

Electronic Supplementary Information

Amplified electrochemical sensor employing a polymeric film and graphene quantum dots/multiwall carbon nanotubes in deep eutectic solvent for sensitive analysis of paracetamol and 4-aminophenol

Nastaran Arab,^a Lida Fotouhi,^{a,b*} Andrea Salis,^{c,d} and Parisa Seyed Dorraji^a

Comment [S]: The second affiliation was added in the article text for corresponding author.

Comment [S]: The second affiliation was added in the article text for corresponding author.

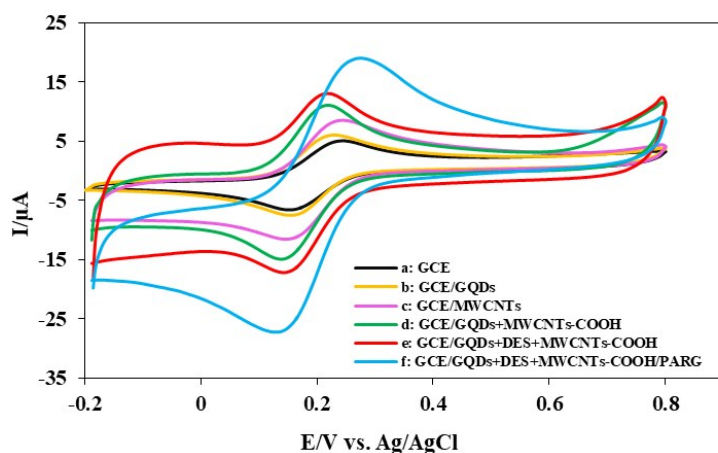


Figure S1 Cyclic voltammograms of 1.0 mmol L⁻¹ of K₃[Fe(CN)₆] containing 0.1 mol L⁻¹ KCl (scan rate: 0.1 V s⁻¹) recorded on bare GCE (a) GCE/GQDs (b), GCE/MWCNTs-COOH (c), GCE/GQDs+MWCNTs-COOH (d) GCE/GQDs+DES+MWCNTs-COOH (e) and GCE/GQDs+DES+MWCNTs-COOH/PARG (f).

^a Department of Chemistry, Faculty of Physics and Chemistry, Alzahra University, Tehran, Iran

^b Analytical and Bioanalytical Research Centre (ABRC), Alzahra University, Tehran, Iran

^c Department of Chemical and Geological Sciences, University of Cagliari, Cittadella Universitaria, SS 554 bivio Sestu, 09042 Monserrato (CA) (Italy)

^d Consorzio Interuniversitario Sistemi a Grande Interfase (CSGI), Florence (Italy).

^e Corresponding author; Lida Fotouhi, E-mail: lfotouhi@alzahra.ac.ir, Fax: +98 21 88035187; Tel: +9821 88044040

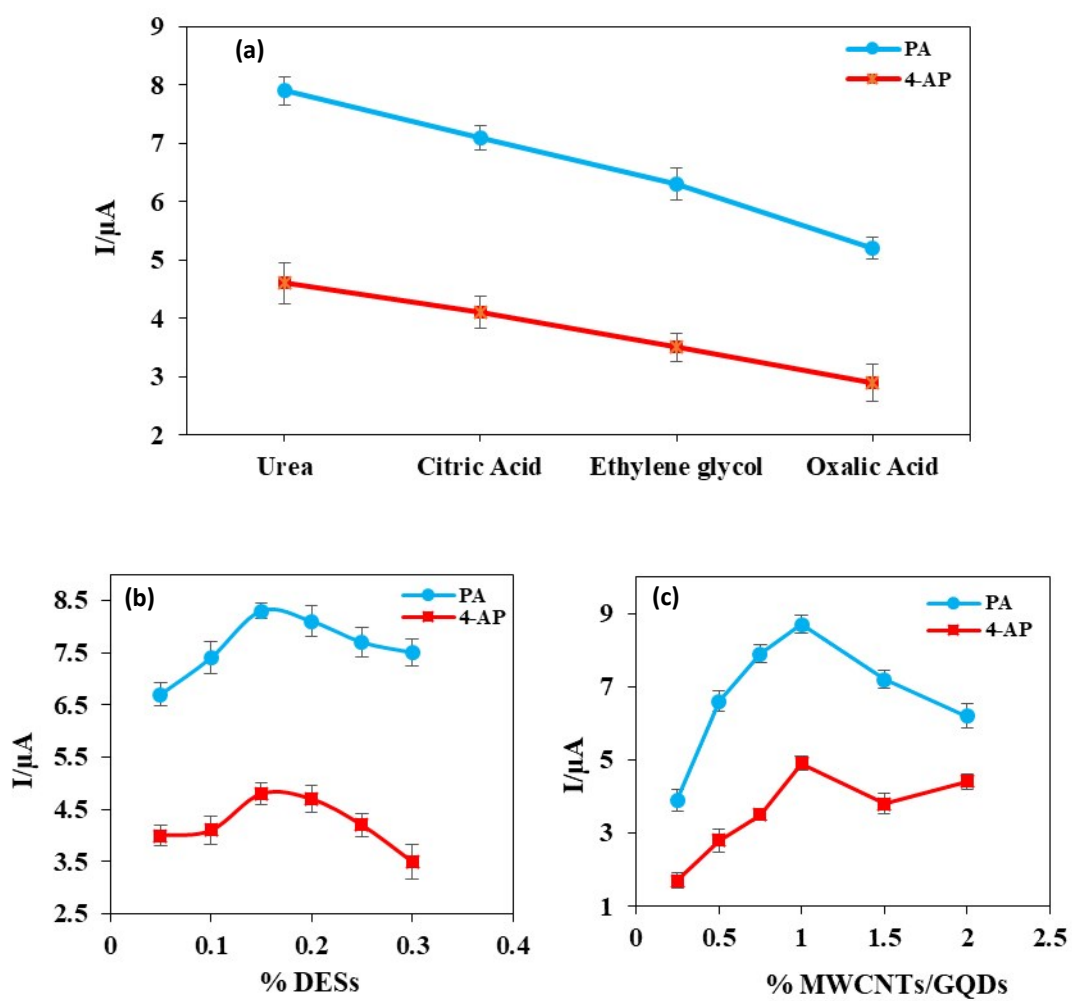


Figure S2 Effects of type of DESs (a) Effects of the amount of DESs (b), and effects of weight ratio of MWCNTs:GQDs (c) on the oxidation peak current of $20.0 \mu\text{mol L}^{-1}$ PA and 4-AP in 0.1mol L^{-1} PBS (pH 6.0) at GCE/GQDs+DES+MWCNTs-COOH/PARG, scan rate: 10 mV s^{-1} .

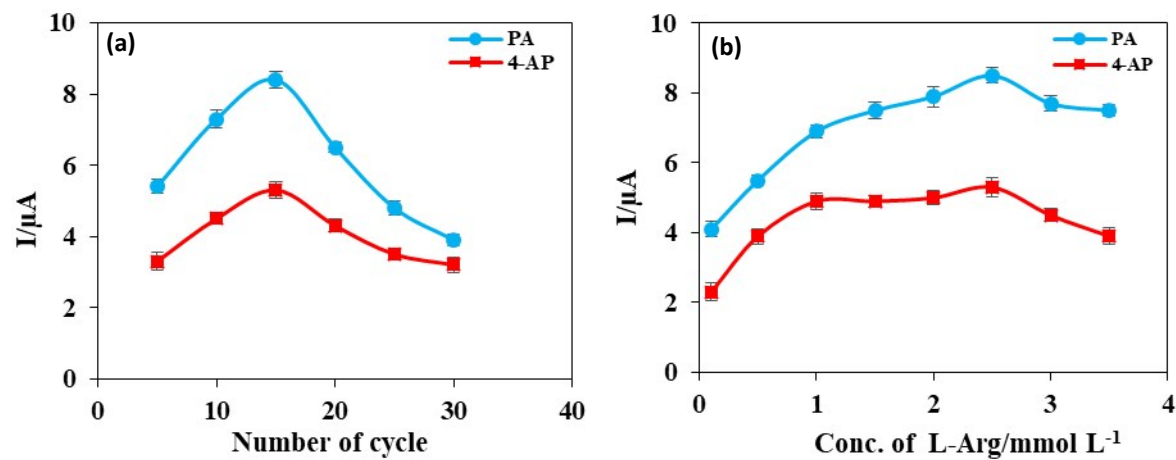


Figure S3 Effects of number of cycles (a) and concentration of L-Arg (b) in the electropolymerization step on the oxidation peak current of 20.0 $\mu\text{mol L}^{-1}$ PA and 4-AP in 0.1 mol L^{-1} PBS (pH 6.0) at GCE/GQDs+DES+MWCNTs-COOH/PARG, scan rate: 100 mV s^{-1} .

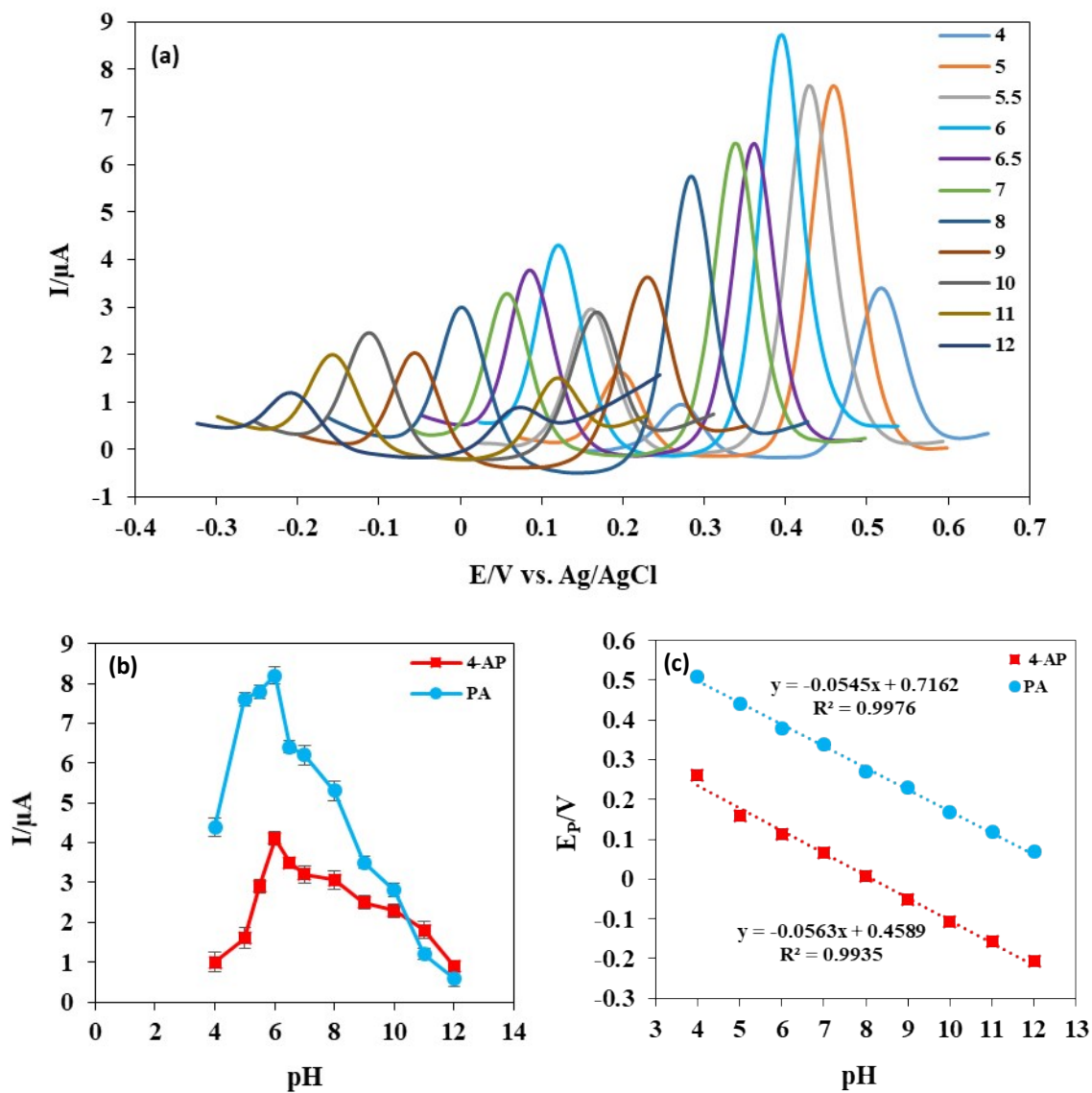


Figure S4 DPV curves of 20.0 $\mu\text{mol L}^{-1}$ PA and 4-AP on GCE/GQDs+DES+MWCNTs-COOH/PARG at different pH values (from 4.0 to 12.0), Scan rate: 0.01 V s^{-1} (a). Dependence of the oxidation peak current of PA and 4-AP to the solution pH (b). Dependence of the oxidation peak potential of PA and 4-AP to the solution pH.

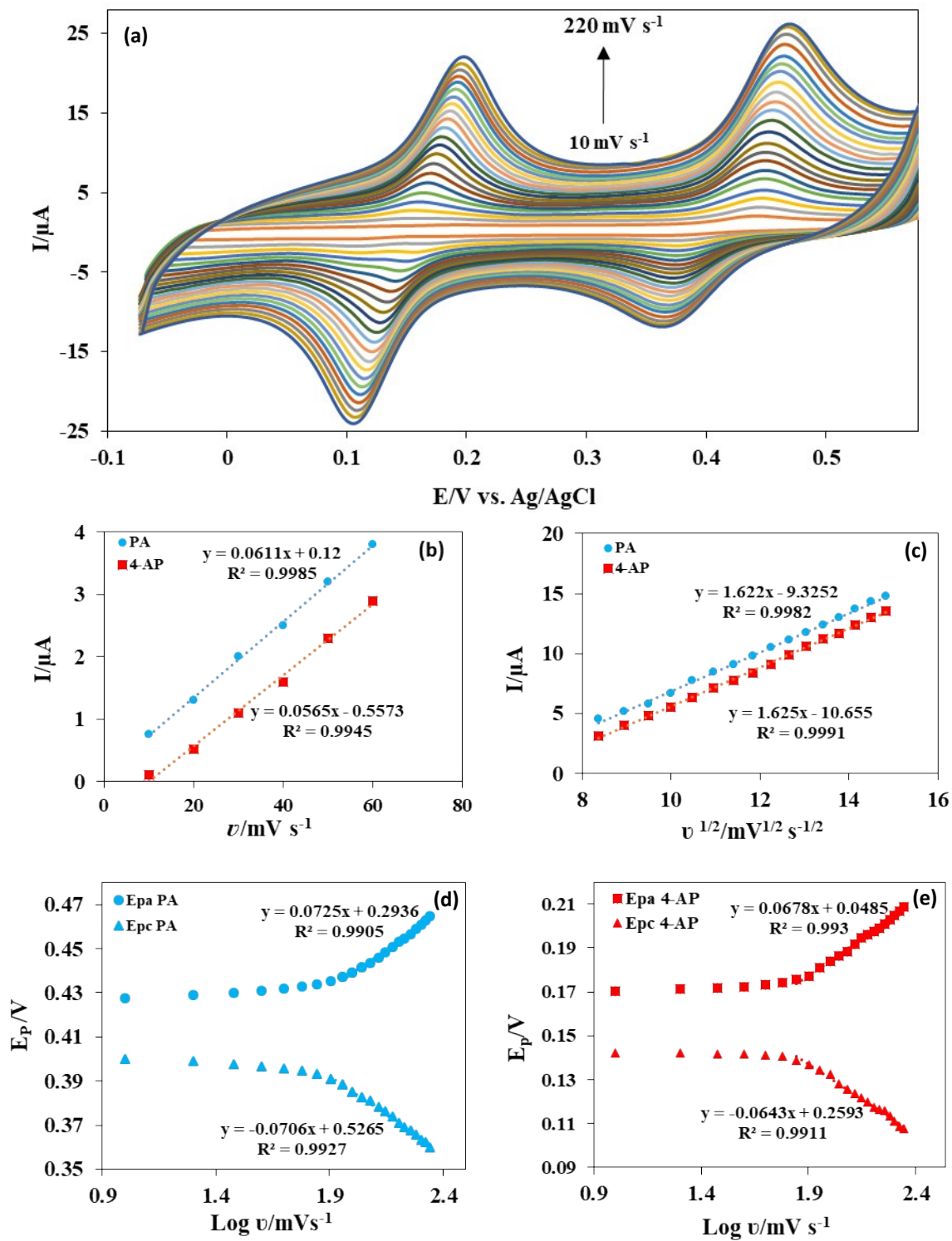


Figure S5 Cyclic voltammograms of 20.0 $\mu\text{mol L}^{-1}$ PA and 4-AP in 0.1mol L^{-1} PBS (pH 6.0) on GCE/GQDs+DES+MWCNTs-COOH/PARG at different scan rate (from 10 to 220 mV s^{-1}) (a). Dependence of the oxidation peak currents of PA and 4-AP with scan rate (b). Dependence of the oxidation peak currents of PA and 4-AP with square root of scan rate (c). Dependence of the peak potential of PA with log scan rate (d). Dependence of the peak potential of 4-AP with log scan rate (e).

Table S1: Comparison of the characteristics of reported electrochemical methods for simultaneous determination of PA and 4-AP.

Electrode	LDR ($\mu\text{mol L}^{-1}$)		LOD ($\mu\text{mol L}^{-1}$)		Sensitivity ($\mu\text{A. } \mu\text{mol}^{-1}\text{L}$)		[Ref.]
	PA	4-AP	PA	4-AP	PA	4-AP	
Co ₃ Ni-MoO ₂ /MoC/GCE	0.05-200.0	0.05-140.0	0.013	0.012	0.1530	0.2633	[1]
CuO-Au/MWCNT/GCE	0.2-6.0	0.5-1.6	0.016	0.1	0.049	35.02	[2]
MoS ₂ @NHCSs/GCE	0.05-20	0.05-20	0.02	0.013	0.2712	0.1978	[3]
CS/Au/Pd/Rgo/GCE	1.0-250	1.0-300	0.3	0.12	0.052	0.1342	[4]
AuNPs/SDS-LDH/GCE	1.0-400.0	0.5-200.0	0.13	-	0.02	0.03	[5]
CILE	2.0-2200	0.3-1000	0.5	0.1	-	-	[6]
PEDOT/GCE	1.0-100.0	4.0-320.0	0.4	1.2	0.284	0.094	[7]
CdSe/GCE	0.5-800.0	1.0-900.0	0.1	-	0.025	0.0147	[8]
Cr-SBC/GCE	0.008-0.125	0.008-0.133	0.0068	0.0056	0.0000411	0.000045	[9]
Poly(PE)Bis-8(hq)/GCE	0.5-200	0.3-150	0.07	0.45	0.0431	0.096	[10]
Paper based devices	50.0-2000	50.0-2000	25.0	10.0	-	-	[11]
RGO-TiN/GCE	0.06-660	0.05-520	0.02	0.013	0.1304	0.2102	[12]
CoTATPAPc/GCE	0.02-0.34	0.02-0.34	0.0063	0.0	248.2	278.1	[13]
GCE/GQDs+DES+MWCNTs-COOH/PARG	0.030-110	0.050-100	0.010	0.016	0.2788	0.2511	This work

MoC: molybdenum carbide; rGO: reduced graphene oxide. NHCS: nitrogen-doped hollow carbon spheres, SDS: sodium dodecyl sulfate; LDH: layered double hydroxide. CILE: carbon ionic liquid electrode; PEDOT: poly (3, 4-ethylenedioxythiophene); Cr-SBC: chromium schiff base complex; poly (PE) bis-8(hq): Poly (2, 2'-(1 4-phenylenedivinylene) bis-8-hydroxyquinaldine); TiN: titanium nitride; CoTATPAPc: cobalt (II) tetra 2-amino-3-(thio)propanoic acid phthalocyanine complex.

Reference

1. Y. Dong, M. Zhou, L. Zhang, 3D multiporous Co, N co-doped MoO₂/MoC nanorods hybrids as improved electrode materials for highly sensitive simultaneous determination of acetaminophen and 4-aminophenol, *Electrochim. Acta*, 2019, **302**, 56-64.
2. P. Shaikshavali, T. M. Reddy, V. N. Palakollu, R. Karpoormath, Y. S. Rao, G. Venkataprasad, T. Venu Gopal, P. Gopal, Multi walled carbon nanotubes supported CuO-Au hybrid nanocomposite for the effective application towards the electrochemical determination of Acetaminophen and 4-Aminophenol, *Synth. Met*, 2019, **252**, 29-39.
3. D. Zhang, J. Qian, Y. Yi, O. J. Kingsford, G. Zhu, Nitrogen-doped hollow carbon nanospheres wrapped with MoS₂ nanosheets for simultaneous electrochemical determination of acetaminophen and 4-aminophenol, *J. Electroanal. Chem.*, 2019, **847**, 113229.
4. H. Wang, S. Zhang, S. Li, J. Qu, Electrochemical sensor based on palladium-reduced graphene oxide modified with gold nanoparticles for simultaneous determination of acetaminophen and 4-aminophenol, *Talanta*, 2018, **178**, 188-194.
5. H. Yin, K. Shang, X. Meng, S. Ai, Voltammetric sensing of paracetamol, dopamine and 4-aminophenol at a glassy carbon electrode coated with gold nanoparticles and an organophilic layered double hydroxide, *Microchim. Acta*, 2011, **175**, 39.
6. A. Safavi, N. Maleki, O. Moradlou, A selective and sensitive method for simultaneous determination of traces of paracetamol and p-aminophenol in pharmaceuticals using carbon ionic liquid electrode, *Electroanalysis*, 2008, **20**, 2158-2162.
7. S. Mehretie, S. Admassie, T. Hunde, M. Tessema, T. Solomon, Simultaneous determination of N-acetyl-p-aminophenol and p-aminophenol with poly (3, 4-ethylenedioxythiophene) modified glassy carbon electrode, *Talanta*, 2011, **85**, 1376-1382.
8. H. Yin, X. Meng, Z. Xu, L. Chen, S. Ai, Electrochemical behavior of phenacetin on CdSe microspheres modified glassy carbon electrode and its simultaneous determination with paracetamol and 4-aminophenol, *Anal. Methods.*, 2012, **4**, 1445-1451.
9. Q. Liang, Z. Liu, C. Liang, G.C. Han, S. Zhang, X.Z. Feng, Electrochemical Simultaneous Detection of Paracetamol and 4-aminophenol Based on bis-Schiff Base Cobalt Complex, *Int. J. Electrochem. Sci.*, 2019, **14**, 7178-7201.
10. H. Filik, S. Aydar, A.A. Avan, Poly (2, 2'-(1, 4-phenylenedivinylene) Bis-8-hydroxyquinoline) Modified Glassy Carbon Electrode for the Simultaneous Determination of Paracetamol and p-Aminophenol, *Anal. Lett.*, 2015, **48**, 2581-2596.
11. L.Y. Shiroma, M. Santhiago, A.L. Gobbi, L.T. Kubota, Separation and electrochemical detection of paracetamol and 4-aminophenol in a paper-based microfluidic device, *Anal. Chim. Acta*, 2012, **725**, 44-50.
12. F.Y. Kong, S.X. Gu, J.Y. Wang, H.L. Fang, W. Wang, Facile green synthesis of graphene-titanium nitride hybrid nanostructure for the simultaneous determination of acetaminophen and 4-aminophenol, *Sens. Actuator B-Chem.*, 2015, **213**, 397-403.
13. M. Palanna, I. Mohammed, S. Aralekallu, M. Nemakal, L.K. Sannegowda, Simultaneous detection of paracetamol and 4-aminophenol at nanomolar levels using biocompatible cysteine-substituted phthalocyanine, *New J. Chem.*, 2020, **44**, 1294-1306.