Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2017

Supporting information

Highly Stable and Conductive PEDOT:PSS/Graphene Nanocomposites for

Biosensor Application in Aqueous Medium

Dongtao Liu^{1, ⊥}, Md. Mahbubur Rahman^{2, ⊥}, Chuangye Ge¹, Jaecheon Kim¹, Jae-Joon Lee^{1,*}

¹Department of Energy & Materials Engineering, Dongguk University, Seoul, 100-715, Korea ²Nanotechnology Research Center and Department of Applied Life Science, College of Biomedical and Health Science, Konkuk University, Chungju 380-701, Korea

[⊥]Both the authors contributed equally

* Author to whom correspondence should be addressed; E-mail: jjlee@dongguk.edu.

Tel.: 82-2-2260-8513.



Figure S1: Schematic illustration of the fabrication of PPG_{AT} onto FTO coated glass substrate.



Figure S2: Optical microscopic images (Magnification: ×100) of (a) GNP_{UT} , (b) GNP_{WT} , (c) PPG_{UT} , (d) PPG_{UT-WT} , (e) PPG_{AT} , and (f) PPG_{AT-WT} .



Figure S3: SEM images of (a) PP_{UT} , (b) PP_{UT-WT} , (c) PP_{AT} , and (d) PP_{AT-WT} .



Figure S4: Survey XPS spectra of different samples.



Figure S5: Core-level S 2p peaks of (a) PP_{UT} and (b) PP_{AT} and O 1s peaks of (c) PP_{UT} and (d) PP_{AT} electrode. The dotted lines indicate the experimental data and the solid lines denote the fitted curves.



Figure S6: Survey XPS spectra of PP_{UT} and PP_{AT} electrodes.



Figure S7: CVs of GNP_{UT}/FTO , PP_{UT}/FTO , and PP_{AT}/FTO electrodes in PBS (pH 7.0) containing $[Fe(CN)_6]^{3-/4-}$ (5 mM each) at a scan rate of 100 mV/s.



Figure S8: Raman spectra of GNPs before and after ball milling.



Figure S9: Consecutive CVs (scan rate 100mV/s) (10th - 90th) of (a) PPG_{UT}/FTO and (b) PPG_{AT}/FTO electrodes and repetitively measured EIS plots of (c) PPG_{UT}/FTO and (d) PPG_{AT}/FTO electrodes in PBS (pH 7.0) containing $[Fe(CN)_6]^{3-/4-}$ (5 mM each). Each of the EIS plot was measured after performing 10 consecutive CV sweeping in the potential range between -0.3 to +0.7 V at a scan rate 100 mV/s.



Figure S10: CVs of PPG_{UT}/FTO and PPG_{AT}/FTO electrodes in PBS (pH 7.0) containing (a) 1 mM AA, (b) 1 mM DA, and (c) 1 mM UA at a scan rate 100 mV/s.



Figure S11: CVs of 1 mM DA (in PBS, pH 7.0) at PPG_{AT}/FTO with varying scan rates (a→h: 25, 50, 75, 100, 125, 150, 200, 300 mV/s).



Figure S12: (a) Consecutive CVs of 1 mM DA (in PBS, pH 7.0) at the PPG_{AT}/FTO sensor at a scan rate of 100 mV/s. (b) DPV responses of three different PPG_{AT}/FTO sensor in a mixture solution of AA (2 mM), DA (30 μ M), and UA (30 μ M).



Figure S13: DPV responses of DA and UA (30 μ M each) at PPG_{AT}/FTO sensor in the absence and presence of AA (2 mM), glucose (1 mM), NaNO₃ (1 mM) and CA (1 mM).

Table S1: Comparison of the sensing performance of PPG_{AT}/FTO sensor for DA detection withsome reported nanocomposites based sensors.

Electrode	Method	Linearity		Detection	Ref.	
		(µM)		limit(µM)		
Electrochemistry based sensor						
^a SPGNE	DPV	0.5~2000 0.		0.12		[S1]
^b GO-BAMB-Co(OH) ₂ /GCE	DPV	3~100		0.4		[S2]
° AGONF	CV	2~30		° 2.2		[S3]
^d TGONF				^d 2.5		
^e GLY-GQDs-Ce (IV)	DPV	0.03~16.7		0.025		[S4]
f rGO-Co ₃ O ₄ /GCE	CA	0~30		0.389		[S5]
^g GR/p-AHNSA/SPCs	SWV	0.05~150		0.003		[S6]
^h PA/GO/GCE	DPV	0.05~10		0.016		[S7]
ⁱ CdTe QDs-Gr/GCE	DPV 1~500			0.33	[S8]	
Tyrosinase/NiO/ITO	CV	2~100		1.04		[S9]
Graphene nanobelts/GCE	DPV	2~200		0.58		[S10]
GO-	CA	0.5~2500		0.17		[S11]
MWCNT/MnO ₂ /AuNP/GCE						
Nitrogen doping graphene/GCE	E DPV	0.5~170		0.25	[S12]	
^j P(TBA _{0.50} Th _{0.50})	EIS	7.8~125		0.3	[S13]	
rGO/CPE	CPE DPV 2.0~2×10 ⁴)4	0.136	[S14]	
Poly(thionine)/GCE	DPV	5~30		0.7	[S15]	
Graphene/Au/GCE	DPV	5~1000		1.86		[S16]
Fe ₃ O ₄ /rGO/GCE	DPV	0.5~100		0.12		[S17]
Acid treated GPP/FTO	DPV	1~30		0.105]	This work
Other technologies based sensor						
- UV	absorbance	0.05~6.00	µg/mL	0.045	µg/mL	[S18]
- Capillary	Electrophoresis	0.001~0.3	μΜ	0.10	nM	[S19]
- Chem	- Chemiluminescence		nM	0.03	nM	[S20]
- ^k L	- ^k LC-MS-MS		μg/L	2.5	μg/L	[S21]
-	¹ LacOF		pg/mL	2.1	pg/mL	[S22]
- m]	^m HPLC-FD		µg/mL	0.031	μg/mL	[823]
- ⁿ I	- ⁿ HPLC-ED		pg/mL	5.2	pg/mL	[S22]
- FI	- Fluorescent		μΜ	40	nM	[S24]
- Neuroc	- Neurochemical Probe		μΜ	-	-	[825]
- ° GQI	° GQD-Fluorescent		μΜ	0.0025	μΜ	[S26]

^aScreen printing graphene electrode; ^b1,4-bis(aminomethyl)benzene (BAMB) and cobalt hydroxide (Co(OH)₂) at graphene oxide (GO); ^cAlanine functionalized GO nanoflakes; ^dTyrosine functionalized GO nanoflakes; ^ePhotoluminescent glycine functionalized graphene quantum dots; ^fCobalt oxide nanograindecorated reduced graphene oxide; ^gGraphene (GR) and poly 4-amino-3-hydroxy-1-naphthalenesulfonic acid modified screen printed carbon sensor; ^hPhytic acid/graphene oxide; ⁱQuantum dots CdTe and graphene; ^jPolymerization of 3-Thienylboronic acid and copolymer Thiophene; ^k Liquid chromatography-mass spectrometry- mass spectrometry; ¹ Laccase-Optical fiber biosensor; ^m High Performance Liquid Chromatography with fluorimetric detection; ⁿ High Performance Liquid Chromatography with electrochemical detection.^o graphene quantum dot-Fluorescent.

Reference

- S1. J. Ping, J. Wu, Y. Wang and Y. Ying, Biosens. Bioelectron., 2012, 34, 70-76.
- S2. A. Ejaz, Y. Joo and S. Jeon, Sens Actuators B Chem., 2017, 240, 297-307.
- S3. M. Kumar, B. E. K. Swamy, M. H. M. Asif and C. C. Viswanath, Appl. Surf. Sci., 2017, 399,

411-419.

- S4. R. Liu, R. Yang, C. Qu, H. Mao, Y. Hu, J. Li and L. Qu, Sens Actuators B Chem., 2017, 241, 644-651.
- S5. A. Numan, M. M. Shahid, F. S. Omar, K. Ramesh and S. Ramesh, *Sens Actuators B Chem.*, 2017, **238**, 1043-1051.
- S6. M. Raj, P. Gupta, R. N. Goyal and Y.-B. Shim, *Sens Actuators B Chem.*, 2017, 239, 993-1002.
- S7. D. Wang, F. Xu, J. Hu and M. Lin, *Mater Sci Eng C Mater Biol Appl.*, 2017, 71, 1086-1089.
- S8. H. W. Yu, J. H. Jiang, Z. Zhang, G. C. Wan, Z. Y. Liu, D. Chang and H. Z. Pan, Anal. Biochem., 2017, 519, 92-99.
- S9. A. Roychoudhury, S. Basu and S. K. Jha, Biosens. Bioelectron., 2016, 84, 72-81.
- S10. P. K. Kannan, S. A. Moshkalev and C. S. Rout, Nanotechnology, 2016, 27, 075504.
- S11. D. Rao, X. Zhang, Q. Sheng and J. Zheng, Microchim. Acta., 2016, 183, 2597-2604.

S12. Z. H. Sheng, X. Q. Zheng, J. Y. Xu, W. J. Bao, F. B. Wang and X. H. Xia, *Biosens. Bioelectron.*, 2012, **34**, 125-131.

- S13. M. Dervisevic, M. Senel and E. Cevik *Mater Sci Eng C Mater Biol Appl.*, 2017, 72, 641-649.
- S14. A. Benvidi, S. Dalirnasab, S. Jahanbani, M. D. Tezerjani, M. M. Ardakani, B.-B. F.Mirjalili and R. Zare, *Electroanalysis*, 2016, 28, 1625-1633.
- S15. A.J.S. Ahammad, X.B. Li, M.M. Rahman, K.-M. Noh, J.-J. Lee, *Int. J. Electrochem. Sci.*, 2013, 8, 7806-7815.
- S16. J. Li, J. Yang, Z. Yang, Y. Li, S. Yu, Q. Xu and X. Hu, Anal Methods., 2012, 4, 1725-1728.
- S17. T. Peik-See, A. Pandikumar, H. Nay-Ming, L. Hong-Ngee and Y. Sulaiman, *Sensors*, 2014, 14, 15227-15243.
- S18. L. Guo, Y. Zhang, Q. Li, Anal Sci, 2009, 25, 1451-1455.
- S19. H. Li, C. Li, Z.Y. Yan, J. Yang, H. Chen, J. Neurosci. Methods, 2010, 189, 162-168.
- S20. X. Xu, H. Shi, L. Ma, W. Kang, S. Li, Luminescence, 2011, 26, 93-100.
- S21. A. El-Beqqali, A. Kussak, M. Abdel-Rehim, J. Sep. Sci, 2007, 30, 421-424.
- S22. L.I. Silva, F.D. Ferreira, A.C. Freitas, T.A. Rocha-Santos, A.C. Duarte, *Talanta*, 2009, 80, 853-857.
- S23. G.E. De Benedetto, D. Fico, A. Pennetta, C. Malitesta, G. Nicolardi, D.D. Lofrumento, F. De Nuccio, V. La Pesa, *J. Pharm. Biomed. Anal*, 2014, 98, 266-270.
- S34. A. Yildirim, M. Bayindir, Anal. Chem, 2014, 86, 5508-5512.
- S25. H.N. Schwerdt, M.J. Kim, S. Amemori, D. Homma, T. Yoshida, H. Shimazu, H.
 Yerramreddy, E. Karasan, R. Langer, A.M. Graybiel, M.J. Cima, *Lab Chip*, 2017, 17, 1104-1115.
 S26. X. Zhou, X. Gao, F. Song, C. Wang, F. Chu, S. Wu, *Appl. Surf. Sci*, 2017, 423, 810-816.