

Instant synthesis of nitrogen-doped Ti_3C_2 MXene quantum dots for fluorescence and electrochemical dual-mode detection of norepinephrine with a portable smartphone assay

Murugesan Chandran, Gayathri Chellasamy, Mekala Veerapandian, Barkavi Dhanasekaran, Saravanan Govindaraju*, Kyusik Yun*

Department of Bionanotechnology, Gachon University, Gyeonggi-do 13120, Republic of Korea

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kyusik@gachon.ac.kr (K.Yun.), biovijaysaran@gmail.com (S.G.)

Table S1. Analytical results of NE in spiked human serum sample using PL (Added concentration,

Samples	Added concentration (μM)	Found concentration (μM)	Recovery (%)	RSD
1	0.1	0.097	97.86	1.73
2	0.5	0.50	100.84	0.72
3	5	4.98	99.67	1.13
4	25	24.95	99.81	1.49
5	100	99.62	99.62	0.92
6	500	511.39	102.27	2.08

Found concentration, Recovery %, RSD)

Samples	Added concentration (μM)	Found concentration (μM)	Recovery (%)	RSD
1	0.1	0.097	97.86	1.73
2	0.5	0.50	100.84	0.72
3	5	4.98	99.67	1.13
4	25	24.95	99.81	1.49
5	100	99.62	99.62	0.92
6	500	511.39	102.27	2.08

Table S2. Analytical results of NE in spiked human serum sample using DPV (Added concentration, Found concentration, Recovery %, RSD)

S. No.	Nanomaterials	Analytical methods	Linear range	LOD	Ref.
1	PNC	Colorimetric	0.2-19 μM	126 nM	1
2	Bifunctionalized AuNPs	Colorimetric	0-1500 μM	0.07 μM	2
3	MA-Ir NPs	Colorimetric	0.1-120 μM	50 nM	3
4	N-CNPs	Fluorescence	0.1-100 μM	91 nM	4
5	Cy-TPC	Fluorescence	0-7000 μM	5.01 μM	5
6	LNE probe	Fluorescence	0-5 μM	40 μM	6
7	AgNPs	SERS	0-1 mM	10 μM	7
8	AuNP	SERS	32-80 μg/mL	-	8
9	MF NPs	Electrochemical	0.03–500 μM	0.02 μM	9
10	1@CFMCN/GCE	Electrochemical	2-1000 μM	1.5 μM	10
11	GQDs/AuNPs/GCE	Electrochemical	0.5-7.5 μM	0.150 μM	11
12	CoFe ₂ O ₄ @NiO/ EMIM Ac	Electrochemical	10-500 μM	2.26 μM	12
13	N-MQDs	Fluorescence	0.1-500	37 nM (PBS)	This work
	N-MQDs/GCE	Electrochemical	0.1-500	54 nM (PBS)	
				33 nM (HS)	

Table S3. Comparison study for proposed NE detection with other reported sensors (Nanomaterials used for detection, analytical methods, linear rage, LOD).

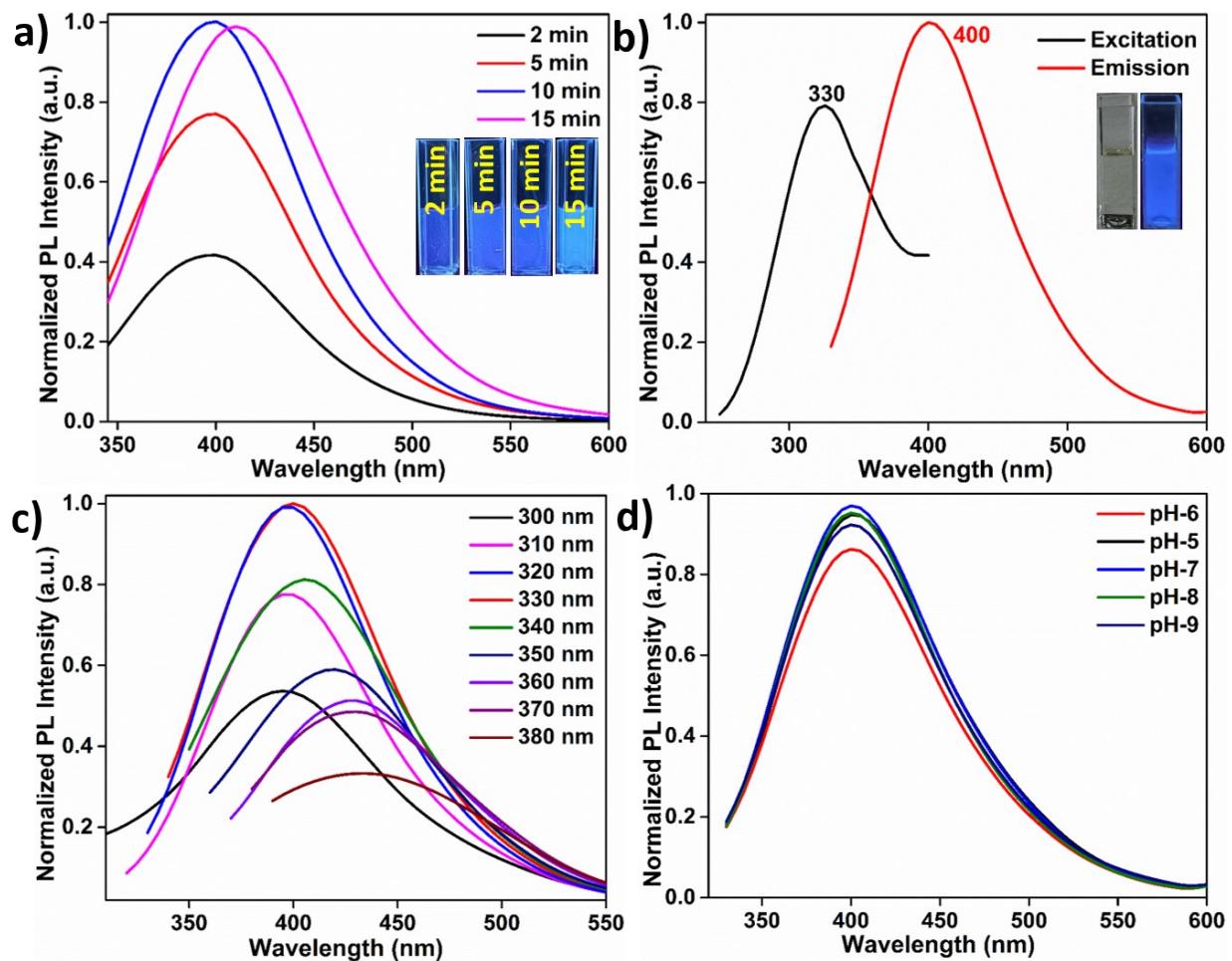


Fig. S1. a) PL spectrum of N-MQDs at different microwave irradiation times from 2-15 min (Inset: microwave synthesized N-MQDs samples under 365 nm UV light), b) Excitation and emission spectrum of N-MQDs (Inset: 5-min synthesized N-MQDs sample in daylight and under 365 nm UV light), c) excitation-dependent emission spectrum of N-MQDs, d) Effect of different pH (6-9) for the fluorescence intensity of N-MQDs.

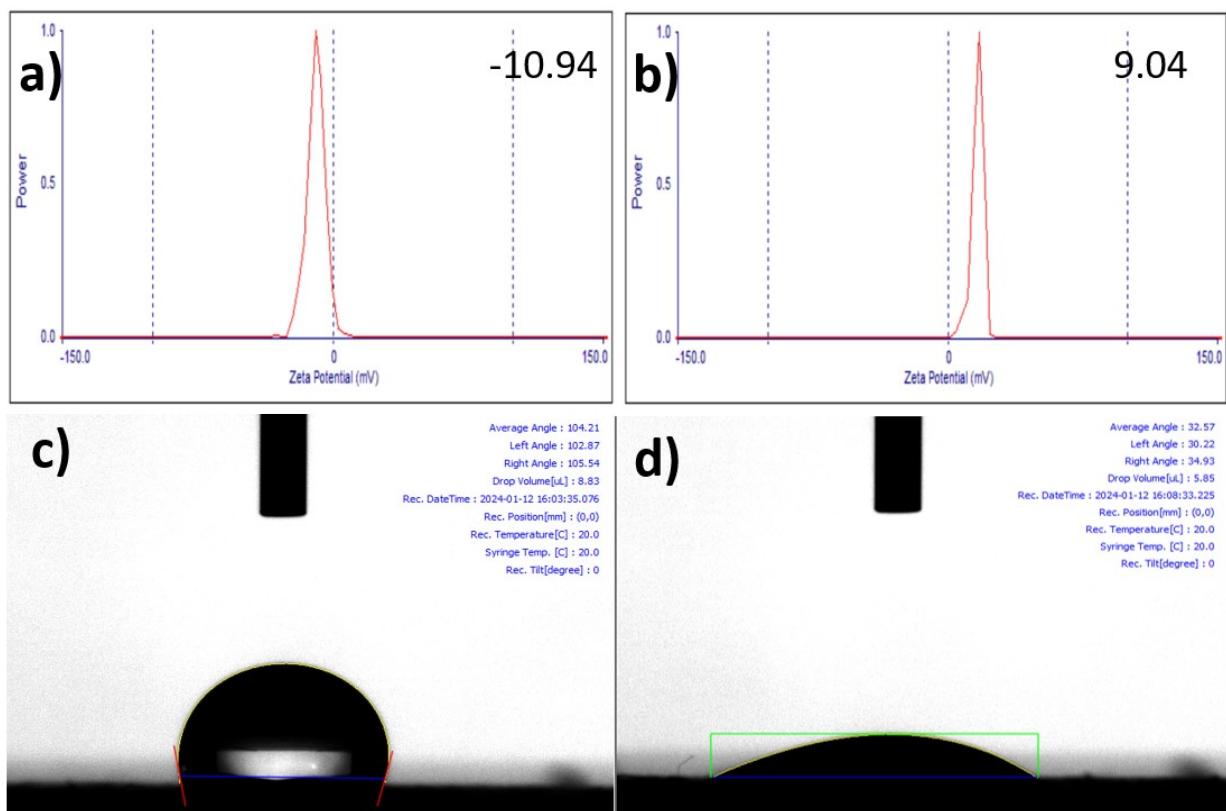


Fig. S2. Zeta potential and contact angel analysis of N-MQDs a) Zeta potential of N-MQDs, b) Zeta potential of N-MQDs with NE c) contact angel analysis of bare carbon paper electrode d) N-MQDs modified carbon paper electrode.

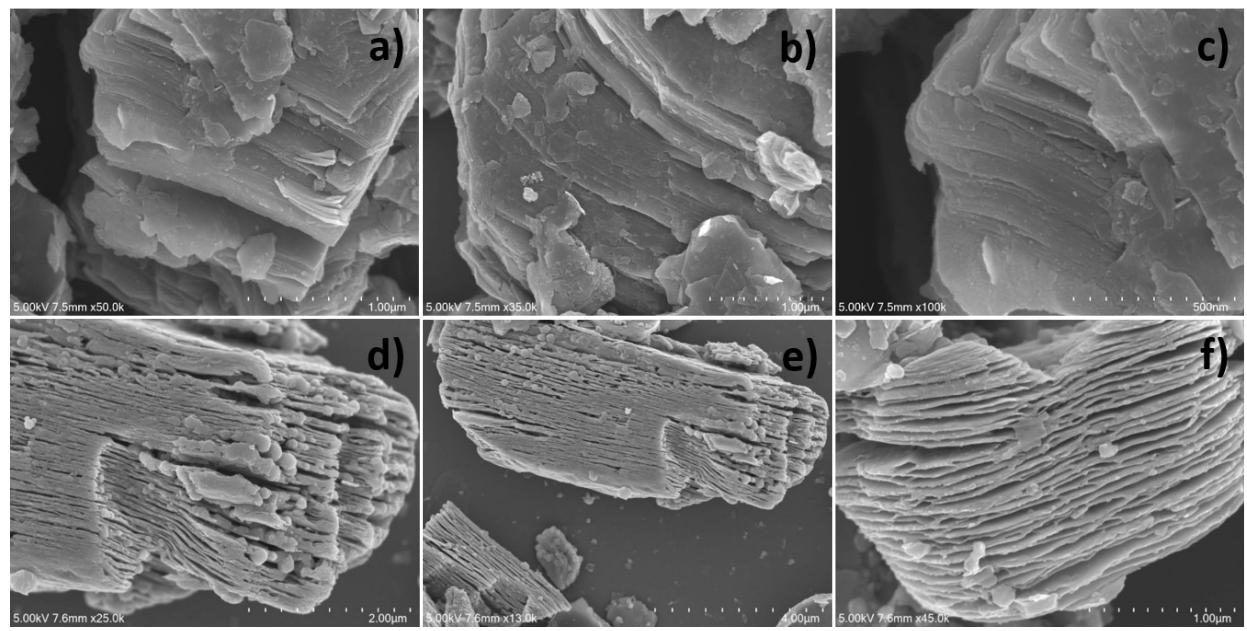


Fig. S3. a-c) SEM images of the MAX phase at different magnifications, d-f) SEM images of HF etched MXene at different magnifications.

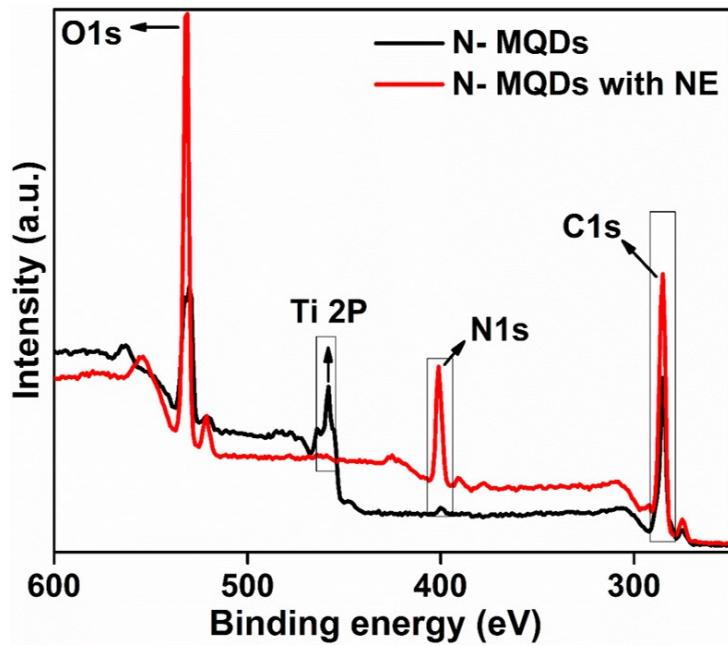


Fig. S4. XPS survey spectrum of N-MQDs (block) and N-MQDs with NE (red).

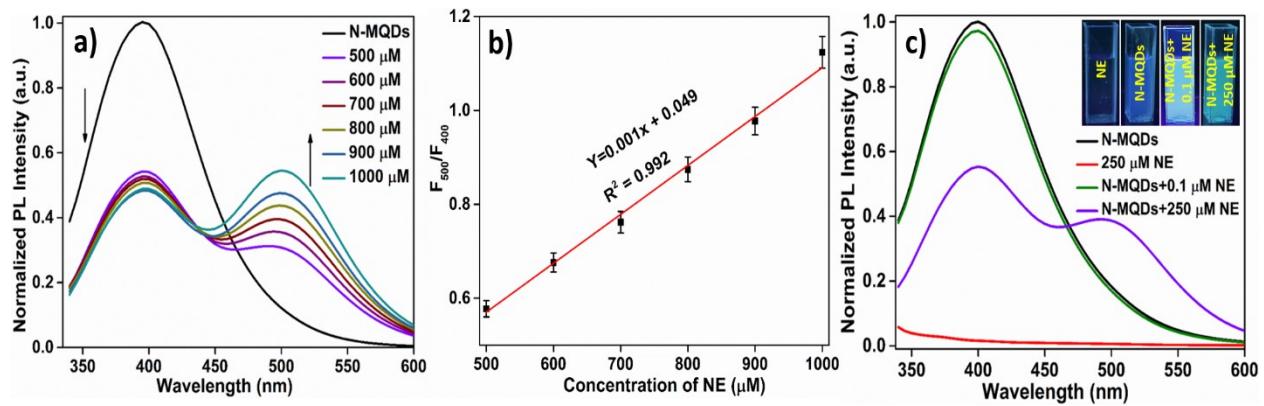


Fig. S5. a) PL spectrum of N-MQDs and 500 to 1000 μM of NE samples, b) The linear relationship between F_{500}/F_{400} ratio of the MQDs and the concentration of NE, c) The PL spectrum of NE, N-MQDs, and N-MQDs with 0.1 and 250 μM of NE samples (Inset: NE, N-MQDs, N-MQDs with 0.1 and 250 μM of NE samples under 365 nm UV light).

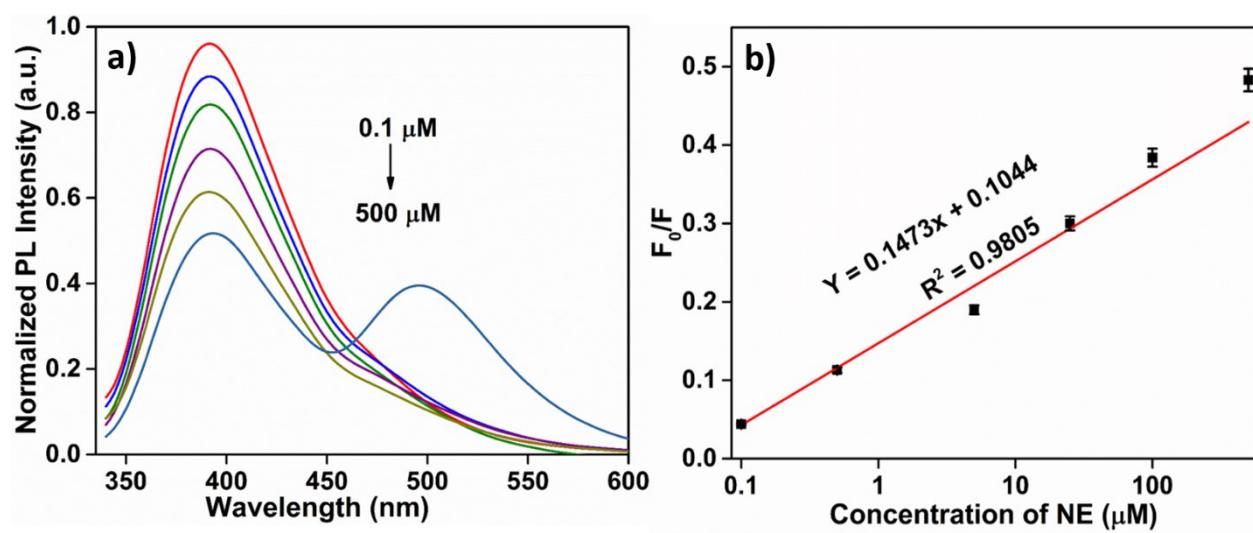


Fig. S6. a) PL spectrum of N-MQDs in the presence of different concentrations of NE from 0.1 to 500 μM were spiked with serum sample, b) corresponding linear regression plot.

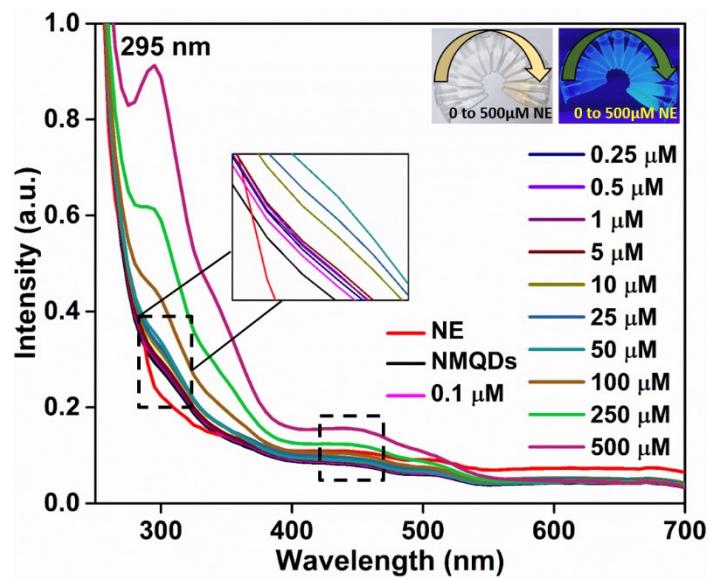


Fig. S7. The UV-visible spectrum of NE, N-MQDs, and N-MQDs with different concentrations of NE from 0.1 to 500 μM . (Inset: N-MQDs with different concentrations of NE (0 to 500 μM) sample in daylight and under 365 nm UV light).

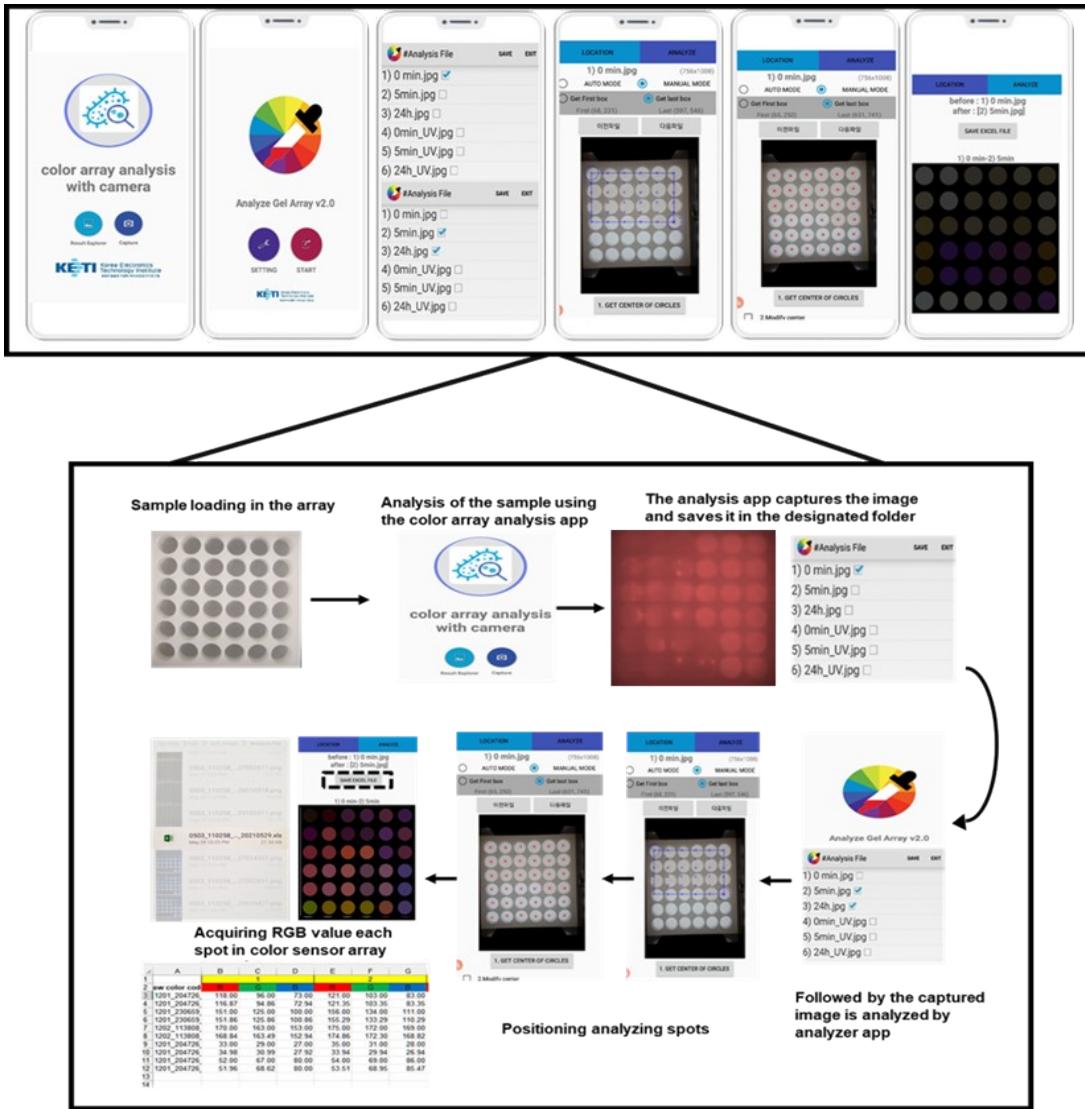


Fig. S8. The step-wise analysis of NE samples using the smartphone-based application.

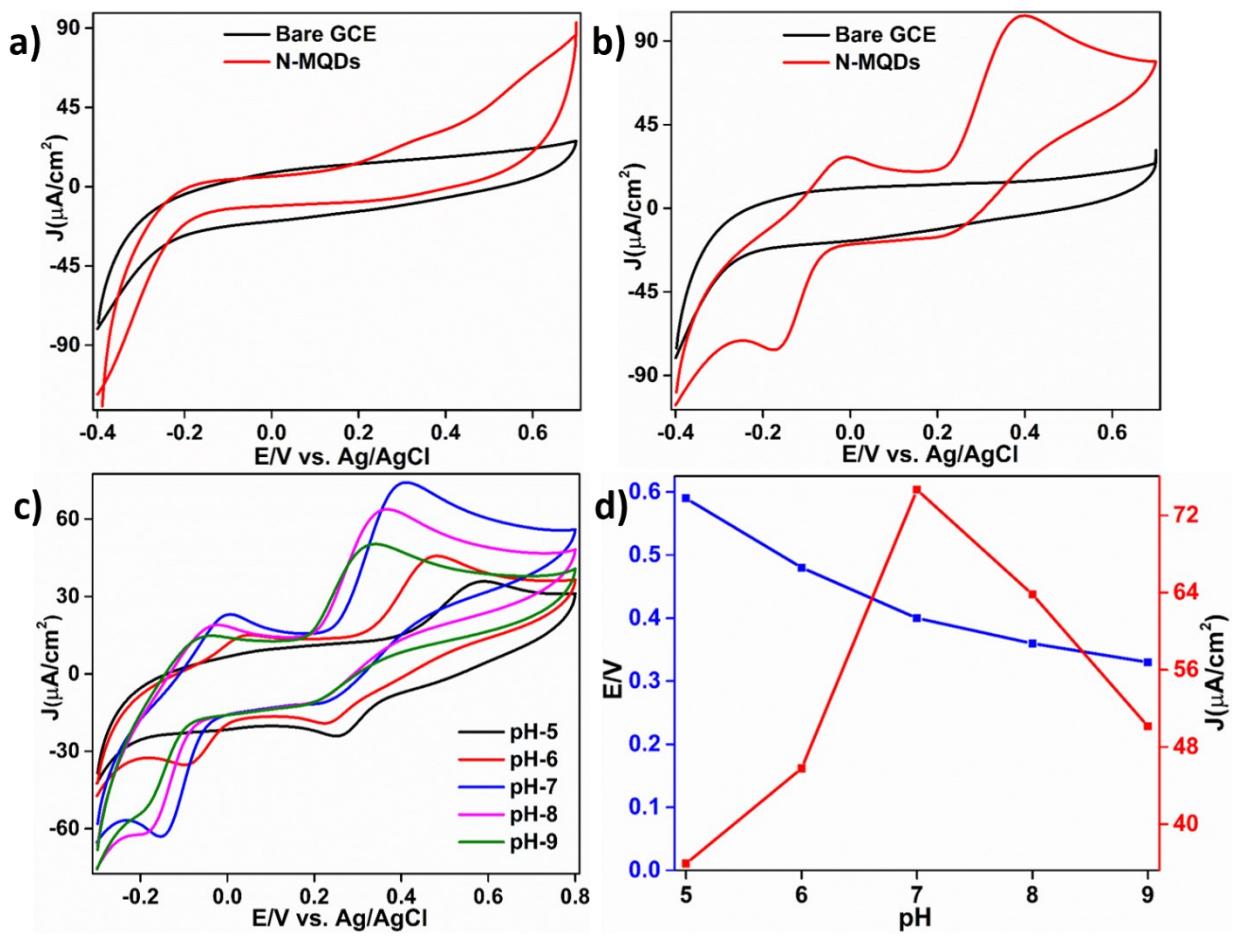


Fig. S9. a) CV of bare GCE and N-MQDs modified GCE in the absence of NE (using PBS, pH = 7.0), b) CV of bare GCE and N-MQDs modified GCE in the presence of NE (using PBS, pH = 7.0), c) Effect of pH (5-9) on N-MQDs modified GCE in 25 μM NE sample in PBS using CV, d) corresponding calibration curve with respect to potential and current.

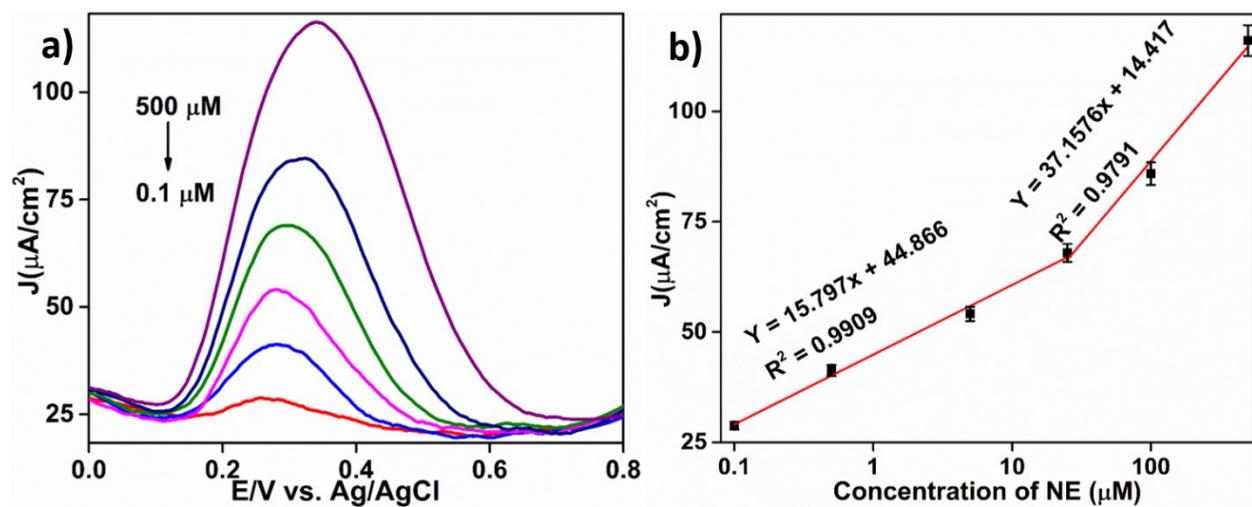


Fig. S10. a) DPV analysis of N-MQDs modified GCE in the presence of spiked serum in different concentrations of NE (0.1 to 500 μM), b) corresponding linear regression plot.

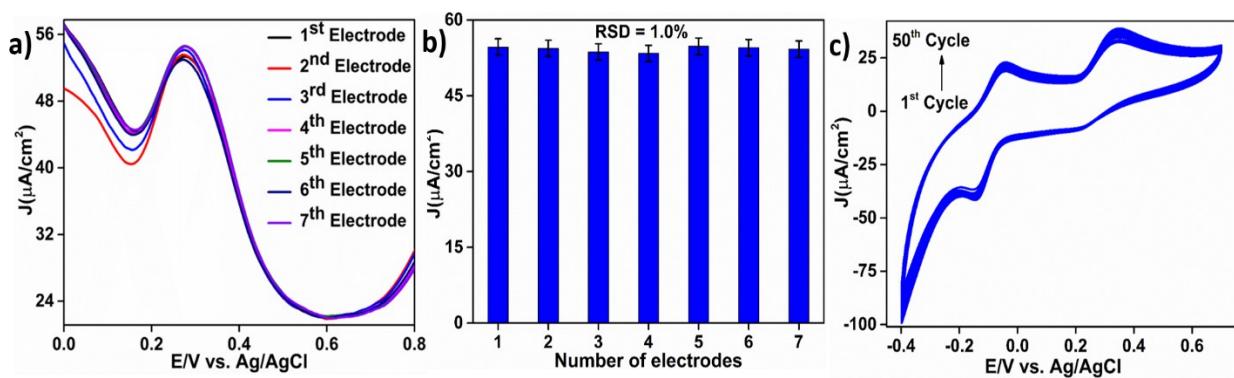


Fig. S11. Reproducibility and stability of NE detection a) reproducibility of N-MQDs modified GCE towards NE detection, b) corresponding bar chart c) stability studies of N-MQDs modified GCE for the detection of NE sample using CV over 50 cycles.

References

- 1 S.E. Son, E. Ko, V.K. Tran, W. Hur, H. Choi, H.B. Lee, Y. Park and G.H. Seong, *ChemElectroChem.*, 2019, **6**, 4666-4673.
- 2 T.M. Godoy-Reyes, A.M. Costero, P. Gavina, R. Martinez-Manez and F. Sancenon, *ACS Appl. Nano Mater.*, 2019. **2**, 1367-1373.
- 3 X. Chen, L. Zhou, Z. Guo and Q. Song, *Mater. Adv.*, 2024, **5**, 1332-1339.
- 4 D. Das and R.K. Dutta, *Dyes Pigm.*, 2022, **203**, 110314.
- 5 F. Zhang, Y.A. Song, H. Yan, H. Yang, Z. Liu, Z. Li, P. Zhang and C. Ding, *Sens Actuators B Chem.*, 2024, 136182.
- 6 P. Gu, L. Li, A. Fu, H. Song, B. Zhao, L. Wei, L. Ji, W. Li, R. Zhang, Q. Wang and G. He, *Bioorg. Chem.*, 2023, **131**, 106306.
- 7 A. Hariharan and P. Vadlamudi, *Mater. Today Commun.*, 2021, **27**, 102429.
- 8 A. Dowek, M. Berge and P. Prognon, *Anal. Bioanal. Chem.*, 2022, **414**, 1163–1176
- 9 S. Jafarei, H. Asadollahzadeh, N. Rastakhiz, M. Ghazizadeh and S.Z. Mohammadi, *J. Mater. Sci.: Mater. Electron.*, 2022, **33**, 11813-11824.
- 10 M. Liu, Y. Zhang, J. Jiang, D. Wang, Y. Li, J. Zhao and L. Chen, *J. Rare Earths.*, 2022, **40**, 1785-1793.
- 11 A. Fajardo, D. Tapia, J. Pizarro, R. Segura and P. Jara, *J. Appl. Electrochem.*, 2019, **49**, 423-432.
- 12 R. Mostafazadeh, Y. Hamidian, N. Erk and E.N. Dragoi, *Carbon Letters*, 2023, **33**, 1827-1837.