Selective and sensitive determination of dopamine by composites of polypyrrole and graphene modified electrodes

*Peng Si, Hailan Chen, Palanisamy Kannan and Dong-Hwan Kim**

Division of Bioengineering

School of Chemical and Biomedical Engineering,

Nanyang Technological University

70, Nanyang Drive, Singapore – 637457

Supporting information

*Corresponding author e-mail: dhkim@ntu.edu.sg; Phone (O): +65-67904111; Fax: (65) 6791-1761.

Raman spectroscopy study of PPy/eRGO film. Raman spectroscopy is a sensitive tool to investigate the chemical structures of carbon-based materials. As shown in Fig. S4, the two peaks on GO spectrum centered at 1325 and 1596 cm^{-1} are assigned for the D and G bands, respectively. D band indicates the defects or edge planes in the structure, while G band is related to the vibration of sp^2 hybridized carbon [1]. Except for D and G bands, two other characteristic bands are observed at 946 and 1095 cm^{-1} on the spectrum of PPy, corresponding to the bipolaron ring deformations and polaron symmetric C-H in-plane bending vibration respectively. The peak observed at 1498 cm^{-1} is assigned to asymmetric C-N stretching vibration of the pyrrole ring.[2, 3]. The D/G intensity ratio of PPy/GO is measured to be 1.2. Upon electrochemical reduction, the ratio was increased to 1.5, resulting from the increase of unrepaired defects in the PPy/eRGO composite after the removal of oxygen-containing groups from GO. [4] The observed result is consistent with the reports previously.[5, 6] The characteristic bands of PPy could also be observed on the spectra of PPy/GO and PPy/eRGO, confirming the presence of PPy in the composite films.

Electrochemical impedance spectroscopy (EIS) study of PPy/eRGO composite film. EIS is a powerful technique which provides useful information on the electrochemical frequency of the system, and allows the measurement of redox reaction resistance and equivalent series resistance of electrodes. The 45° slopped portion at the low frequency region of impedance spectrum (Nyquist plot) is the typical Warburg resistance reflecting the ion diffusion behavior of the electrolyte. Smaller Warburg region means lower electronic transport resistance, less obstruction for ion diffusion and higher conductivity of the electrode material[7]. Fig. S5 presents the Nyquist plots of PPy and PPy/eRGO-films modified electrodes. Pure PPy film-modified GCE shows a large Warburg region, indicating the poor conductivity and high resistance of the modified electrode. However, the PPy/eRGO composite film-modified GCE exhibits a nearly vertical Nyquist curve with much smaller Warburg region, indicating the conductivity of PPy film is significantly improved after doping with graphene.

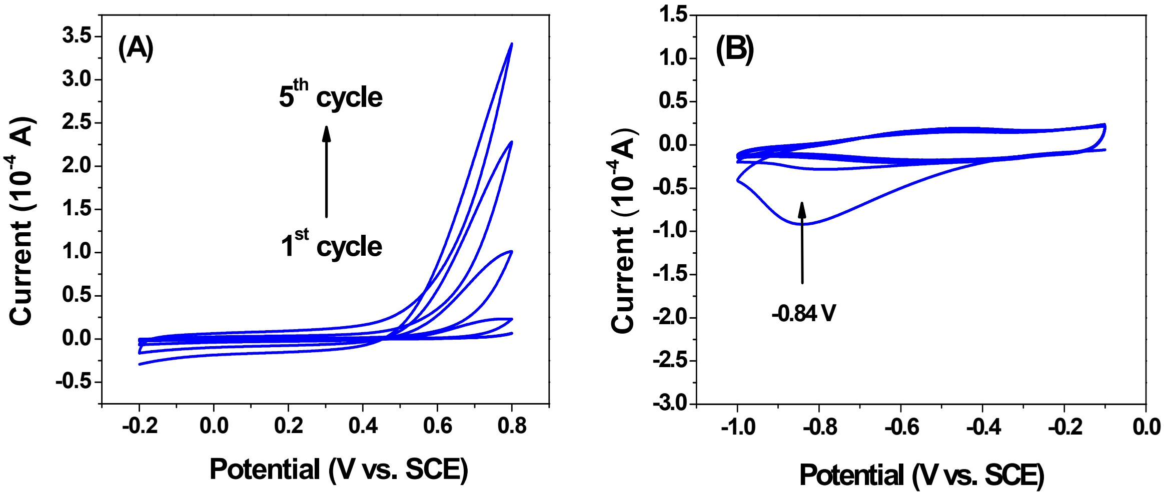

Fig. S1 (A) CVs obtained for GCE in 10 mg mL^{-1} GO solution containing 0.1 M pyrrole at a scan rate of 20 mV s^{-1}. (B) CVs obtained for PPy/GO-modified GCE in nitrogen-saturated 0.5 M Na_2SO_4 solution at scan rate of 50 mV s^{-1}.

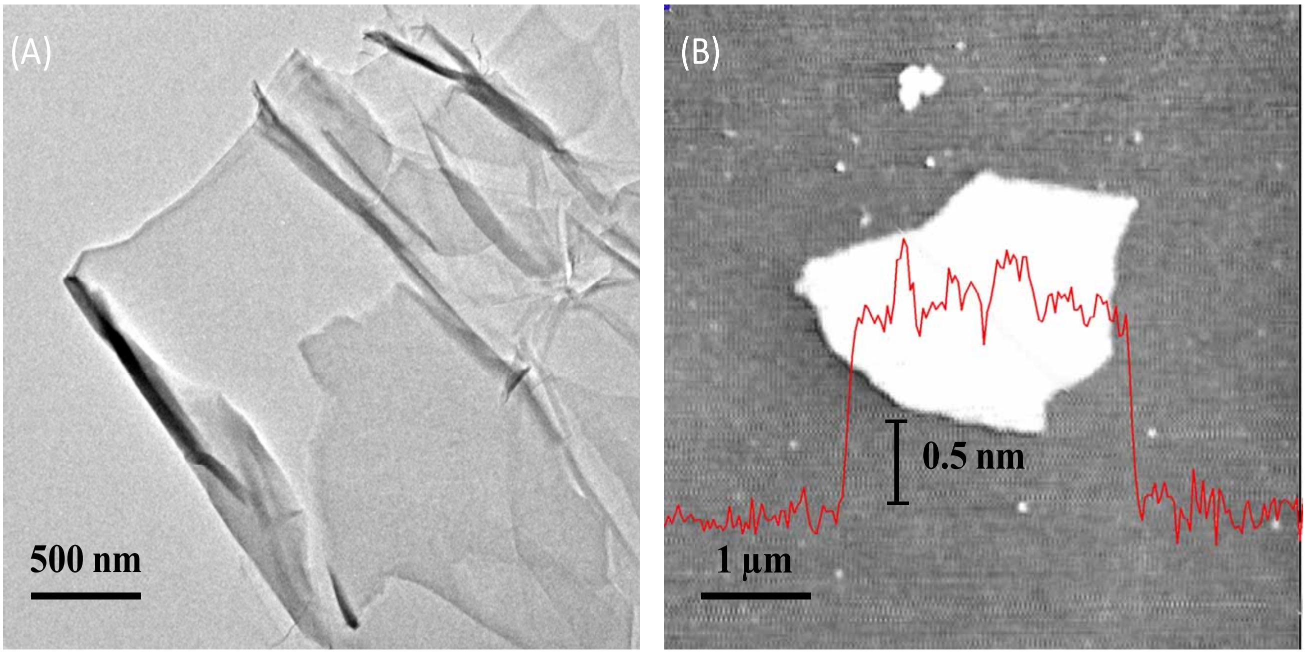

Fig. S2 TEM (A) and AFM (B) images of GO.

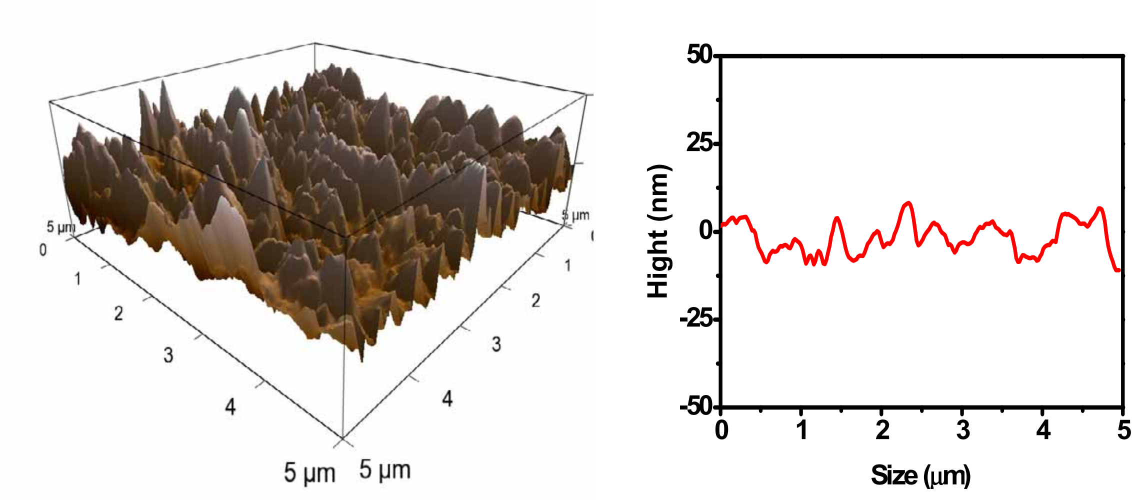

Fig. S3 AFM image and the corresponding height profile graph of the PPy/eRGO film.

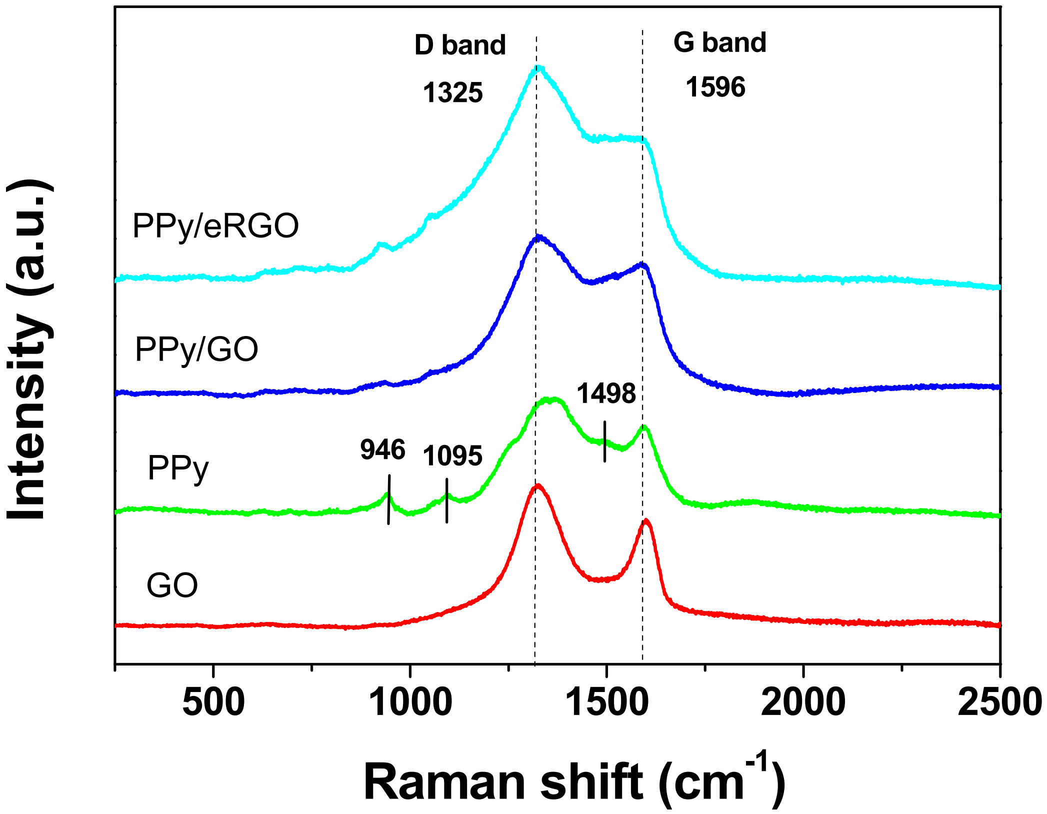

Fig. S4 Raman spectra of GO, PPy, PPy/GO and PPy/eRGO.

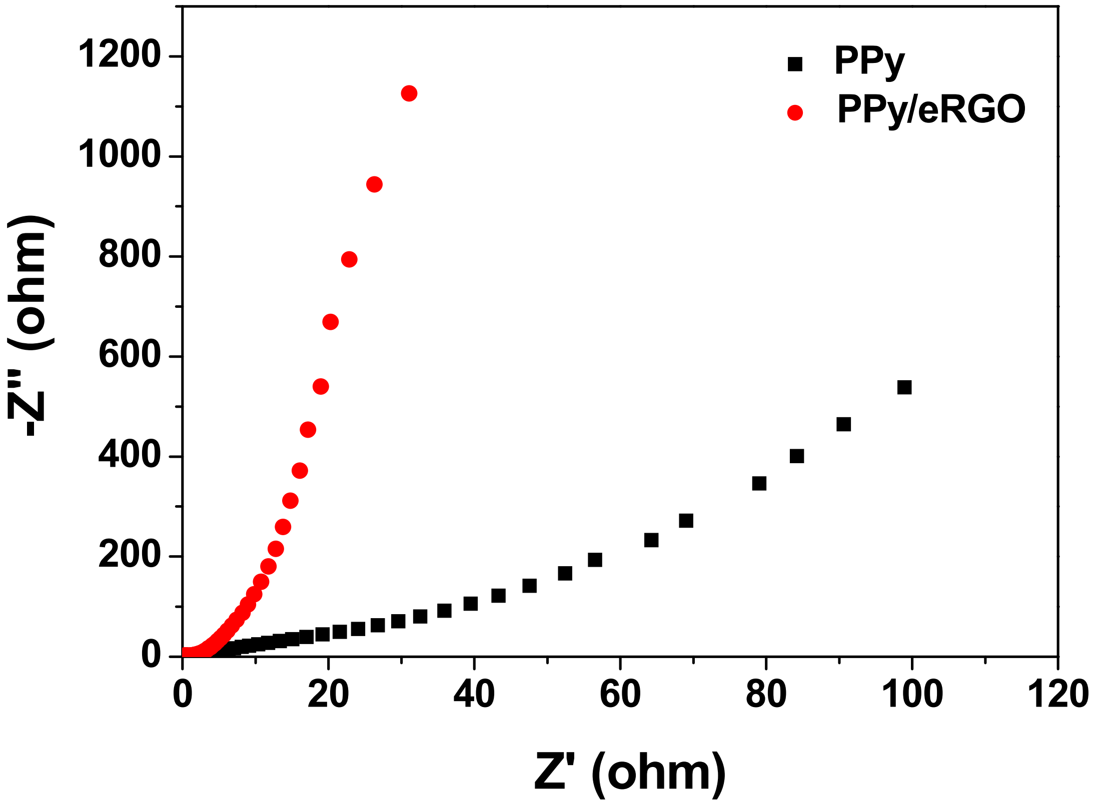

Fig. S5 Nyquist plots of PPy (black) and PPy/eRGO (red) obtained by electrochemical impedance spectroscopy (EIS) in 1.0 M KCl containing 10 mM $Fe(CN)_6^{-3/-4}$.

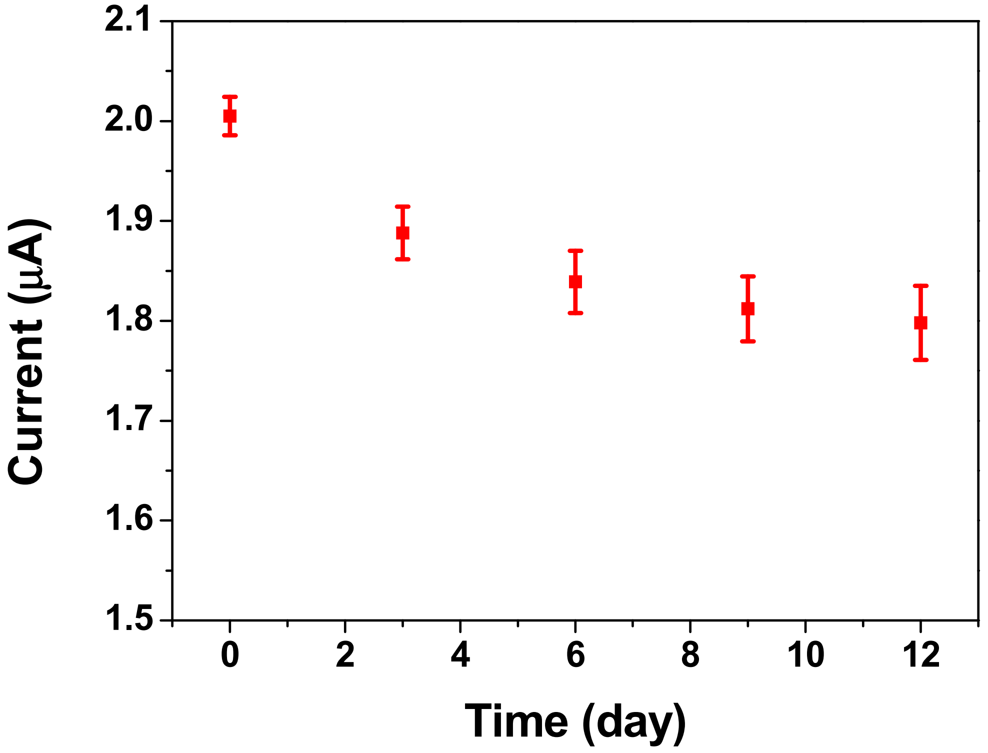

Fig. S6 The DPV current response of the PPy/eRGO-GCE for 50 μM DA in 0.1 M PBS for 12 days.

Table S1. Determination of DA at different materials modified electrodes.

Modified electrodes	Detection limit (μM)	Linear range (μM)	References
PPy/eRGO	0.023	0.1-150	This study
Carbon nanofibers	0.04	0.04-5.6	[8]
Au nanoparticles	0.13	0.13-20	[9]
PPy/SWCNT	1	1-50	[10]
Graphene/chitosan	1	1-24	[11]
Graphene	2.64	4-100	[12]

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