and was readily dispersed in water via a few minutes of sonication.

Reference

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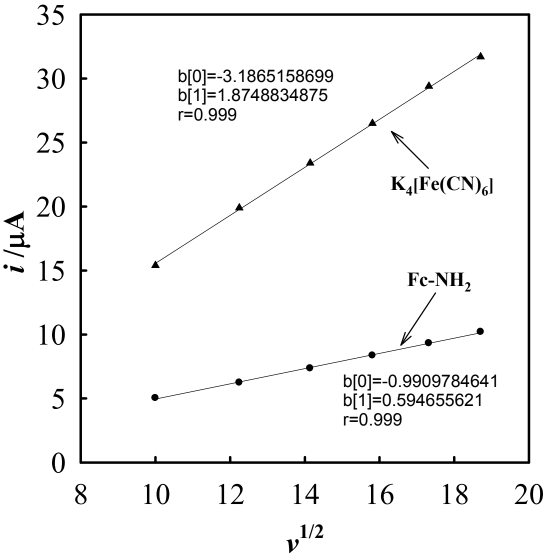

Fig. S1 The relationship between i_p and $v^{1/2}$ in 1 mM $K_4[Fe(CN)_6]$ (0.2 M KCl solution) and Fc-NH_2 (CH_3CN, containing 0.1 M $LiClO_4$ as electrolyte) at different scan rates.

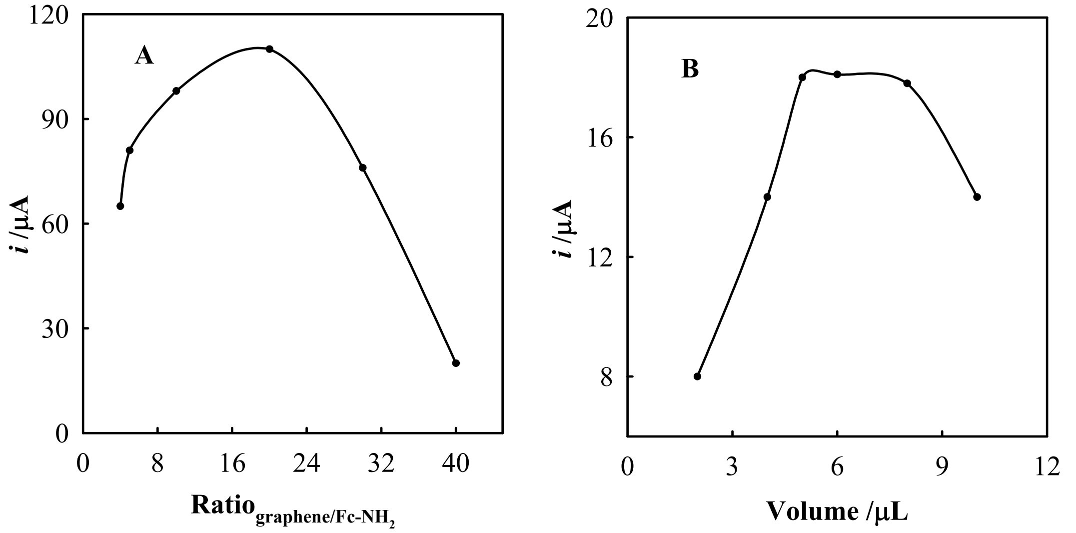

Fig. S2 The effect of (A) the ratio of graphene/Fc-NH_2 and (B) the amount of graphene/Fc-NH_2. 0.1 mM DA in pH=7.0 PBS.

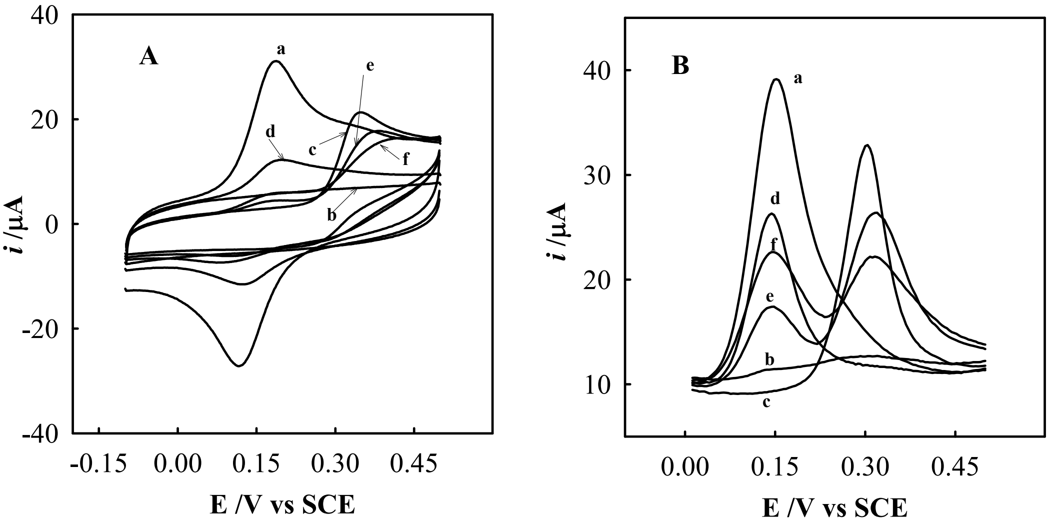

Fig.S3 Cyclic voltammograms of Nafion/graphene/Fc-NH_2/GCE in PBS buffer solution with the given concentration of DA, AA and UA in the Table below.

Curve	Concentration of DA (mM)	Concentration of UA (mM)	Concentration of AA (mM)
a	1	0	0
b	0	0	1
c	0	1	0
d	0.4	0	0.6
e	0.1	0.5	0.4
f	0.2	0.3	0.5