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Praseodymium ferrite nano-particles based modified electrode and its application in determination of dopamine

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ABSTRACT

The present works report the graphite based electrochemical sensor modified by nano-sized praseodymium ferrite (np-$PrFeO_3$) materials for the detection of dopamine. The combustion technique was used to synthesize these nanomaterials of np-$PrFeO_3$ using praseodymium oxide and ferric nitrate as precursor materials. The nanomaterials were characterized by field emission scanning electron microscopy and transmission electron microscopy techniques. The crystallite sizes of synthesized nanoparticles (nps) were in the range from 40-45 nm with cubic crystal system. Cyclic voltammetry and Differential pulse voltammetry techniques were used to study the electrochemical property and were observed to be superior to earlier reports. The limit of detection of dopamine at $PrFeO_3$/GP electrode was 600 nM with 5 to 200 µM for linearity range. The phosphate buffer solution of pH 6.0 was used for all experimental work with maintaining the scan rate 100mVs^{-1} and 50mVs^{-1} for cyclic voltammetry and Differential pulse voltammetry, respectively.

Keywords: *Dopamine; Sensor; Cyclic Voltammetry; Differential pulse voltammetry; np-$PrFeO_3$.*

1. INTRODUCTION

Dopamine [Fig 1, DA], a biologically available important molecule recognized for its "inhibitory neurotransmitter", and generated in the mid-brain "Dargic Neurons" connected to the brain such as memory, propulsion, understanding and cognitive behavior. Being a hormone, it not often activates the development of the central and peripheral nervous system throughout physical activity [1, 2] however it is also accountable for the emotional and endocrine process. Small DA concentrations can resulted in to burning mouth syndrome [3], unstable leg syndrome [4], senile dementia, fibromyalgia [5, 6], and uncommon depression [7]. Reduced DA in the cerebral zone could lead to Parkinson's disorder [8] whereas higher DA level may affect sympathetic nervous system and trigger unusual blood pressure and heart rate census. It becomes evident to identify biomolecules such as DA in bio-fluids that can serve a significant part in regulating drug efficacy.

Several analytical techniques have been used for the identification of DA in bio-fluids and dosage forms, such as "titmetry [9], high-performance liquid chromatography [10-12], spectrophotometry [13], chemiluminescence [14], gas-chromatography-mass spectrometry [15] and ultraviolet spectrophotometry" [16]. Nevertheless, these techniques are less suitable for clinical practics, because of their cumbersome extraction method. On the other hand, electrochemical techniques have gained considerable interest due to their high selectivity, reasonable expense, simple processing and less laborious design [17,18] for the identification of DA in bio-fluids.

The nano materials with porous morphology and larger surface area have been extensively employed as electrode material for the identification of pharmaceutically important compounds in biological fluids and dosage formulations [19-22]. A number of different type of electrodes including (MWCNTs) modified carbon paste electrode [23], MWCNTs "graphene oxide nanocomposite-modified glassy carbon electrode" (GCE) [24], activated graphene-Nafion modified GCE [25], carbon paste electrode modified with 4-porphyrin [26], and "tyrosine glassy carbon electrode modified with a nano-composite" [27] were established for identification of DA.

Alothman *et al*. reported "functionalized MWCNTs-modified GCE for the simultaneous estimation of DA & paracetamol (PCM) [28]. Keeley *et al*. developed a thin pyrolytic carbon films based sensor for simultaneous electrochemical detection of DA and PCM [29].

To the best of author's knowledge, there is no report is available on the detection of DA using praseodymium ferrite nano-particles (np$PrFeO_3$/GP) electrode. Herein, we report an economical and efficient electrode designated as np-$PrFeO_3$ modified with graphite for the identification of DA. The electrode material was synthesized and characterized using several analytical techniques "Field Emission Scanning Electron Microscope" (FESEM), "transmission electron microscopy" (TEM) etc. The electrochemical activity of the modified electrode (np-$PrFeO_3$/GP) was investigated for the detection of DA.

2. MATERIALS AND METHODS

2.1. Chemical and reagents.

Praseodymium oxide (Pr_2O_3), ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), nitric acid (HNO_3), paraffin oil, ethanolamine ($HOCH_2CH_2NH_2$) and sugar (glucose, $C_6H_{12}O_6$) etc. were obtained from Merck (India) and graphite flakes and dopamine ($C_8H_{11}NO_2$) were

purchased from Sigma Aldrich, USA. All the reagents were of analytical grade and used without further purification. Double distilled water was used in all studies.

2.2. Synthesis of lanthanide orthoferrites nanoparticles (np).

Praseodymium oxide (Pr_2O_3) (1.0 mM) was dissolved in 50 mL of aq. nitric acid (3.5 mM) and warmed until a browinsh clear solution was obtained. After that ferric nitrite (1.0 mM), ethanolamine (1.7 mM) and sugar (2.5 mM) were added in the above solution and the mixture obtained was placed on hot plate at 150 ^oC until evaporated to dryness. A black fluffy mass obtained was calcined in muffle furnace at 800 ^oC for 6 h to get npPr_2O_3 orthoferrite nanocomposite.

2.3. Preparation of electrode.

Preparation of the electrode was carried out by mixing the graphite powder and praseodymium ferrites in the ratio 4:1 thoroughly in "mortar and pastel". Also few drops paraffin oil was added to get a uniform paste of the mixture. The paste was then filled in a capillary glass tube (2 mm i.d.) and packed firmly by pressing with metal rod. A Pt wire was introduced from the rear-side of the capillary tube for electrical connection. Similarly, bare GP electrode was fabricated using the same procedure. The surface of electrode was cleaned by using 0.3 mM and 0.05 mM Al_2O_3 slurries successively. Lastly, the electrodes were rinsed with ethanol and dried under N_2 gas prior to investigation.

2.4. Apparatus and measurements.

FESEM model (Hitachi SU-8010) and TEM model (FP 5032/21 Tecnai G2 30 S-TWIN (serial No. 9921621/D934) Model No. 943205032211 made in Czech Republic) were used for the morphology and size of synthesized nanomaterials. All electrochemical investigations were performed using "three electrode systems by Autolab Potentiostate/Galvanostate 101" (Netherlands). In this three electrode system the Ag/AgCl electrode, Pt electrode and $PrFeO_3$/GP electrodes were used as a reference, counter and the working electrode, respectively. The electrochemical study was carried out in phosphate buffer (0.1M, pH 6.0) at 25±2 ^oC with a scan rate 100 mVS^{-1} for CV & 50 mVS^{-1} for DPV in the voltage range from 0.0 to 0.6V and 0.15 to 0.4 V, respectively for CV & DPV experiments.

3. RESULTS

3.1. FESEM and TEM analysis of $PrFeO_3$ nanoparticles.

FESEM analysis was carried out for surface studies of synthesized praseodymium ferrite nanoparticles (np-$PrFeO_3$). Fig 1a demonstrated a "uniform cubic structural morphology" with a fine size distribution of the materials. Fig 1b presented a TEM analysis that also supported the FESEM results.

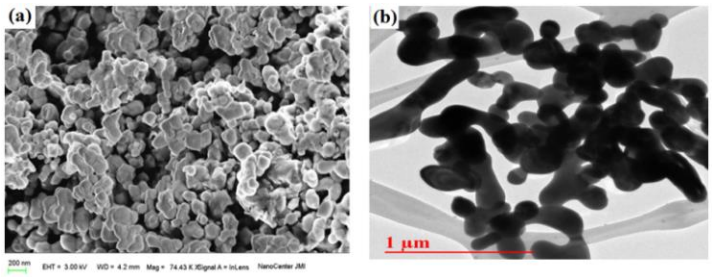

Figure 1. (a) FESEM image and (b) TEM image of $PrFeO_3$ nano materials

3.2. Electrochemical studies of $PrFeO_3$/GP electrode.

Firstly, the electrochemical measurements of newly prepared $PrFeO_3$/GP electrode and the bare GP electrode were performed by applying the standard redox system $[Fe(CN)_6]^{-4}$/ $[Fe(CN)_6]^{-3}$ as reference. The comparative CV plots of 3 mM $K_4[Fe(CN)_6]$ solution at bare GP, $PrFeO_3$/GP electrodes are represented in Fig. 2.

Certain factors, such as "particle size, surface defects, electrochemical band gap, structure, optical band gap & capping ligand" carry essential functions in the voltammetric study of semiconductor substances [31-35]. Nanomaterials are extremely relevant for electro-chemical research for such purposes. Fig. 2 represents CV plots for bare GP and $PrFeO_3$/GP obtained at 100 mV sec^{-1} scan rates using phosphate buffer (pH 6.0). The peak potential separation (ΔEp) at $PrFeO_3$/GP was observed 250 mV and at bare GP electrode it was 429mV. As shown by "Velasco equation", the lower value of ΔEp implies the quicker electronic movement through the electrode surface and analyte.

Based on the correlation of prepared electrodes to bare GP electrode, np-PrFeO3/GP electrode can be assumed to be better for electron transport over GP. CV analysis for DA indicates that the peak oxidation currents at the PrFeO3/GP electrode were observed to be 3.506 and that is approximately 1.5 times greater than bare GP.

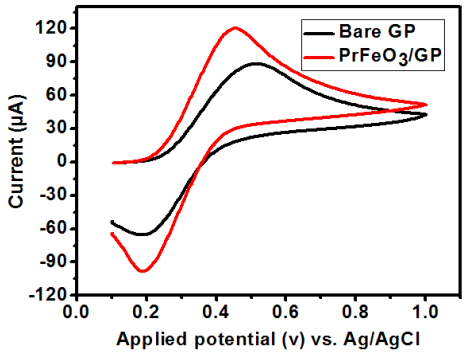

Figure 2. "Cyclic Voltammogram obtained for 3.0 mM $Fe(CN)_6^{-4}$ at $PrFeO_3$/GP and bare GP electrodes at 100 $mVsec^{-1}$ scan rate with phosphate buffer solution of pH 6.0".

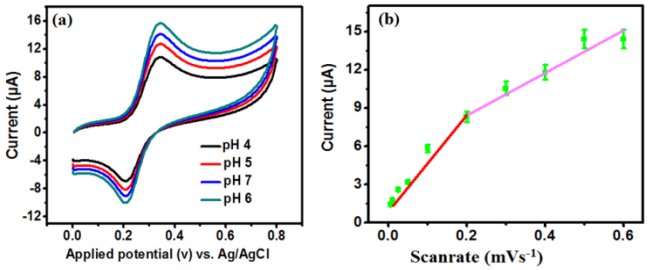

Figure 3. (a) pH study with making variation from pH 4 to 7 and (b) Current in µA during scan rate study with making variation from 5 to 600 mVS^{-1} using 100 µM concentration of dopamine

3.3. Effect of the scan rate and pH on the oxidation of DA

The effect of scanning rate for electro-catalytic oxidation of DA was examined by varying the scan rates from 5 mVs^{-1} to 600 mVs^{-1} in CV technique. The results obtained indicated a linear increase in the peak current with an increase of scan rate. Fig. 3b displays diffusion regulated at the electrode surface during the oxidation phase. The pH of supporting electrolyte serves as a critical part in electrochemical molecular oxidation. To investigate the effect of pH on DA oxidation, pH of 0.1 M phosphate buffer solution varies in the range between 4.0 and 7.0.

It was observed that when the pH was increased from 4.0 to 6.0, the peak currents of DA also get increased and then decreased with a further increase in pH value. As the highest peak current value at npPrFeO$_3$/GP was observed with pH 6.0, the buffer with pH 6.0 was taken as standard for all other studies. Fig. 3a displays the oxidation behavior at different pH.

3.4. Electrocatalytic oxidation of DA at PrFeO$_3$/GP electrode.

The electro-catalytic activity of modified electrodes was determined by CV and DPV techniques. The CV and DPV plots for the np-PrFeO$_3$/Gp electrode and bare GP electrode are displayed in Fig. 4.

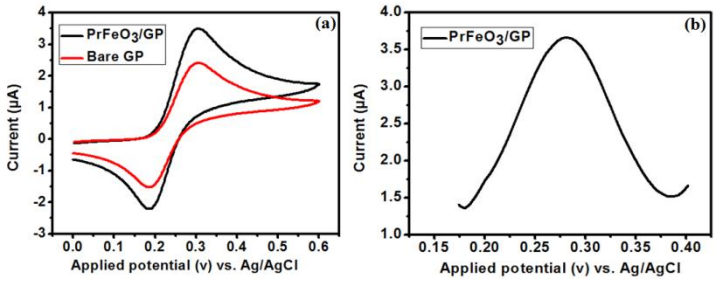

Figure 4. (a) Cyclic voltamogram and (b) diffrantial pule voltammogram at PrFeO$_3$/GP electrode using 100 µM concentration of dopamine in 0.1(M) phosphate buffer pH 6.0 for CV, scan rate 100 mVs^{-1} and for DPV, scan rate 50 mVs^{-1}.

The results obtained from the above study indicated that the oxidation peak potential at bare GP electrode and PrFeO$_3$/GP electrode were 305 mV for DA.

3.5. Comparison of present study with literature

A comparison of the current electrode with the literature reported electrode is present in Table 1. It may be concluded that the newly developed npPrFeO$_3$/GP electrode is superior to the previously reported electrode for the detection of DA in sensitivity i.e. linearity range and lower detection limit.

Table 1. Comparison of sensitivity of praseodymium-ferrite modified graphite paste electrodes with other previously developed electrodes.

Modified Electrode	detection limit (nM)	Liner range (µM)	Ref.
f-MWCNT	800	3-200	[28]
Pyrolytic carbon films	2300	18-270	[29]
PrFeO$_3$/GP	600	5-200	Our Work

3.6. Repeatability, stability and reproducibility of electrodes.

To test the stability of the modified electrode (PrFeO$_3$/GP), it was stored at 30^o C ± 1^o C for a month. It was observed after storing for a month the electrode is capable of provides 95% retention sensitivity which further indicates the stability of electrode. The electrode behaviors were recorded for ten successive tests, and consistent output was observed which suggests strong repeatability of the method. Also a set of four electrodes were designed using a similar fabrication method to test reproducibility. The results of all four electrodes were identical, indicating strong reproducibility. Fig. 5 indicates the repeatability study with the four electrodes.

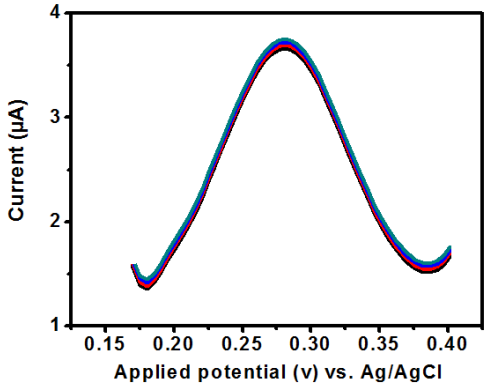

Figure 5. Repeatability of the prepared electrode by preparing four electrodes using 100 µM concentration of dopamine solution in 0.1(M) phosphate buffer pH 6.0 using scan rate @ 100 mVs^{-1}.

4. CONCLUSIONS

In this work, we have synthesized a nanocomposite of Lanthanide ferrite using the combustion technique and praseodymium oxide and ferric nitrate as precursor material. Further, the nanocomposite was characterized using various analytical techniques viz. FESEM, TEM etc. The crystallite sizes of synthesized nanoparticles were in the range from 40-45 nm with cubic crystal system. CV and DPV techniques were used for electrochemical behavior of synthesized materials. The detection limit of DA at PrFeO$_3$/GP electrode was 600 nM with 5 to 200 µM for linearity range. The phosphate buffer solution of pH 6.0 was used for all experimental work with maintaining the scan rate 100mVs^{-1} and 50mVs^{-1} for CV and DPV, respectively. The modified electrode displayed excellent sensitivity in detection of DA. The method developed can be used for the detection of related pharmaceutical both in dosage and in biological fluids.

5. REFERENCES

1. Wise, R.A. Dopamine, learning and motivation. *Nature reviews neuroscience* **2004,** *5*, 483-494, https://doi.org/10.1038/nrn1406.
2. Evtugyn, G.A.; Shamagsumova, R.V.; Sitdikov, R.R.; Stoikov, I.I.; Antipin, I.S.; Ageeva, M.V.; Hianik, T. Dopamine sensor based on a composite of silver nanoparticles implemented in the electroactive matrix of calixarenes. *Electroanalysis* **2011,** *23*, 2281-2289, https://doi.org/10.1002/elan.201100197.
3. Wood, P.B.; Schweinhardt, P.; Jaeger, E.; Dagher, A.; Hakyemez, H.; Rabiner, E.A.; Bushnell, M.C.; Chizh, B.A. Fibromyalgia patients show an abnormal dopamine response to pain. *European Journal of Neuroscience* **2007,** *25*, 3576-3582, https://doi.org/10.1111/j.1460-9568.2007.05623.x.
4. Červenka, S.; Pålhagen, S.E.; Comley, R.A.; Panagiotidis, G.; Cselényi, Z.; Matthews, J.C.; Lai, R.Y.; Halldin, C.; Farde, L. Support for dopaminergic hypoactivity in restless legs syndrome: a PET study on D2-receptor binding. *Brain* **2006,** *129*, 2017-2028, https://doi.org/10.1093/brain/awl163.
5. Dursun, Z.; Gelmez, B. Simultaneous determination of ascorbic acid, dopamine and uric acid at Pt nanoparticles decorated multiwall carbon nanotubes modified GCE. *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis* **2010**, *22*, 1106-1114, https://doi.org/10.1002/elan.200900525.
6. Yang, Z.; Huang, X.; Li, J.; Zhang, Y.; Yu, S.; Xu, Q.; Hu, X. Carbon nanotubes-functionalized urchin-like In 2 S 3 nanostructure for sensitive and selective electrochemical sensing of dopamine. *Microchimica Acta* **2012,** *177*, 381-387, https://doi.org/10.1007/s00604-012-0791-8.

7. Kollins, S.H.; Adcock, R.A. ADHD, altered dopamine neurotransmission, and disrupted reinforcement processes: implications for smoking and nicotine dependence. *Progress in Neuro-Psychopharmacology and Biological Psychiatry* **2014,** *52*, 70-78, https://doi.org/10.1016/j.pnpbp.2014.02.002.
8. Rice, M.E. Ascorbate regulation and its neuroprotective role in the brain. *Trends in neurosciences* **2000,** *23*, 209-216, https://doi.org/10.1016/S0166-2236(99)01543-X.
9. de Carvalho, R.M.; Freire, R.S.; Rath, S.; Kubota, L.T. Effects of EDTA on signal stability during electrochemical detection of acetaminophen. *Journal of pharmaceutical and biomedical analysis* **2004,** *34*, 871-878, https://doi.org/10.1016/j.jpba.2003.11.005.
10. Jensen, L.S.; Valentine, J.; Milne, R.; Evans, A. The quantification of paracetamol, paracetamol glucuronide and paracetamol sulphate in plasma and urine using a single high-performance liquid chromatography assay. *Journal of pharmaceutical and biomedical analysis* **2004,** *34*, 585-593, https://doi.org/10.1016/S0731-7085(03)00573-9.
11. Nebot, C.; Gibb, S.W.; Boyd, K.G. Quantification of human pharmaceuticals in water samples by high performance liquid chromatography–tandem mass spectrometry. *Analytica Chimica Acta* **2007,** *598*,87-94, https://doi.org/10.1016/j.aca.2007.07.029.
12. Baranowska, I.; Markowski, P.; Baranowski, J., Simultaneous determination of 11 drugs belonging to four different groups in human urine samples by reversed-phase high-performance liquid chromatography method. *Analytica chimica acta* **2006,** *570*, 46-58, https://doi.org/10.1016/j.aca.2006.04.002.
13. Khaskheli, A.R.; Shah, A.; Bhanger, M.I.; Niaz, A.; Mahesar, S. Simpler spectrophotometric assay of paracetamol in tablets and urine samples. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2007,** *68*, 747-751, https://doi.org/10.1016/j.saa.2006.12.055.
14. Easwaramoorthy, D.; Yu, Y.C.; Huang, H.J. Chemiluminescence detection of paracetamol by a luminol-permanganate based reaction. *Analytica chimica acta* **2001,** *439*, 95-100, https://doi.org/10.1016/S0003-2670(01)00968-0.
15. Speed, D.; Dickson, S.; Cairns, E.; Kim, N. Analysis of paracetamol using solid-phase extraction, deuterated internal standards, and gas chromatography-mass spectrometry. *Journal of analytical toxicology* **2001,** *25*, 198-202, https://doi.org/10.1093/jat/25.3.198.
16. Kumar Talluri, M.; Bairwa, M.K.; Theja Dugga, H.; Srinivas, R. Development and validation of RP-HPLC and ultraviolet spectrophotometric methods of analysis for simultaneous determination of paracetamol and lornoxicam in pharmaceutical dosage forms. *Journal of liquid chromatography & related technologies* **2012,** *35*, 129-140, https://doi.org/10.1080/10826076.2011.597064.
17. Chen, J.; He, P.; Bai, H.; He, S.; Zhang, T.; Zhang, X.; Dong, F. Poly (β-cyclodextrin)/carbon quantum dots modified glassy carbon electrode: preparation, characterization and simultaneous electrochemical determination of dopamine, uric acid and tryptophan. *Sensors and Actuators B: Chemical* **2017,** *252*, 9-16, https://doi.org/10.1016/j.snb.2017.05.096.
18. Huang, J.; Yue, G.; Yang, J.; Bai, S.; Hu, Q.; Wang, L. Design, synthesis and application of carboxylic multi-walled carbon nanotubes/tetrahexahedral platinum nanocrystals nanocomposites biosensor for simultaneous determination of guanine and adenine in DNA. *Journal of Electroanalytical Chemistry* **2017,** *801*, 536-544, https://doi.org/10.1016/j.jelechem.2017.07.048.
19. Pradhan, S.; Biswas, S.; Das, D.K.; Bhar, R.; Bandyopadhyay, R.; Pramanik, P. An efficient electrode for simultaneous determination of guanine and adenine using nano-sized lead telluride with graphene. *New Journal of Chemistry* **2018,** *42*, 564-573, https://doi.org/10.1039/C7NJ03308G.
20. Pradhan, S.; Das, R.; Biswas, S.; Das, D.K.; Bhar, R.; Bandyopadhyay, R.; Pramanik, P. Chemical synthesis of nanoparticles of nickel telluride and cobalt telluride and its electrochemical applications for determination of uric acid and adenine. *Electrochimica Acta* **2017,** *238*, 185-193, https://doi.org/10.1016/j.electacta.2017.04.023.
21. Kumar, Y.; Pradhan, S.; Pramanik, S.; Bandyopadhyay, R.; Das, D.K.; Pramanik, P. Efficient electrochemical detection of guanine, uric acid and their mixture by composite of nano-particles of lanthanides ortho-ferrite XFeO3 (X= La, Gd, Pr, Dy, Sm, Ce and Tb). *Journal of Electroanalytical Chemistry* **2018,** *830*, 95-105, https://doi.org/10.1016/j.jelechem.2018.10.021.
22. Kumar, Y.; Singh, P.; Pramanik, P.; Das, D. Electrochemical Determination of Guanine and Uric Acid using NdFeO3 Nps Modified Graphite Paste Electrode. *JSIR* **2019,***78*, 177-181.
23. Raoof, J.B.; Baghayeri, M.; Ojani, R. A high sensitive voltammetric sensor for qualitative and quantitative determination of phenobarbital as an antiepileptic drug in presence of acetaminophen. *Colloids and Surfaces B: Biointerfaces* **2012,** *95*, 121-128, https://doi.org/10.1016/j.colsurfb.2012.02.038.
24. Cheemalapati, S.; Palanisamy, S.; Mani, V.; Chen, S.M. Simultaneous electrochemical determination of dopamine and paracetamol on multiwalled carbon nanotubes/graphene oxide nanocomposite-modified glassy carbon electrode. *Talanta* **2013,** *117*, 297-304, https://doi.org/10.1016/j.talanta.2013.08.041.
25. Kim, D.; Lee, S.; Piao, Y. Electrochemical determination of dopamine and acetaminophen using activated graphene-Nafion modified glassy carbon electrode. *Journal of Electroanalytical Chemistry* **2017,** *794*, 221-228, https://doi.org/10.1016/j.jelechem.2017.04.018.
26. Kemmegne-Mbouguen, J.C.; Ngameni, E. Simultaneous quantification of dopamine, acetaminophen and tyrosine at carbon paste electrodes modified with porphyrin and clay. *Analytical Methods* **2017,** *9*, 4157-4166, https://doi.org/10.1039/C7AY01173C.
27. Chen, D.; Tian, C.; Li, X.; Li, Z.; Han, Z.; Zhai, C.; Quan, Y.; Cui, R.; Zhang, G. Electrochemical determination of dopamine using a glassy carbon electrode modified with a nanocomposite consisting of nanoporous platinum-yttrium and graphene. *Microchimica Acta* **2018,** *185*, https://doi.org/10.1007/s00604-017-2624-2.
28. Alothman, Z. A.; Bukhari, N.; Wabaidur, S. M.; Haider, S. Simultaneous electrochemical determination of dopamine and acetaminophen using multiwall carbon nanotubes modified glassy carbon electrode. *Sensors and Actuators B: Chemical* **2010,** *146*, 314-320, https://doi.org/10.1016/j.snb.2010.02.024.
29. Keeley, G.P.; McEvoy, N.; Nolan, H.; Kumar, S.; Rezvani, E.; Holzinger, M.; Cosnier, S.; Duesberg, G.S. Simultaneous electrochemical determination of dopamine and paracetamol based on thin pyrolytic carbon films. *Analytical Methods* **2012,** *4*, 2048-2053, https://doi.org/10.1039/C2AY25156F.
30. Wan, Q.; Wang, X.; Yu, F.; Wang, X.; Yang, N. Effects of capacitance and resistance of MWNT-film coated electrodes on voltammetric detection of acetaminophen. *Journal of applied electrochemistry* **2009,** *39*, 1145-1151, https://doi.org/10.1007/s10800-008-9773-2.
31. Haram, S.K.; Quinn, B.M.; Bard, A.J. Electrochemistry of CdS nanoparticles: a correlation between optical and electrochemical band gaps. *Journal of the American Chemical Society* **2001,** *123*, 8860-8861, https://doi.org/10.1021/ja0158206.
32. Querner, C.; Reiss, P.; Sadki, S.; Zagorska, M.; Pron, A. Size and ligand effects on the electrochemical and spectroelectrochemical responses of CdSe nanocrystals. *Physical Chemistry Chemical Physics* **2005,** *7*, 3204-3209, https://doi.org/10.1039/B508268B.

33. Gaponik, N.; Poznyak, S.K.; Osipovich, N.P.; Shavel, A.; Eychmüller, A. Electrochemical probing of thiol-capped nanocrystals. *Microchimica Acta* **2008,** *160*, 327-334, https://doi.org/10.1007/s00604-007-0765-4.
34. Zhong, H.; Lo, S.S.; Mirkovic, T.; Li, Y.; Ding, Y.; Li, Y.; Scholes, G.D. Noninjection gram-scale synthesis of monodisperse pyramidal CuInS2 nanocrystals and their size-dependent properties. *ACS nano* **2010,** *4*, 5253-5262, https://doi.org/10.1021/nn1015538.
35. Inamdar, S.N.; Ingole, P.P.; Haram, S.K. Determination of Band Structure Parameters and the Quasi-Particle Gap of CdSe Quantum Dots by Cyclic Voltammetry. *ChemPhysChem* **2008,** *9*, 2574-2579, https://doi.org/10.1002/cphc.200800482.

6. ACKNOWLEDGEMENTS

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