Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B
This journal is © The Royal Society of Chemistry 2014

A metal-catalyst free flexible and free-standing chitosan/vacuum-stripped graphene/polypyrrole three dimensional electrode interface for high performance dopamine sensing

Jing Liu, Ziming He, Jingwen Xue and Timothy Thatt Yang Tan*

School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, 637459, Singapore

*E-mail: tytan@ntu.edu.sg

Experimental Section

Preparation of CHI/VSG scaffolds: Graphite oxide was first prepared via modified hummers' method[1,2] using graphite as starting material and was then heated at 250 °C for 5 min under vacuum condition to obtain VSG. Subsequently, 50 mg of VSG powder was dispersed in 5 ml chitosan solution (1 wt.% in 0.05 M acetic acid aqueous solution) and this precursor suspension was stirred overnight to ensure the uniform dispersion of VSG. After that, the precursor suspension was drawn into syringes and dipped into a liquid nitrogen bath at a constant dipping rate of 5 mm min^{-1}. The unidirectionally frozen samples were then freeze-dried using a freeze-dryer (Labconco FreeZone 2.5) to obtain CHI/VSG scaffolds.

Preparation of CHI/VSG/PPy scaffolds: The prepared CHI/VSG scaffolds were connected with electrical leads and sealed using epoxy, and then dried in room temperature to obtain free-standing scaffold electrode. 0.1 M pyrrole monomer was dispersed in 0.1 M sodium dodecylsulfate (SDS) aqueous solution under ultrasonication for 15 min to form a homogenous suspension. The PPy nanofilm was electropolymerized on CHI/VSG scaffold by cyclic voltammetry (CV) scanning of the CHI/VSG electrode in the above mentioned solution as reported (Figure S1).[3] The obtained CHI/VSG/PPy electrode was then carefully rinsed with DI water before use.

Characterization of VSG powder and CHI/VSG scaffolds: The structure of VSG powder, CHI/VSG and CHI/VSG/PPy scaffolds was observed using field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). The specific surface area of CHI/VSG and

This journal is © The Royal Society of Chemistry 2014

CHI/VSG/PPy scaffolds were measured with a commercial pore and surface analyzer (Quantachrome Adsorb-1) and calculated using the Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) methods. The chemical structures of the scaffolds were analyzed with fourier transform infrared spectroscopy (FTIR, Thermo Nicolet, USA) in potassium bromide, recording with a scan range from 4000 to 400 cm^{-1}.

Electrochemical measurements: Electrochemical measurements were performed using PGSTAT30 Autolab system (Ecochemie, Utrecht, Netherlands) in a three-electrode system, consisted of a working electrode (CHI/VSG or CHI/VSG/PPy scaffold), a saturated calomel electrode (SCE) as reference electrode, and a platinum foil counter electrode.

Supplementary results

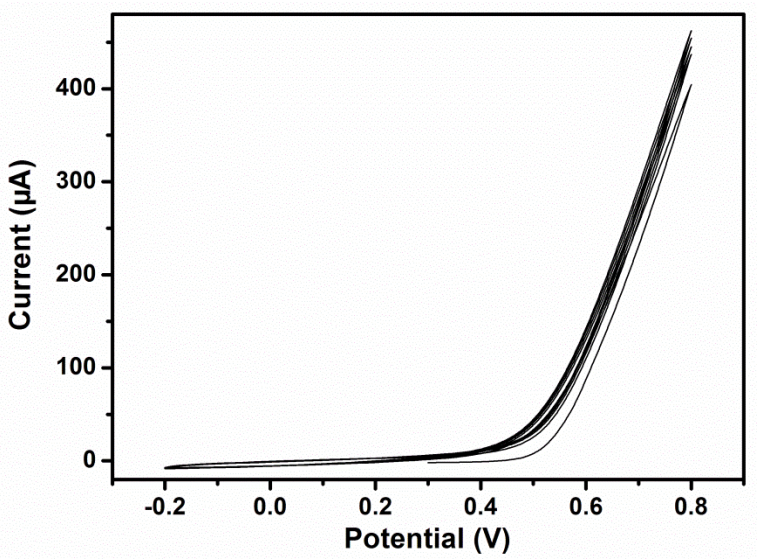

Figure S1. Cyclic voltammograms recorded during the pyrrole electropolymerization on the CHI/VSG scaffold.

This journal is © The Royal Society of Chemistry 2014

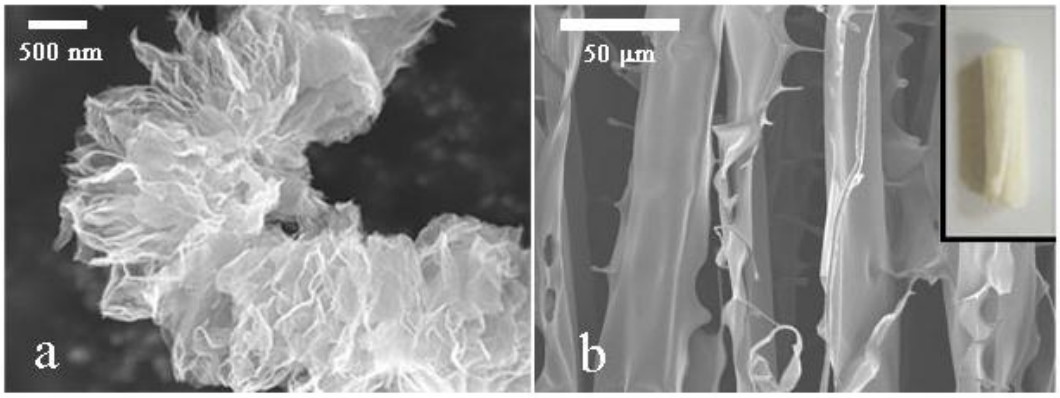

Figure S2. FESEM image of pure VSG powder (a) and CHI scaffold (b), inset of (b) is the photograph of CHI scaffold.

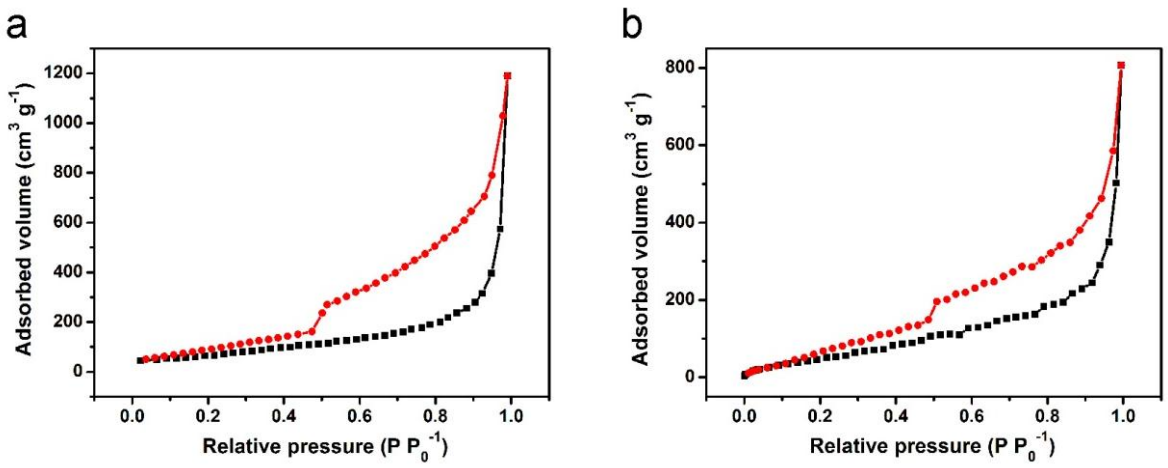

Figure S3. N_2 adsorption-desorption isotherm of the CHI/VSG and CHI/VSG/PPy.

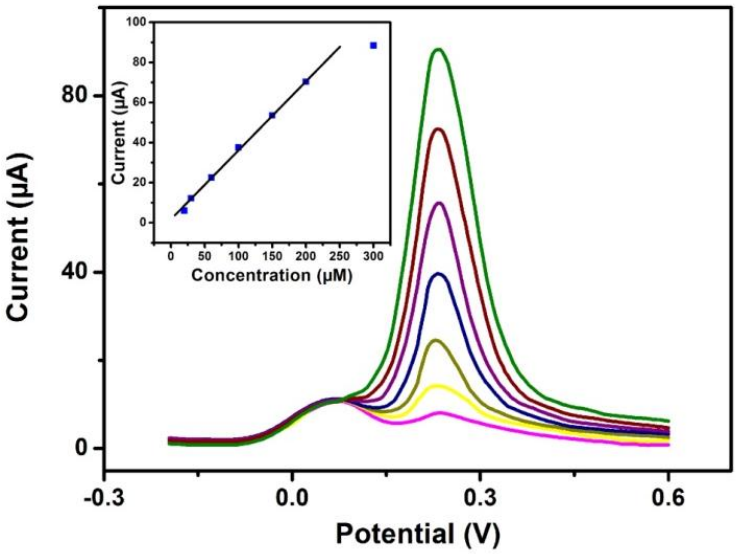

Figure S4. DPVs of DA at the CHI/VSG/PPy electrode in the presence of 0.2 mM AA in 0.1 M PBS (pH=6.0). From bottom to top DA concentration= 20, 30, 60, 100, 150, 200, 300 μM. Inset: the relation between the peak current and the DA concentration.

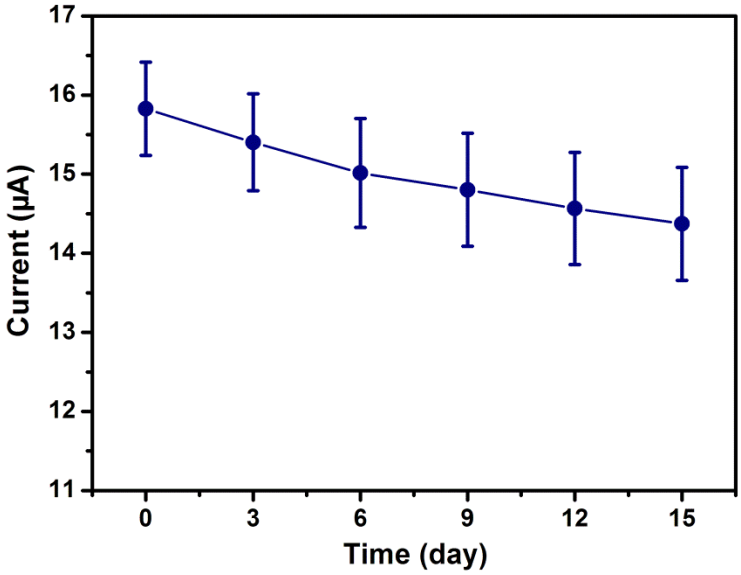

Figure S5. The DPV current response of the CHI/VSG/PPy sensor in 0.1 M PBS containing 40 μM DA for 15 days.

This journal is © The Royal Society of Chemistry 2014

Table S1 Recovery of DA from the human blood serum sample.

	Spiked/μM	**Found/μM**	**RSD (%)**	**Recovery (%)**
1	2.00	2.07	2.30	104
2	3.00	3.06	2.85	102
3	4.00	3.91	2.95	98

Reference

1 He, Z. *et al.* Nanostructure control of graphene-composited TiO_2 by a one-step solvothermal approach for high performance dye-sensitized solar cells. *Nanoscale* **3**, 4613-4616 (2011).

2 Hummers, W. S. & Offeman, R. E. Preparation of Graphitic Oxide, *J. Am. Chem. Soc.* **80**, 1339-1339 (1958).

3 Si, P., Chen, H. L., Kannan, P. & Kim, D. H. Selective and sensitive determination of dopamine by composites of polypyrrole and graphene modified electrodes. *Analyst* **136**, 5134-5138 (2011).