Electronic Supplementary Material (ESI) for Nanoscale.

***Supporting information** for*

Efficient optical-electrochemical dual probe for highly sensitive recognition of dopamine based on terbium complexes functionalized reduced graphene oxide

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Experimental Section

Chemicals and Materials

Tb_4O_7 (99.9%) was purchased from Shanghai Yuelong company. Terbium perchlorate was obtained by dissolving Tb_4O_7 in concentrated perchloric acid. N-Boc-1,4-butanediamine (97%), diethylenetriamine pentaacetic acid dianhydride (DTPAda, 98%), trifluoroacetic acid (TFA, 99%) and dopamine hydrochloride (DA, 98%) were purchased from Aladdin Reagent Company. Natural graphite flakes were supplied by Qingdao Tianhe Graphite Co., Ltd. Sulphuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%), sodium nitrate (AR) and all the other reagents were purchased from Guangzhou Chemical Reagent Factory and used without further purification.

Preparation of amino-functionalized reduced graphene oxide (RGO-NH_2)

Graphene oxide (GO) was synthesized from natural graphite by a modified Hummer's method.[1, 2] For the preparation of RGO-NH_2, GO (200 mg) in $SOCl_2$ (100 mL) and dimethylformamide (DMF, 5 mL) was allowed to react at 70℃ for 24 h to convert the carboxyl groups into acyl chlorides. Solvent was evaporated under vacuum and the remaining solid was washed with anhydrous tetrahydrofuran (THF) to remove residual $SOCl_2$ and DMF. N-Boc-1,4-butanediamine (1 g) was added to 100 mg acylchlorinated GO in 30 mL dry THF and allowed to react at 100℃ for 4 days. After cooling to room temperature, RGO-NHBoc was washed with ethanol for several times to remove excess N-Boc-1,4-butanediamine and dried at room temperature overnight under vacuum. RGO-NHBoc (80 mg) was dispersed in

50 mL dimethyl sulfoxide (DMSO) by sonication and vigorous stirring for 1 h at room temperature. Then trifluoroacetic acid (TFA, 20 mL) was added dropwise to the above solution. The mixture was stirred at room temperature for another 24 h to cleave the Boc group from the end of alkyl chain. RGO-NH_2 was isolated by centrifugation and washed repeatedly with ethanol/water (v/v, 1:1), filtered, and dried at room temperature under vacuum for 12 h.

Preparation of diethylenetriamine pentaacetic acid (DTPA) modified RGO (RGO-DTPA)

RGO-NH_2 (50 mg) was dispersed by sonication in 20 mL of bicarbonate buffer (0.1M, pH 9.6) at room temperature. 200 mg of diethylenetriamine pentaacetic acid dianhydride (DTPAda) was then slowly added to the solution during stirring. After 12 h, the RGO-DTPA was separated by centrifugation and then thoroughly washed with bicarbonate buffer and deionized water.

Preparation of terbium containing RGO sensor (RGO-DTPA-Tb)

RGO-DTPA (40 mg) was dispersed in ethanol solution of $Tb(ClO_4)_3$ (20 mL, 0.01 M) by sonication, 3~5 drops of aq. NH_3 were added, and the mixture was stirred for 5 h at room temperature. After centrifugation, the precipitate was washed with ethanol three times to remove the excess amounts of un-reacted Tb^{3+} and dried under vacuum to obtain the target sensor RGO-DTPA-Tb.

Preparation of RGO-DTPA-Tb modified glassy carbon electrode (GCE)

The GC disk electrode (3 mm diameter) was polished with 3 μm and 0.1 μm alumina paste on a polishing cloth (Buehler) and then ultrasonically washed in absolute ethanol for 2 min and then ultrapure water for 2 min. Then it was dried at room temperature. A suspension of RGO-NH-DTPA-Tb (5 μ L, 0.5 mg / mL) was applied to the GC electrode and the electrode was dried at room temperature to obtain the RGO-DTPA-Tb modified GCE (RGO-DTPA-Tb/GC). Similarly, GO modified GCE (GO/GCE) and RGO-DTPA modified GCE (RGO-DTPA/GCE) were prepared.

Characterizations of the probe

Fluorescence spectra were measured on an Agilent 8453 spectrophotometer and an Edinburgh FLS920 spectrometer. Luminescence sensing experiments of the RGO-DTPA-Tb were performed by adding various concentrations of DA to the RGO-DTPA-Tb (1 mg/L) in buffered solution (PBS, pH 7.4). Differential-pulse voltammetry (DPV) measurements were carried out with a CHI660a electrochemical system in 100 mM PBS (pH 7.4) with a conventional three-electrode system comprised of a platinum wire as the auxiliary electrode, an Ag/AgCl as the reference electrode and the modified GC electrode used as working electrode. Fourier transform infrared spectra were measured using a Prestige-21, Shimadzu. The X-ray diffraction (XRD) measurements were carried out on powdered samples in a BRUKER D8 diffractometer (40 mA/40kV), using monochromated Cu-Kα_1 radiation (λ = 1.54 Å) over the 2θ range of 5° to 70°. TEM images, HR-TEM images and SAED patterns were obtained with a JEOL JEM-2100HR transmission electron microscope. SEM was measured using a Tescan 5136MM scanning electron microscope.

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

2. X. Z. Zhou, X. Huang, X. Y. Qi, S. X. Wu, C. Xue, F. Y. C. Boey, Q. Y. Yan, P. Chen and H. Zhuang, *J. Phys. Chem. C*, 2009, **113**, 10842.

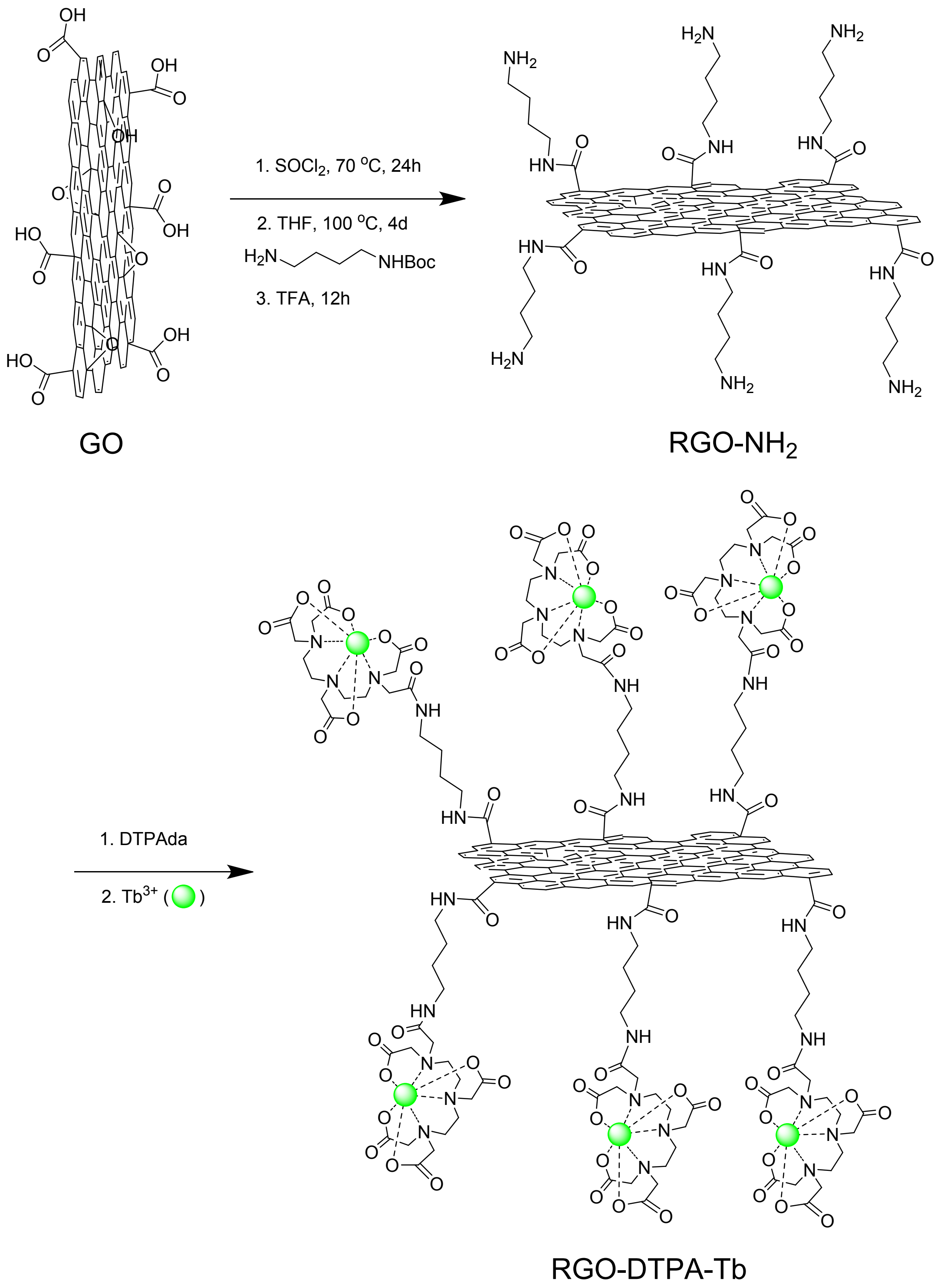

Fig. S1 Synthesis of RGO-DTPA-Tb.

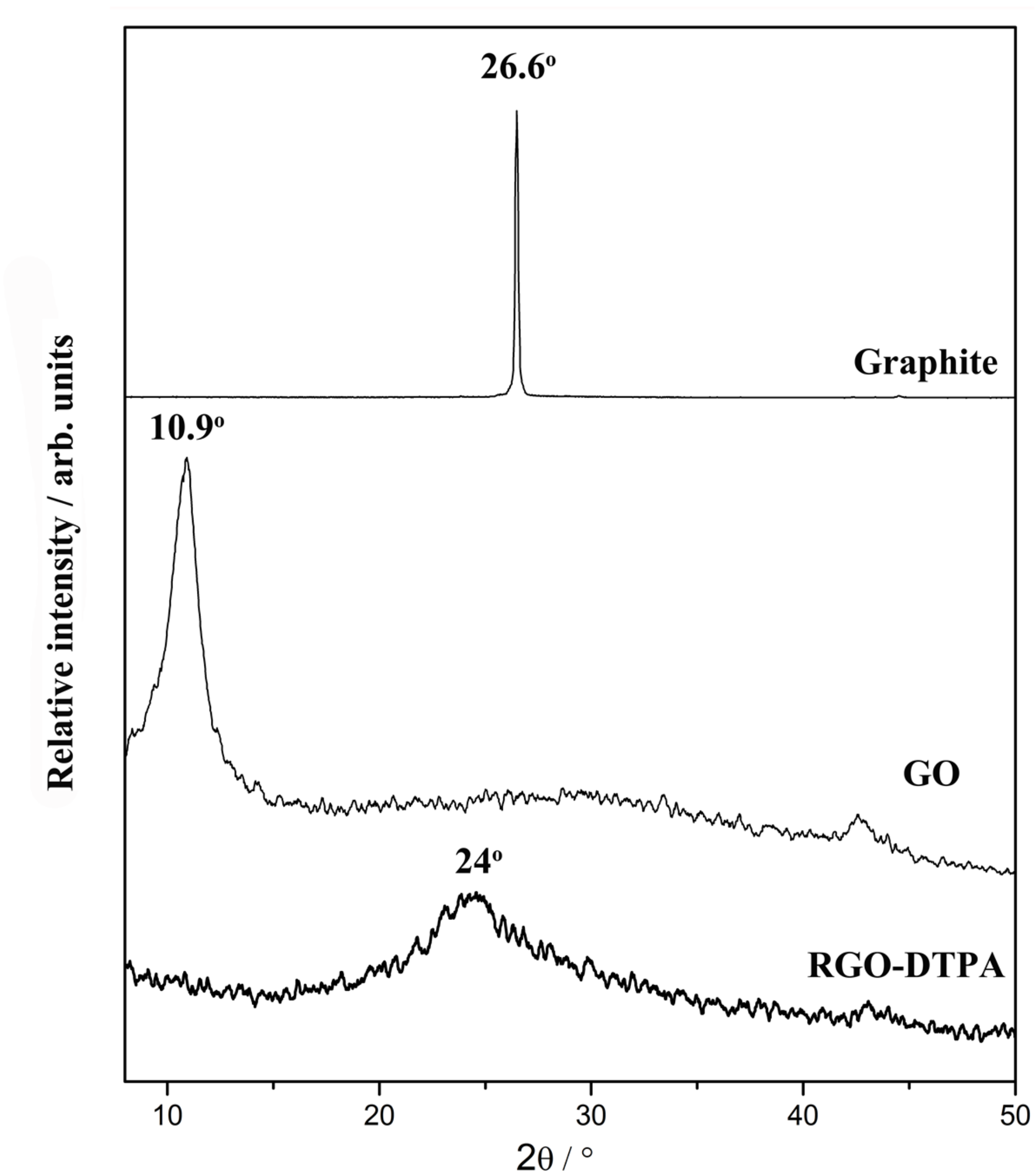

Fig. S2 XRD patterns of graphite, GO and RGO-DTPA.

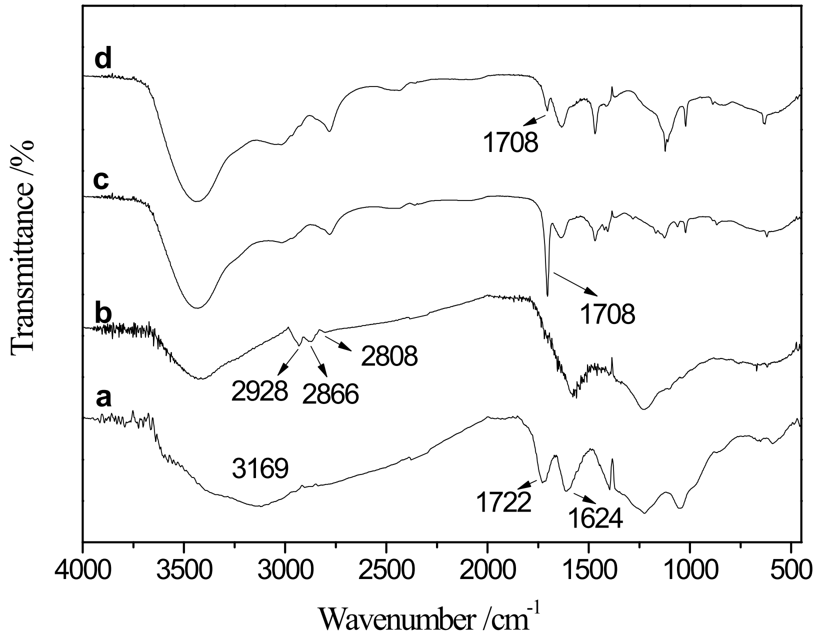

Fig. S3 IR spectra of (a) GO, (b) RGO-NH_2, (c) RGO-DTPA and (d) RGO-DTPA-Tb.

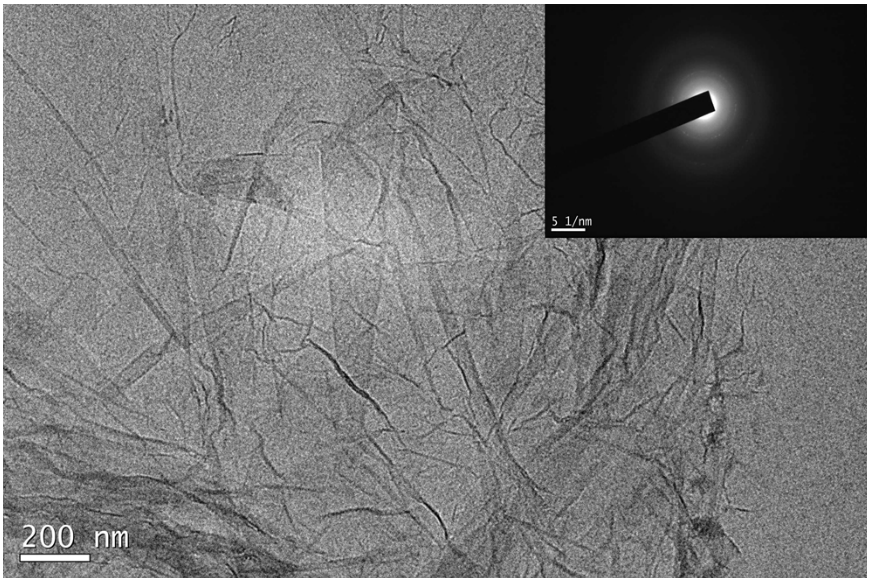

Fig. S4 SEM image of GO. The inset is the selected area electron diffraction pattern (SAED).

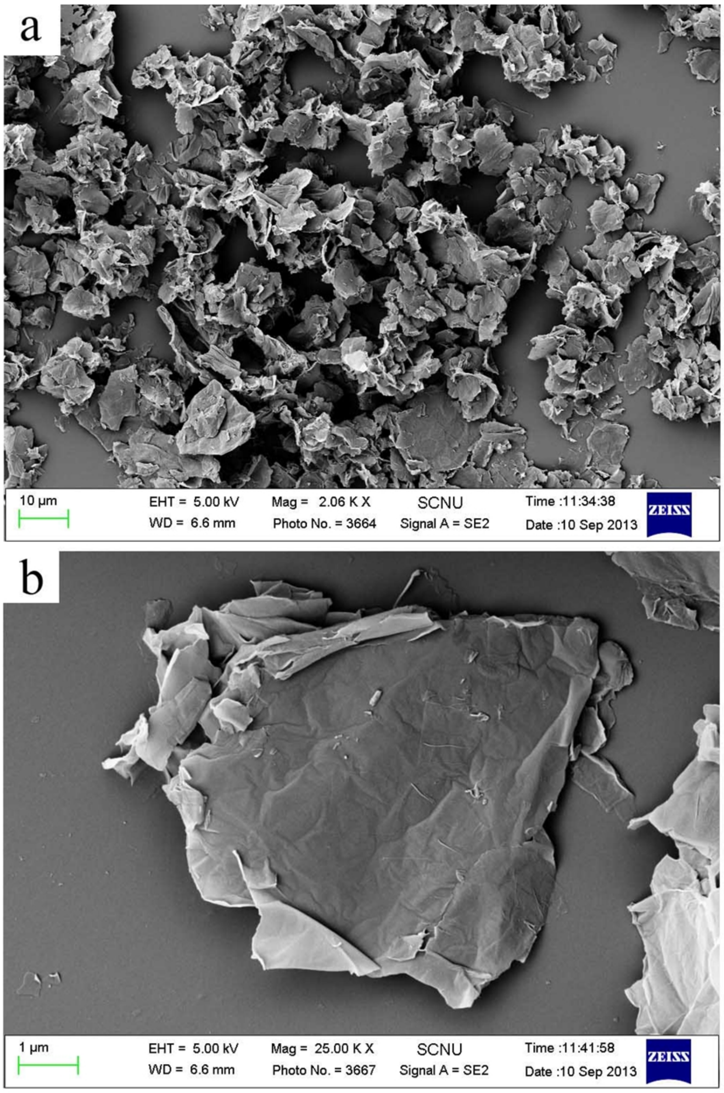

Fig. S5 SEM (a) and HR-SEM (b) images of RGO-DTPA-Tb.

Method	Concentration of dopamine (μM)	Fluorescent intensity / Current (μA)	Detection limit (nM)
Luminescence Method	0	45	80
	0.5	96	
	1	146	
	1.5	197	
	2	258	
	2.5	315	
	3	385	
	4	477	
	5	589	
	6	690	
	7	853	
	8	941	
	9	1087	
	10	1265	
Electrochemical Method	0	-1.65	12
	0.2	-1.67	
	0.3	-1.71	
	0.4	-1.76	
	0.5	-1.81	
	1	-2.03	
	1.5	-2.31	
	2	-2.51	
	3	-2.96	
	4	-3.46	
	5	-4.05	
	6	-4.49	
	7	-4.91	
	8	-5.2	
	9	-5.56	
	10	-6.07	

Table S1 Fluorescent intensity or current (μA) at indicated dopamine concentrations obtained by the luminescence and electrochemical methods. The detection limit (DL) of RGO-DTPA-Tb for dopamine (DA) was determined from the following equation:

DL = K*SD/S, where K is 3, SD is the standard deviation of the blank solution (obtained by

10 consecutive scans of the blank sample), and S is the slope of the calibration curve.).

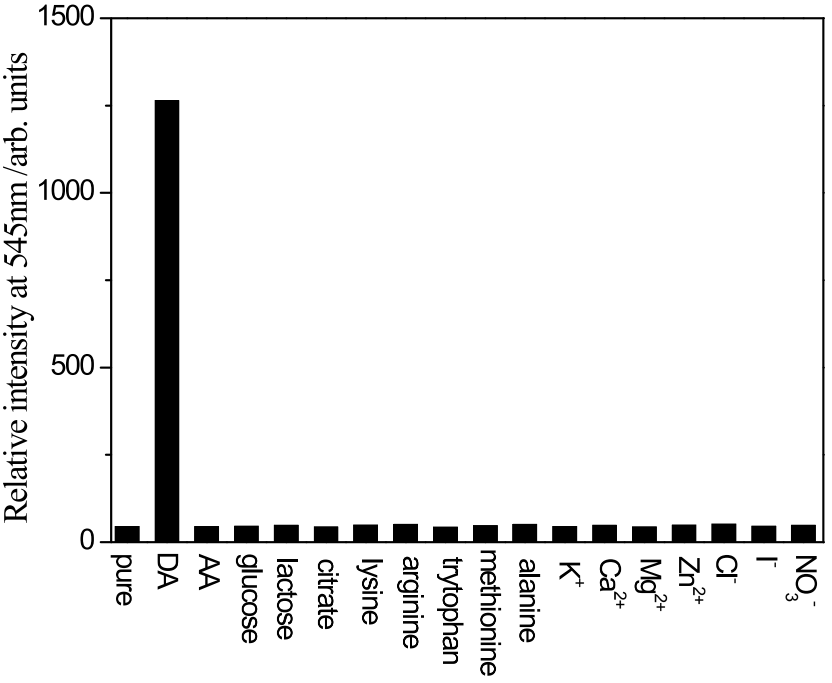

Fig. S6 Selectivity of RGO-DTPA-Tb for DA (10 μM) in the presence of excess amounts of potential interfering compounds (1 mM) or ions (1 mM). Fluorescence intensity of RGO-DTPA-Tb was monitored at 545 nm.

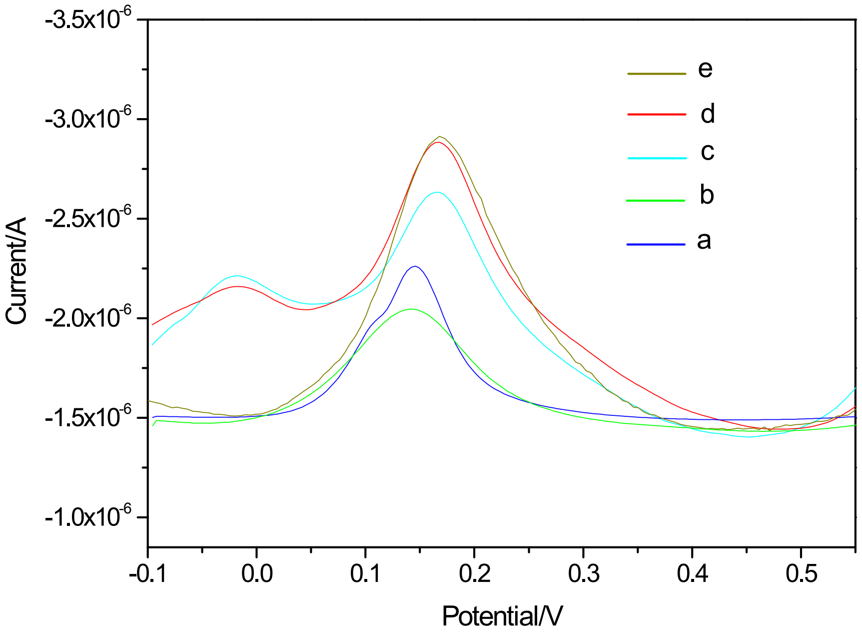

Fig. S7 DPVs obtained for DA (3 μM) in presence of AA (300 μM) recorded at bare GCE (a), GO/GCE (b), RGO-DTPA/GCE (c) and RGO-DTPA-Tb/GCE (d) in 0.1 M PBS (pH 7.4) and DPV of RGO-DTPA-Tb/GCE for 3 μM DA in absence of AA (e) in 0.1 M PBS (pH 7.4).