Supporting Information

One-pot *in situ* synthesis of $CoFe_2O_4$ nanoparticles-reduced graphene oxide nanocomposite with high performance for levodopa sensing

Junhua Li [a,b,c], Haibo Feng [a], Jianbo Jiang [a], Yonglan Feng [b], Zhifeng Xu [b], Dong Qian [a,c,*]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China

[b] College of Chemistry and Material Science, Hengyang Normal University, Hengyang 421008, PR China

[c] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China

Corresponding author. Tel/Fax: +86-731-88879616. E-mail address: qiandong6@vip.sina.com (D. Qian).

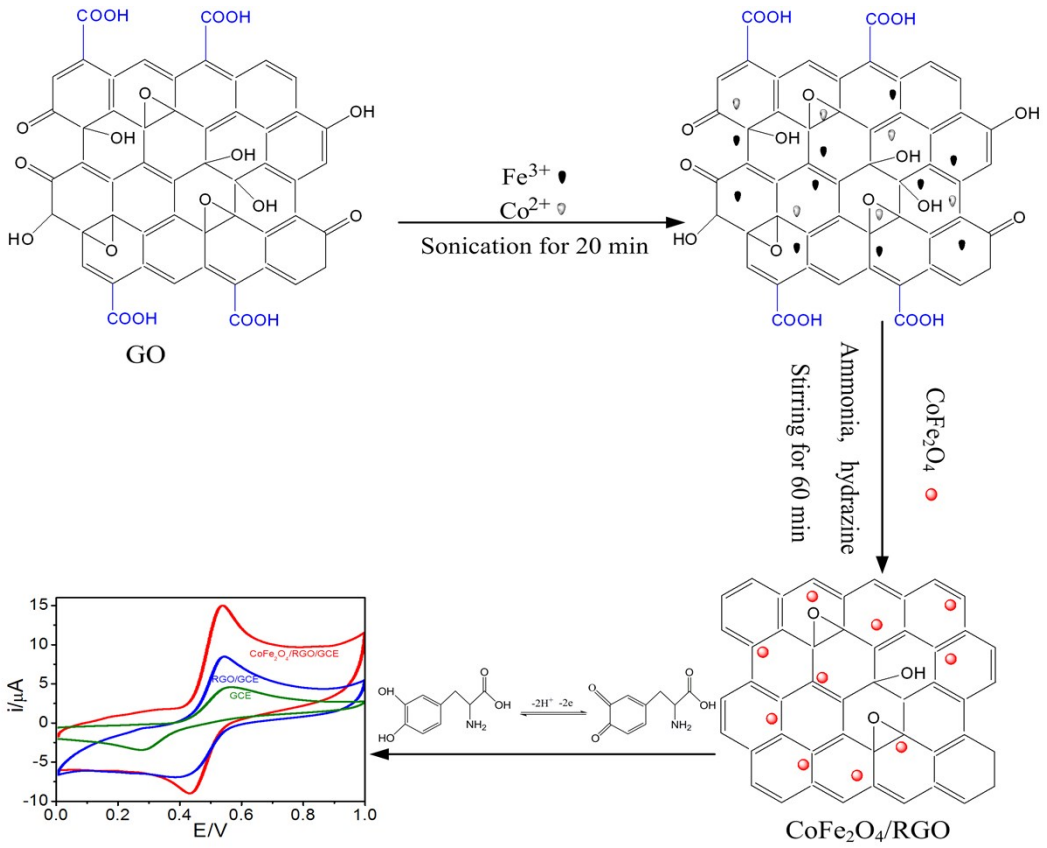


Fig. S1 Schematic diagram of synthesis of $CoFe_2O_4$/RGO composite and levodopa oxidation at $CoFe_2O_4$/RGO film.

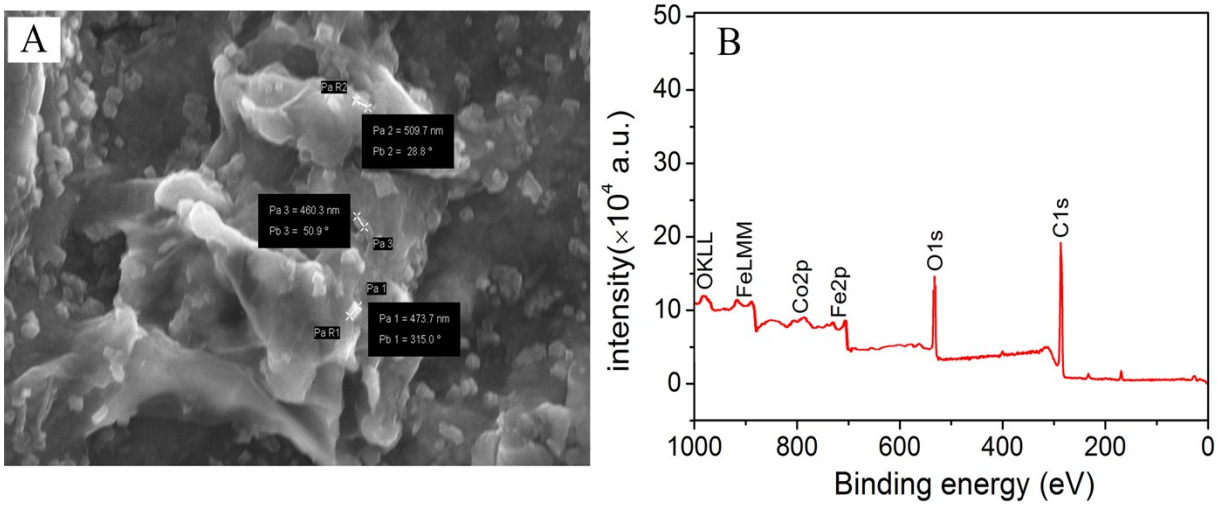


Fig. S2 (A) The particle sizes of $CoFe_2O_4$ nanoparticles and (B) wide scan XPS spectrum of $CoFe_2O_4$/RGO composite.

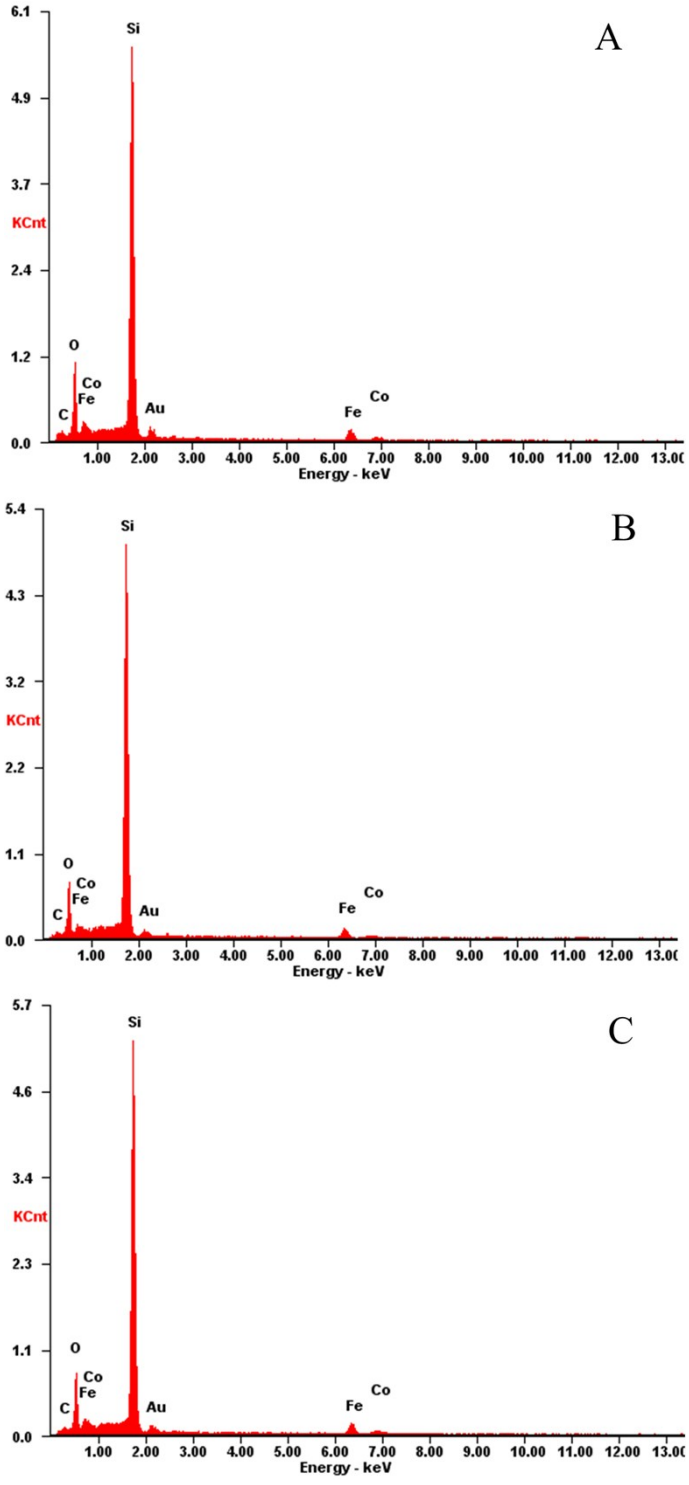


Fig. S3 EDX images obtained at different regions of $CoFe_2O_4$/RGO composite.

Electrochemical effective surface area

As shown in Fig. S3A and B, the electrochemical effective surface areas for GCE, RGO/GCE and $CoFe_2O_4$/RGO/GCE can be calculated by the slope of plot of Q *vs.* $t^{1/2}$, which is obtained by chronocoulometry using 0.5 mM $K_3[Fe(CN)_6]$ as the model complex based on Equation (1) given by Anson[1]:

$$Q(t) = \frac{2nFAC_0D^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads} \qquad (1)$$

where n is the number of transferred electron (n of $K_3[Fe(CN)_6]$ is 1), A is the surface area of the working electrode, C_0 is the concentration of substrate, D is the diffusion coefficient (D of $K_3[Fe(CN)_6]$ is 7.6×10^{-6} cm^2 s^{-1}), Q_{dl} is the double layer charge which can be eliminated by the background subtraction, Q_{ads} is the Faradic charge. As shown in Fig. S3B, the slopes of the linear relationship between Q and $t^{1/2}$ for $CoFe_2O_4$/RGO/GCE, RGO/GCE and bare GCE can be obtained to be 42.83, 26.48 and 8.05 μC s$^{-1/2}$, respectively. Thus A can be calculated as 0.285, 0.176 and 0.0536 cm^2, correspondingly. The results indicate that the electrochemical effective surface area increases obviously after the modification of GCE with $CoFe_2O_4$/RGO, which could enhance the total adsorption capacity of levodopa, leading to the increase of current response of levodopa.

References:

[1] F. Anson, Application of potentiostatic current integration to the study of the adsorption of cobalt(iii)-(ethylenedinitrilo(tetraacetate) on mercury electrodes, Anal. Chem. 36 (1964) 932–934.

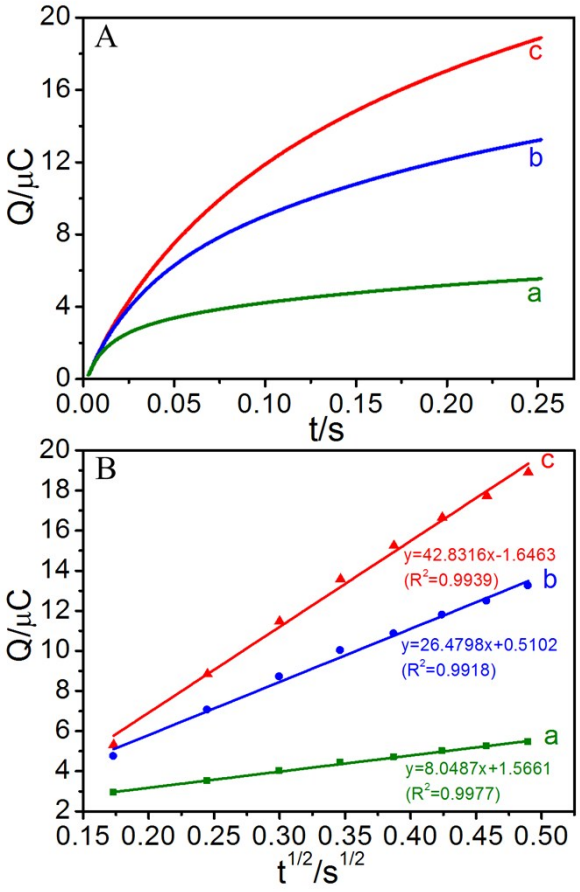
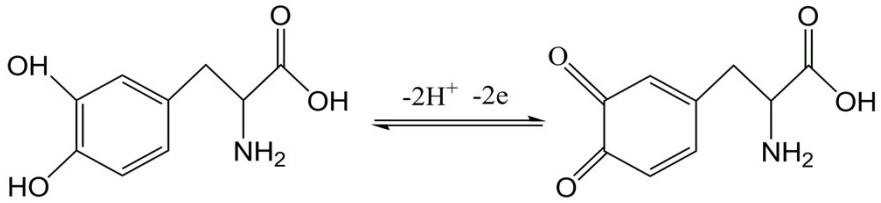


Fig. S4 (A) Plots of *Q*–*t* curves acquired at GCE (a), RGO/GCE (b) and $CoFe_2O_4$/RGO/GCE (c) in 1 M KCl containing 0.5 mM $K_3[Fe(CN)_6]$; (B) plots of Q–$t^{1/2}$ curves derived from the data of chronocoulometry for GCE (a), RGO/GCE (b) and $CoFe_2O_4$/RGO/GCE (c). The pulse width, sample interval and quiet time of chronocoulometry were 0.25 s, 0.25 ms and 2 s, respectively.



Scheme 1 The possible mechanism of the levodopa oxidation at $CoFe_2O_4$/RGO/GCE.

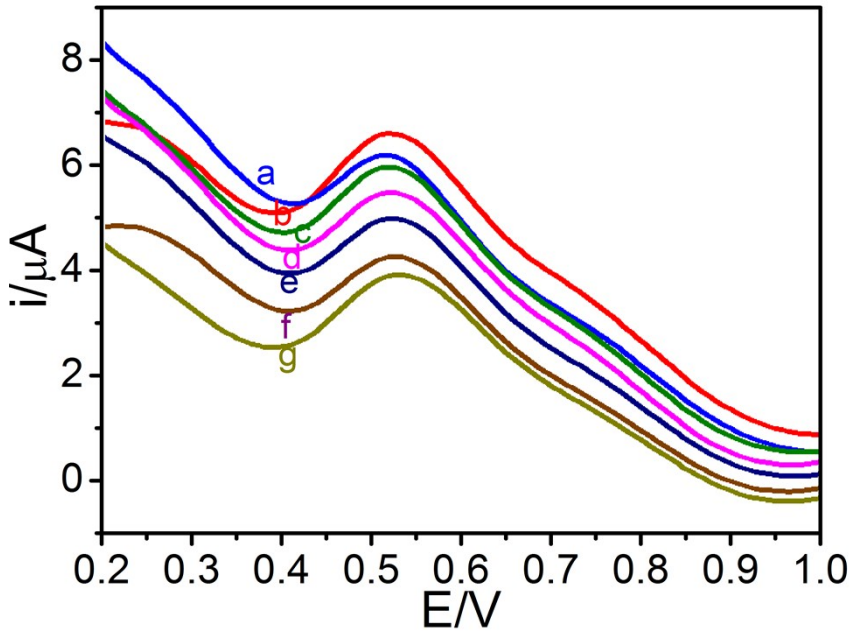


Fig. S5 The influence of different accumulation potential on the DPV response of 10 μM levodopa (accumulation potentials of cuvres a−g: −0.4, −0.3, −0.2, −0.1, 0, 0.1 and 0.2 V).

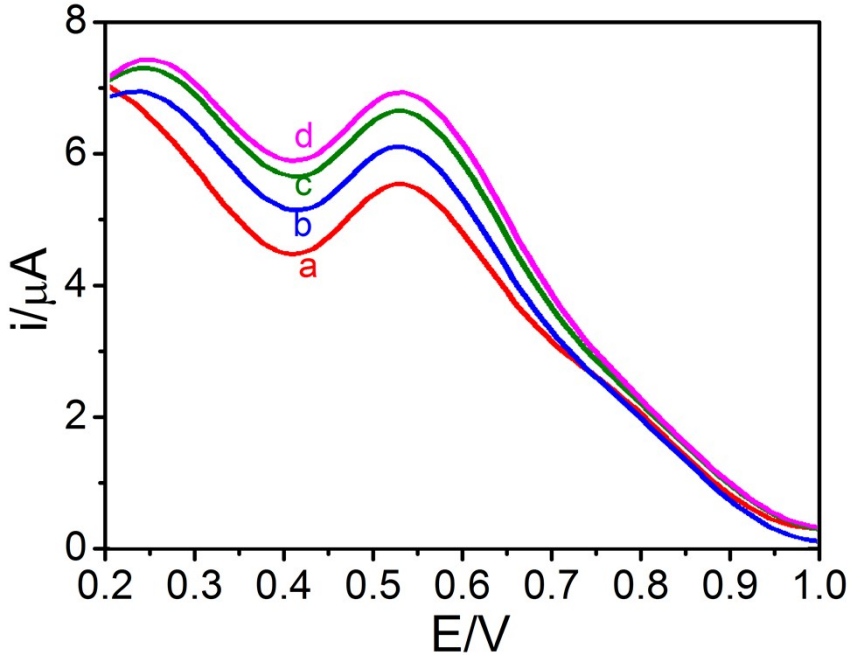


Fig. S6 The influence of different accumulation time on the DPV response of 10 μM levodopa (accumulation times of cuvres a−d: 50, 100, 150 and 200 s).

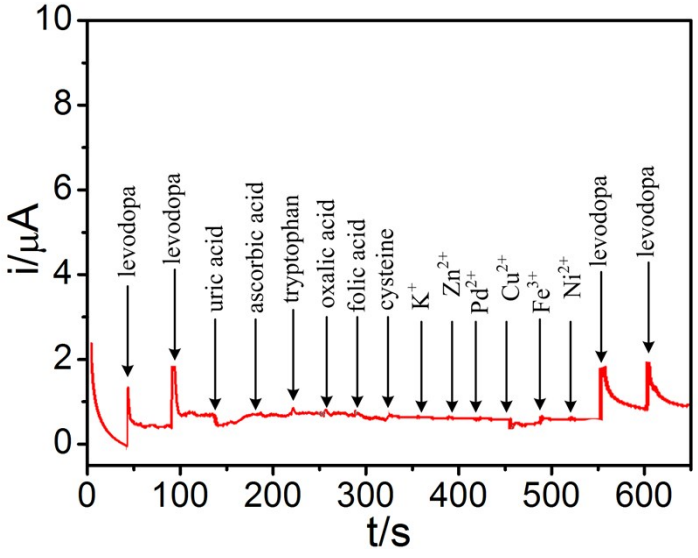


Fig. S7 The effects of some interfering substances (20 μM uric acid, ascorbic acid, tryptophan, oxalic acid, folic acid, cysteine, K^+, Zn^{2+}, Pd^{2+}, Cu^{2+}, Fe^{3+} and Ni^{2+}) on the determination of levodopa at $CoFe_2O_4$/RGO/GCE. Applied potential is 0.5 V.

Table S1 Influences of some possible interfering substances on the DPV determination of 1.0 μM levodopa (n = 3).

Interfering substance	Concentration (μM)	Oxidation peak current [b] (μA)	Relative error(%)
– [a]	1.0	3.885	–
Ascorbic acid	10.0	3.992	2.75
Uric acid	10.0	3.965	2.06
Adrenaline	10.0	3.696	−4.86
benzene	10.0	3.812	−1.88
hydroquinone	10.0	3.712	−4.45
4-aminophenol	10.0	3.768	−3.01
2-chlorophenol	10.0	3.722	−4.20
Guanine	10.0	4.033	3.81
Adenine	10.0	3.996	2.86
Vitamin B_1	10.0	4.011	3.24
Glucose	10.0	3.980	2.45
Dopamine	10.0	4.386	12.9
D-dopa	10.0	4.457	14.7

[a] No interfering substance for levodopa determination.

[b] Oxidation peak current for 1.0 μM levodopa.

Table S2 Electrochemical determination of levodopa in human urine samples (n = 6).

Sample No.	Spiked (μM)	Found (μM)	Recovery (%)	RSD (%)
1	0	–	–	–
2	5.00	4.89	97.8	2.86
3	10.00	10.16	101.6	1.75
4	20.00	20.63	103.2	3.11

Note: No obvious DPV signal was found for the unspiked urine samples, indicating that the concentration of levodopa in the urine samples is lower than the detection limit of the proposed method, so levodopa with known concentrations was added and further evaluated by the standard addition method.