# NJC

# PAPER

Check for updates

Cite this: New J. Chem., 2021, **45**. 11644

Received 8th April 2021 Accepted 27th May 2021

DOI: 10.1039/d1nj01718g

rsc.li/njc

# 1. Introduction

Neurotransmitters play a vital role in the human body that helps in communication between the brain and nerve cells. Among the various neurotransmitters, dopamine (DA) is an

- National Taipei University of Technology, Taipei 106, Taiwan.
- E-mail: smchen78@ms15.hinet.net; Fax: +886 2270 25238; Tel: +886 2270 17147 <sup>d</sup> Research and Development Center for Smart Textile Technology, National Taipei
- University of Technology, Taipei 106, Taiwan

# A disposable electrochemical sensor based on iron molybdate for the analysis of dopamine in biological samples<sup>†</sup>

Elumalai Ashok Kumar,<sup>ab</sup> Tse-Wei Chen,<sup>cde</sup> Shen-Ming Chen, <sup>b</sup>\*<sup>c</sup> Tzyy-Jiann Wang, 🕑 a Allen Joseph Anthuvan, f Suliman Yousef AlOmar, g Naushad Ahmad<sup>h</sup> and Yu-Hsu Chang<sup>b</sup>

Developing cost-effective approaches for the fabrication of electrochemical devices is instantly needed for transferring from basic research to point-care technology. Herein, we report an electrochemical sensing platform based on an iron molybdate (Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>)-modified screen-printed carbon electrode (SPCE) for the sensitive and selective sensing of dopamine (DA). The formation and purity of  $Fe_2(MOQ_4)_3$ was characterized via multiple spectroscopic techniques. Likewise, the electrochemical performance of the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> modified SPCE was probed via cyclic voltammetry and differential pulse voltammetry. Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE exhibited a 1.44-fold increase in electrochemical sensing activity towards DA than bare SPCE. In a range as wide as from 0.01 to 225  $\mu$ M, a linear relationship is well established with the value of correlation coefficient being 0.9914. The limit of detection (S/N = 3) is well defined as 0.002  $\mu$ M, which is lower than that reported previously. The fabricated Fe2(MoO<sub>4</sub>)<sub>3</sub>/SPCE shows good antiinterference ability towards DA detection in the presence of numerous co-interfering compounds at a higher level. Moreover, a biological analysis indicated that spiked DA can be determined accurately by Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> modified SPCE with the recovery rate in the range of 99.30–99.80% in human serum samples. Based on the above-mentioned results, the proposed electrochemical sensor has great potential in the fields of biological detection.

> important catecholamine and neurotransmitter for living organisms.<sup>1,2</sup> It plays an essential role in the cardiovascular, central nervous, and endocrine regulation systems.<sup>3,4</sup> The inadequate level of DA in biological fluids causes diseases such as schizophrenia, hyperactivity disorder, Tourette syndrome, senile dementia, and Huntington's, Parkinson's, and Alzheimer's diseases.5-7 Besides, some toxic agents in the environment would damage the human brain, liver, and kidney, which may lead to inadequate DA level.<sup>8-10</sup> Therefore, it is of excessive importance to develop accurate, sensitive, and low-cost analytical techniques for detecting DA in biological samples. At present, numerous techniques, such as fluorescence, chemiluminescence, colorimetry, capillary electrophoresis, high-performance liquid chromatography, electrochemical sensing, and liquid chromatography/tandem mass spectrometry, are available for the detection of DA.11-20 Among them, electrochemical sensing gained considerable attention due to its simplicity, low cost, rapid response, user-friendliness, and real-time detection.21-24

> Transition metal molybdates (TMMs) have been widely used in electrochemical application due to their efficient catalytic performance.<sup>25-27</sup> Sundaresan et al. reported barium molybdate as a promising electrocatalyst for the detection of DA.28



**View Article Online** 

ROYAL SOCIETY

<sup>&</sup>lt;sup>a</sup> Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei 106, Taiwan

<sup>&</sup>lt;sup>b</sup> Department of Materials and Mineral Resources Engineering, Institute of Mineral Resources Engineering, National Taipei University of Technology, Taipei 106, Taiwan

<sup>&</sup>lt;sup>c</sup> Department of Chemical Engineering and Biotechnology,

<sup>&</sup>lt;sup>e</sup> Department of Materials, Imperial College London, London, SW7 2AZ, UK

<sup>&</sup>lt;sup>f</sup>DRDO-Centre for Life Sciences, Bharathiar University, Coimbatore 641 046, India

<sup>&</sup>lt;sup>g</sup> Doping Research Chair, Zoology Department, College of Science,

King Saud University, Kingdom of Saudi Arabia

<sup>&</sup>lt;sup>h</sup> Chemistry Department, College of Science, King Saud University, Kingdom of Saudi Arabia

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/ d1nj01718g

#### Paper

Fan et al. developed an electrochemical sensor based on cobalt porphyrin/tantalum molybdate for the simultaneous detection of DA.<sup>29</sup> Nanomaterials owing to their high surface area and high activity are almost utilized in all sensor applications.<sup>30</sup> Zhang et al. reported nickel molybdate nanosheets as a potential catalytic platform for NADH and ethanol sensing.<sup>31</sup> Among these different TMMs, iron molybdate  $(Fe_2(MoO_4)_3)$  is crystallized in a structure of monoclinic with 16-FeO<sub>6</sub> octahedra and 24-MoO<sub>4</sub> tetrahedra, which share corners in a unit cell, which has the advantages of low cost, good conductivity, environmental friendliness, high theoretical specific capacity, chemical stability and natural abundance, and it is the most promising electrode material.<sup>32,33</sup> However,  $Fe_2(MoO_4)_3$  have some limitations, such as poor conductivity and electrochemical stability, due to structural breakdown during redox reactions that leads to low electrochemical performance.<sup>34</sup> Arumugam et al. reported nanoplate-like iron molybdate for the selective determination of promethazine hydrochloride.35 Different methods such as the sol-gel method, co-precipitation method, impregnation method and hydrothermal method have been used for the synthesis of  $Fe_2(MoO_4)_3$ .<sup>36-46</sup> Among the abovementioned synthesis techniques, the hydrothermal technique has been widely used as an electrocatalyst owing to its simple, environmentally, high phase purity, well-defined structural morphology, low-cost, and highly efficient method.47,48 Several hydrothermally prepared materials offer low detection limit due to their precise morphology and functionality.<sup>49</sup> To the best of our knowledge, the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> modified electrode was utilized the first time for the electrochemical determination of DA.

In this study, we utilized a  $Fe_2(MOO_4)_3$  modified electrode for the electrochemical detection of DA. The as-prepared  $Fe_2(MOO_4)_3$  was analyzed by different spectroscopic, microscopic, and voltammetric techniques. The electrochemical performance was scrutinized by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The effect of various parameters such as pH, scan rate, different concentration and detection limit was evaluated. Significantly, the  $Fe_2(MOO_4)_3$ modified electrode exhibits an improved electrocatalytic activity towards DA *via* various physicochemical properties. Notably, the  $Fe_2(MOO_4)_3$  modified electrode delivers a low limit of detection, wide linear range and acceptable selectivity. Compared with previously reported electrodes for the detection of DA, the fabricated  $Fe_2(MOO_4)_3$  sensor provides several significant merits such as (1) superior conductivity, (2) wide linear range because of the large surface area, (3) excellent selectivity ability due to the specific DA recognition, (4) high accuracy, and (5) good biocompatibility for real-time monitoring of DA.

### 2. Experimental

#### 2.1. Materials

Iron acetate  $(Fe(CO_2CH_3)_2)$  and sodium molybdate dihydrate  $(Na_2MoO_4)$  were purchased from Sigma Aldrich. Urea  $(NH_2CONH_2)$  and ethanol were purchased from Fluka chemical companies. All chemicals were of analytical grade and used without further purification. Phosphate buffer solutions (PBS) 0.05 M were used in all the electrochemical studies. Double distilled water (DI) was used for all the experiments.

#### 2.2. Instrumentation

The structural morphology, crystalline structure and chemical composition of the as-prepared Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> were characterized *via* transmission electron microscopy (TEM) (JEOL: JEM-1200EX), and mapping analysis was performed *via* FE-SEM (SEM Hitachi S-3000H) and X-ray diffraction (XRD; XPERT-PRO spectrometer from PANalytical B.V. with Cu K $\alpha$  radiation  $\lambda = 1.5406$  Å). The functional groups were identified *via* FT-IR (FT-IR-6600 spectrometer). The electrochemical measurements were conducted at room temperature on an electrochemical workstation (CH Instrument, USA) connected to a computer. A typical three-electrode system consisting of a saturated KCl silver–silver chloride (sat. KCl Ag/AgCl) as the reference electrode, platinum wire as the counter electrode, and a SPCE (0.071 cm<sup>2</sup>) as the working electrode was used. All the experiment was carried in a nitrogenous atmosphere.

#### 2.3. Synthesis of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>

In this study,  $Fe_2(MOO_4)_3$  were prepared by the simple hydrothermal method, as represented in Scheme 1. Briefly, 0.1 M Fe  $(CO_2CH_3)_2$  and 0.1 M Na<sub>2</sub>MoO<sub>4</sub> were dissolved in 20 mL DI water and stirred until a homogeneous mixture was obtained at atmospheric temperature. Then, 5 mg urea was dissolved in 10 mL DI water, and the mixture was added to the above-



Scheme 1 The synthesis procedure of  $(Fe_2MoO_4)_3$  by the hydrothermal method.



mentioned solution and stirred for another 30 min. The final solution is transferred to a Teflon-lined stainless steel autoclave, shield tightly, maintained at 140 °C for 12 h and left undisturbed until it reached room temperature. Then, it was washed with DI water and ethanol several times and dried at 50 °C for 12 h and finally calcined at 600 °C for 4 h. The obtained Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> were ground and used for further electrochemical studies. Scheme 1 shows the schematic representation of the synthesis methodology of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>.

#### 2.4. Fabrication of the DA sensor

Initially, the bare SPCE was cleaned with DI water and ethanol every few seconds to remove unwanted impurities over the SPCE surface. The SPCE electrode was modified with  $Fe_2(MOO_4)_3$  for the sensitive electrochemical detection of DA. For the preparation of an  $Fe_2(MOO_4)_3$  suspension, the assynthesized  $Fe_2(MOO_4)_3$  electrocatalyst was ultrasonically dispersed in DI water to form a 2 mg mL<sup>-1</sup>. Then, 8 µL of  $Fe_2(MOO_4)_3$  dispersed in 1 mL DI water was gently drop-coated



Fig. 2 (A-C) TEM image of (D) line EDX spectra and (E-G) mapping image of Fe<sub>2</sub>(MoO4)<sub>3</sub>.



Fig. 3 (A) CV curves of bare SPCE and Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE in the absence and presence of 150  $\mu$ M DA in 0.05 M PBS (pH 7.0) at a scan rate of 50 mV s<sup>-1</sup>. (B) CV curves at different DA concentrations at a scan rate of 50 mV s<sup>-1</sup>. (C) CV curves at different scan rates with a DA concentration of 150  $\mu$ M. (D) Corresponding calibration plot of the redox current response and the scan rates.

on the electrode surface and dried to dehydrate the water content at 50  $^{\circ}$ C for 15 min. Later, the modified SPCE was rinsed to remove the loosely bounded particles with water, and electrochemical studies were carried out.

### 3. Results and discussion

#### 3.1. Material characterization

The structural and phase analyses of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> were characterized via XRD in Fig. 1A. The XRD patterns of the product can be indexed to the monoclinic phase Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> structure (JCPDS file Card No. 35-0183) without other possible impurities.<sup>50,51</sup> The sharpness of the XRD peak indicates the high crystallinity nature of materials. Raman spectroscopy analysis was used further to confirm the  $(Fe_2MoO_4)_3$  formation, which is shown in Fig. 1B. The Raman spectrum of the MoO<sub>4</sub> units of  $Fe_2(MoO_4)_3$  was characterized by a triple peak feature at 995, 972 and 937 cm<sup>-1</sup>, corresponding to the symmetric stretching mode of the Mo=O bonds of three distinct MoO<sub>4</sub> units. The two bands at 785 and 824 cm<sup>-1</sup> correspond to the asymmetric stretching vibration mode. A broad feature at around 350 cm<sup>-1</sup> corresponds to the bending modes of the MoO<sub>4</sub> overlaying bands.<sup>52,53</sup> The morphology of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> was investigated by TEM measurements. The TEM images of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> present a uniform sphere-like structure with good

crystallinity and a more specific area, and the active site will improve the redox process<sup>54</sup> (Fig. 2(A–C)). The corresponding elemental mapping of  $Fe_2(MOO_4)_3$  confirms the presence of Fe, Mo and O elements (Fig. 2(E–G)). The line energy dispersive spectrum shows that Fe, Mo and O elements are distributed evenly in  $Fe_2(MOO_4)_3$ .

#### 3.2. Electrochemical studies

The concentration (mg) of  $Fe_2(MOO_4)_3$  for the SPCE preparation will influence the performance of the developed electrochemical sensor. Fig. S1 (ESI<sup>†</sup>) displays the electrochemical oxidation of DA with respect to variation in the concentration of  $Fe_2(MOO_4)_3$ . 2 mg mL<sup>-1</sup> of  $Fe_2(MOO_4)_3$  presented the highest oxidation current for the detection of DA. The effect of the amount of  $Fe_2(MOO_4)_3$  on the electrode response to 150 µM DA is shown in Fig. S2 (ESI<sup>†</sup>). The oxidation peak current progressively increases with the loading amount (2.0–6.0 µL), and the highest peak current response appears at 8 µL of  $Fe_2(MOO_4)_3$ . Therefore, 8.0 µL of  $Fe_2(MOO_4)_3$  was selected as the optimal loading volume in the subsequent electrochemical experiment.

**3.2.1 Electrochemical performance for the detection of DA.** The CV technique in Fig. 3A show the bare SPCE and  $Fe_2(MoO_4)_3$ /SPCE in the absence and presence of DA (150  $\mu$ M). No obvious redox peaks were observed on the bare SPCE and  $Fe_2(MoO_4)_3$ /SPCE in 0.05 M PBS (pH 7.0) without 150  $\mu$ M DA, which suggests that no electrocatalytic reaction took on the electrodes. The bare SPCE exhibits quasi-reversible redox performance with weak oxidation  $(E_{pa})$  and reduction  $(E_{pc})$  peaks for DA observed at 0.35 and 0.02 V, respectively. As expected, Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE shows a well-defined quasi-reversible behaviour for DA, and the redox peaks are observed at 0.28 V  $(E_{pa})$ and 0.03 V ( $E_{pc}$ ), respectively. Besides, the anodic peak current response of DA is about 1.44 fold higher than that of those observed at bare SPCE. The good redox current response at Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE is due to good specific area, better electrocatalytic activity and more active sites. The electrochemical reaction of DA occurs by exchanging two-electron and two protons on the surface of Fe<sub>2</sub>(MoO4)<sub>3</sub>/SPCE, thus forming dopamine-o-quinone (DOQ). The mechanism for the electrooxidation of DA is depicted in Scheme 2. Fig. 3B shows the CV curves of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE in the different concentrations of DA ranging from 30 to 150 µM. As shown in the CV signals, the redox currents progressively increase with the concentration of DA. The result indicates that  $Fe_2(MoO_4)_3/SPCE$  has a good electrochemical activity for the electrochemical sensing of DA.

3.2.2 Effect of scan rate and pH. The effect of the scan rate on the electrochemical performance of DA at Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE was examined by the CV method. Fig. 3C displays the CV curves of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE in 150 µM DA containing 0.05 M PBS (pH 7.0) at different scan rates from 40 to 240 mV s<sup>-1</sup>. As the scan rate increases, the redox peak currents of DA for  $Fe_2(MoO_4)_3$ /SPCE increases continuously, suggesting a quasireversible process. The redox peak current of DA had a linear dependence on the scan rates with the correlation coefficient of 0.9975 and 0.9984 (Fig. 3D). The obtained results indicate that the electrochemical reaction was controlled by a typical surfacecontrolled electrochemical process on the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE. The solution pH is an important parameter for high sensitivity in the detection system.55-57 The effect of pH on the redox reaction of 150 µM DA at Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE was investigated by the CV method in the pH range from 3.0 to 11.0. As shown in Fig. 4A, the redox peak current of DA increased gradually with the increase in the pH of the solution from 3.0 to 7.0, and the maximum redox current was achieved at pH 7.0. With further increasing pH, the redox peak current gradually reduced.58-61



Fig. 4 (A) CV curves obtained at  $Fe_2(MoO_4)_3$ /SPCE in 150  $\mu$ M DA containing different pH at a scan rate of 50 mV s<sup>-1</sup>. (B) Calibration plot of the formal potential ( $E^{0'}$ ) of DA vs. pH.



Fig. 5 (A) DPV responses at Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE of various concentrations of DA. (B) Calibration plots of the oxidation peak current vs. different DA concentrations.

Table 1 Comparison of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> with previously reported DA sensors

Electrode materials	Methods	Linear range ( $\mu M$ )	$LOD\;(\mu M)$	Ref.
YVO/GA	DPV	0.009-89	0.0015	6
Cu/Cu <sub>x</sub> O NP <sub>s</sub> /PGE	DPV	0.3-53	1.06	63
CuCrO <sub>2</sub> -TiO <sub>2</sub>	DPV	1-230	0.14	64
Fe <sub>3</sub> O <sub>4</sub> @Au	CV	10-1000	0.058	65
CB-Nafion/p-BDD	SWV	0.1-100	0.054	66
NPC	DPV	30-90	0.0027	67
Ni-MOF	DPV	0.2-100	0.06	68
Poly-ET	SWV	0.1-20	0.007	69
Au-C@Ni/BDD	DPV	0.05-100	0.015	70
rGO-CMNs	DPV	34-125	0.158	71
$Fe_2(MoO_4)_3$	DPV	0.01-225	0.002	This work

Hence, pH 7.0 was chosen for the subsequent analytical experiments. The linear plot between the formal potential and pH was plotted (Fig. 4B). The number of electron was calculated by the following Nernst equation:<sup>62</sup>

$$E_{\rm p} = E_{\rm formal}^0 - \frac{2.303 RTm}{nf} \rm pH$$

where  $E_p$ , *R*, *T*, *m*, *n*, and *f* are the electric potential, universal gas constant, temperature, number of protons, number of electrons, and Faraday constant, respectively. We estimated the slope value of  $-50.6 \text{ mV pH}^{-1}$ , which is an equal number of protons and electrons process.

3.2.3 Determination of DA. The DPV technique was applied to assess the electrochemical performance of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE towards the DA determination. Fig. 5A shows the DPV signals for various concentrations of DA at  $Fe_2(MoO_4)_3/$ SPCE. The oxidation peak current of DA increased linearly with the concentration in the range of 0.01-849 µM. The linear range for DA was determined in the range from 0.01 to 225  $\mu$ M with the correlation coefficient of 0.9913, as shown in Fig. 5B. The limit of detection (LOD) was calculated to be 0.002 µM by utilizing the formula as shown in previous literature.<sup>6,62-71</sup> Table 1 shows the electrochemical comparison of the proposed sensor with that of previously reported DA sensors.  $Fe_2(MOO_4)_3/$ SPCE presents a better electrochemical performance towards DA with a dynamic linear range and a very low LOD. The fabricated  $Fe_2(MoO_4)_3$ /SPCE sensor is effective for analyzing DA in biological samples.

**3.2.4 Interference and analytical application.** The selectivity of DA electrochemical oxidation on  $Fe_2(MoO_4)_3/SPCE$  was assessed by the DPV method with numerous interferents in human serum samples. Thus, uric acid (b), ascorbic acid (c), glucose (d), sucrose (e), caffeic acid (f), catechol (g), iron (h), zinc (i) and sodium chloride (j) were taken as interfering substances for DA. Fig. 6A displays the DPV performances of DA oxidation with a 20-fold excess of b–g and a 50-fold excess of h–j. It can be seen that common interfering substance lead to a minimum relative error ( $\pm 5\%$ ) in the determination of DA (Fig. 6B).



Fig. 6 (A) DPV signals of  $Fe_2(MoO_4)_3/SPCE$  towards DA (a) in the presence of various common interference compounds (b–j). (B) A plot of the current response of DA (%) with different interfering compounds. (C) DPV signals for the detection of DA in the spiked human serum sample based on  $Fe_2(MoO_4)_3/SPCE$ . (D) Calibration plot of the oxidation intensity against DA.

Table 2 Determination of DA in human serum samples by  ${\rm Fe}_2({\rm MoO}_4)_3/$  SPCE

Samples	Detected (µM)	Added (µM)	Found (µM)	Recovery (%)
Human serum samples	_	1.00	0.99	99.00
	_	3.00	2.99	99.70
	_	6.00	5.96	99.30
	_	10.00	9.98	99.80
	—	15.00	14.94	99.60

These results confirmed that  $Fe_2(MoO_4)_3/SPCE$  has good selectivity towards DA.

The analysis of DA present in human serum samples was studied *via* the DPV method using the Standard addition approach (Fig. 6C). Human serum samples were diluted 20 times with 0.05 M PBS (pH 7.0). Human serum samples are free from DA; therefore, injected a known level of standard DA in human serum samples. The plot for DA at  $Fe_2(MOO_4)_3$ / SPCE in Fig. 6D displays that the oxidation current increased with the DA concentration in the range from 1 to 15  $\mu$ M with the correlation coefficient of 0.9982, and the obtained recovery results are presented in Table 2. The recovery results of DA in human serum samples were found in the range from 99.30 to 99.80% (Table 2). These results confirmed that  $Fe_2(MOO_4)_3$  is the most promising electrode material for the sensitive and selective detection of DA in real biological samples.

# 4. Conclusion

We describe the simple fabrication of an effective and fast electrochemical sensor for the analysis of DA. A novel  $Fe_2(MoO_4)_3$  was synthesized *via* a hydrothermal method and used as the sensing material. The sensing material was extensively examined via X-ray diffraction, Fourier-transform infrared spectroscopy, transmission electron microscopy, line energydispersive X-ray spectroscopy and elemental mapping. Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/ SPCE exhibits a better electrochemical performance than bare SPCE, which is attributed to the good surface area, electrocatalytic activity and active sites. The pH values were highly influenced and the pH 7.0 was effective for efficient DA detection.  $Fe_2(MoO_4)_3/$ SPCE has proven to be promising for DA detection with low LOD  $(0.002 \ \mu\text{M})$  and good linear range  $(0.01-225 \ \mu\text{M})$ . Importantly, the presence of various coexisting compounds did not adversely affect during DA detection. Compared to other literature reported in Table 1, our proposed sensor was a better linear range, LOD and selectivity. Furthermore, the as-prepared Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>/SPCE shows comparable electrochemical performance for DA sensing in human serum samples with satisfying recoveries. In the future, our Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> based sensor shows promising electrochemical performance as a potential DA sensor.

# Conflicts of interest

There are no conflicts to declare.

# Acknowledgements

This work was supported by the Ministry of Science and Technology, Taiwan (MOST 107-2113-M-027-005-MY3). The authors are grateful to the Deanship of Scientific Research, King Saud University, for funding through Vice Deanship of Scientific Research Chairs. The authors would keenly thank Dr. Thangavelu Kokulnathan for their outstanding support throughout the work.

### References

- S. Madhu, P. Manickam, M. Pierre, S. Bhansali,
   P. Nagamony and V. Chinnuswamy, *Sens. Actuators, A*, 2018, 269, 401–411.
- 2 Y. Gwon, V. D. Phung, Y. D. Son, J. H. Kim and S. W. Lee, *Electron. Mater. Lett.*, 2021, 1–7.
- 3 K. M. Diederen and P. C. Fletcher, *Neuroscientist*, 2021, 1, 30–46.
- 4 S. Priyatharshni, D. Navadeepthy, G. Srividhya, C. Viswanathan and N. Ponpandian, *Colloids Surf.*, *A*, 2021, 126387.
- 5 D. Murugesan, K. Moulaee, G. Neri, N. Ponpandian and C. Viswanathan, *Nanotechnology*, 2019, **30**(26), 265501.
- 6 T. Kokulnathan, F. Ahmed, S. M. Chen, T. W. Chen, P. M. Hasan, A. L. Bilgrami and R. Darwesh, ACS Appl. Mater. Interfaces, 2021, 13, 10987–10995.
- 7 P. M. Shafi, N. Joseph, R. Karthik, J. J. Shim, A. C. Bose and V. Ganesh, *Microchem. J.*, 2021, **164**, 105945.
- 8 M. R. Awual, M. M. Hasan, A. Islam, M. M. Rahman, A. M. Asiri, M. A. Khaleque and M. C. Sheikh, *J. Cleaner Prod.*, 2019, 231, 214–223.
- 9 M. R. Awual, J. Environ. Chem. Eng., 2019, 7(3), 103087.
- 10 M. R. Awual, M. M. Hasan, J. Iqbal, M. A. Islam, A. Islam, S. Khandaker, A. M. Asiri and M. M. Rahman, *J. Environ. Chem. Eng.*, 2020, 8(1), 103591.
- 11 X. Wei, Z. Zhang and Z. Wang, *Microchem. J.*, 2019, 145, 55–58.
- 12 T. Zhou, Z. Su, Y. Tu and J. Yan, *Spectrochim. Acta, Part A*, 2021, 252, 119519.
- 13 U. Nishan, U. Sabba, A. Rahim, M. Asad, M. Shah, A. Iqbal,
  J. Iqbal and N. Muhammad, *Mater. Chem. Phys.*, 2021,
  262, 124289.
- 14 P. Li, X. H. Ma, L. Jin and J. Chen, J. Chromatogr. B: Anal. Technol. Biomed. Life Sci., 2021, 1167, 122582.
- 15 F. Chen, B. Fang and S. Wang, *J. Anal. Methods Chem.*, 2021, 2021.
- 16 B. S. Aydin and I. Bulduk, *Eurasian J. Bio. Chem. Sci.*, 2020, 3(2), 116–120.
- 17 D. Wenk, V. Ignatchenko, A. Macklin, H. Hübner,
  P. Gmeiner, D. Weikert, M. Pischetsrieder and
  T. Kislinger, *Sci. Rep.*, 2021, 11(1), 1–4.
- 18 A. Shahat, H. M. Hassan, M. F. El-Shahat, O. El Shahawy and M. R. Awual, *Chem. Eng. J.*, 2018, 334, 957–967.
- 19 R. Ramachandran, X. Leng, C. Zhao, Z. X. Xu and F. Wang, *Appl. Mater. Today*, 2020, **18**, 100477.

- 20 J. Zou, S. Wu, Y. Liu, Y. Sun, Y. Cao, J. P. Hsu, A. T. Wee and J. Jiang, *Carbon*, 2018, **130**, 652–663.
- 21 T. Kokulnathan and S. M. Chen, *ACS Sustainable Chem. Eng.*, 2019, 7(4), 4136–4146.
- 22 S. Priyatharshni, M. Divagar, C. Viswanathan, D. Mangalaraj and N. Ponpandian, *J. Electrochem. Soc.*, 2016, **163**(8), B460.
- 23 K. Rajendran, T. Kokulnathan, S. M. Chen, J. A. Allen, C. Viswanathan and H. A. Therese, *Microchim. Acta*, 2019, 186(3), 141.
- 24 B. Sriram, M. Govindasamy, S. F. Wang and X. B. Joseph, New J. Chem., 2020, 44(25), 10250–10257.
- 25 T. Kokulnathan, T. W. Chen, S. M. Chen, J. V. Kumar, S. Sakthinathan and E. R. Nagarajan, *Composites, Part B*, 2019, **169**, 249–257.
- 26 S. Zou, J. Gao, L. Liu, Z. Lin, P. Fu, S. Wang and Z. Chen, J. Alloys Compd., 2020, 817, 152785.
- 27 J. N. Baby, B. Sriram, S. F. Wang, M. George, M. Govindasamy and X. B. Joseph, *Nanoscale*, 2020, **12**(38), 19719–19731.
- 28 P. Sundaresan, Y. C. Chen, S. M. Chen, T. W. Chen, P. Latha and B. S. Lou, *Int. J. Electrochem. Sci.*, 2018, 13, 10809–10820.
- 29 Z. Fan, B. Zhao, S. Wu, H. Wang, T. Cao, T. Zhu, X. Zhang, L. Liu and Z. Tong, J. Mater. Res., 2021, 1–9.
- 30 M. R. Awual and T. Yaita, Sens. Actuators, B, 2013, 183, 332-341.
- 31 D. Zhang, R. Zhang, C. Xu, Y. Fan and B. Yuan, *Sens. Actuators, B*, 2015, **206**, 1–7.
- 32 K. V. Raun, L. F. Lundegaard, P. Beato, C. C. Appel, K. Nielsen, M. Thorhauge, M. Schumann, A. D. Jensen, J. D. Grunwaldt and M. Høj, *Catal. Lett.*, 2019, 1.
- 33 Y. Y. Wu, B. Y. Song, X. F. Zhang, Z. P. Deng, L. H. Huo and S. Gao, J. Alloys Compd., 2021, 867, 158994.
- 34 G. Boopathy, M. Keerthi, S. M. Chen, M. J. Umapathy and B. N. Kumar, *Mater. Chem. Phys.*, 2020, 239, 121982.
- 35 B. Arumugam, B. Muthukutty, S. M. Chen, S. K. Ramaraj, J. V. Kumar and E. R. Nagarajan, *Ultrason. Sonochem.*, 2020, **66**, 104977.
- 36 J. Lv, X. Liu, X. Zhang and Q. Lu, Mater. Lett., 2021, 290, 129456.
- 37 A. P. Soares, M. F. Portela, A. Kiennemann and L. Hilaire, *Chem. Eng. Sci.*, 2003, 58(7), 1315–1322.
- 38 A. A. Alkahlaway, M. A. Betiha, D. Aman and A. M. Rabie, Environ. Technol. Innovation, 2021, 22, 101386.
- 39 A. V. Soares, M. F. Portela, A. Kiennemann, L. Hilaire and J. M. Millet, *Appl. Catal.*, A, 2001, **206**(2), 221–229.
- 40 J. W. Heo, J. Hyoung and S. T. Hong, *Inorg. Chem.*, 2018, 57, 11901–11908.
- 41 V. Nguyen, Y. Liu, Y. Li, S. A. Hakim, X. Yang and W. Chen, ECS J. Solid State Sci. Technol., 2015, 4(5), M25.
- 42 M. Niwa and J. Y. Igarashi, Catal. Today, 1999, 52(1), 71-81.
- 43 A. P. Dias, V. V. Rozanov, J. C. Waerenborgh and M. F. Portela, *Appl. Catal.*, A, 2008, 345(2), 185–194.
- 44 H. Liu and E. Iglesia, J. Phys. Chem. B, 2005, 109(6), 2155-2163.
- 45 W. Li, H. Liu and E. Iglesia, *J. Phys. Chem. B*, 2006, **110**(46), 23337–23342.
- 46 Y. Ding, S. H. Yu, C. Liu and Z. A. Zang, *Chem. Eur. J.*, 2007, 13(3), 746–753.
- 47 M. Z. Ahmad, I. A. Bhatti, K. Qureshi, N. Ahmad, J. Nisar,
  M. Zuber, A. Ashar, M. I. Khan and M. Iqbal, *J. Mol. Liq.*,
  2020, 301, 112343.

- 48 A. K. Kulkarni, M. S. Tamboli, D. Y. Nadargi, Y. A. Sethi, S. S. Suryavanshi, A. V. Ghule and B. B. Kale, *J. Solid State Chem.*, 2020, **281**, 121043.
- 49 M. R. Awual, M. M. Hasan, A. Islam, M. M. Rahman, A. M. Asiri, M. A. Khaleque and M. C. Sheikh, *J. Cleaner Prod.*, 2019, **228**, 778–785.
- 50 K. Seevakan, A. Manikandan, P. Devendran, S. A. Antony and T. Alagesan, *Adv. Sci. Eng. Med.*, 2016, **8**(7), 566–572.
- 51 L. Zhang, X. F. Cao, Y. L. Ma, X. T. Chen and Z. L. Xue, New J. Chem., 2010, 34(9), 2027–2033.
- 52 A. Gaur, M. Schumann, K. V. Raun, M. Stehle, P. Beato, A. D. Jensen, J. D. Grunwaldt and M. Hoj, *ChemCatChem*, 2019, **11**(19), 4871-4883.
- 53 M. M. Rashad, A. A. Ibrahim, D. A. Rayan, M. M. Sanad and I. M. Helmy, *Environ. Nanotechnol. Monit. Manage.*, 2017, 8, 175–186.
- 54 H. Znad, K. Abbas, S. Hena and M. R. Awual, J. Environ. Chem. Eng., 2018, 6(1), 218-227.
- 55 A. Islam, S. H. Teo, M. R. Awual and Y. H. Taufiq-Yap, J. Cleaner Prod., 2019, 238, 117887.
- 56 M. R. Awual and M. M. Hasan, J. Mol. Liq., 2019, 294, 111679.
- 57 M. R. Awual, T. Yaita, T. Kobayashi, H. Shiwaku and S. Suzuki, *J. Environ. Chem. Eng.*, 2020, 8(2), 103684.
- 58 M. R. Awual, A. Islam, M. M. Hasan, M. M. Rahman, A. M. Asiri, M. A. Khaleque and M. C. Sheikh, *J. Cleaner Prod.*, 2019, 224, 920–929.
- 59 M. R. Awual, Chem. Eng. J., 2015, 266, 368-375.
- 60 R. M. Kamel, A. Shahat, W. H. Hegazy, E. M. Khodier and M. R. Awual, *J. Mol. Liq.*, 2019, 285, 20–26.
- 61 M. R. Awual, M. M. Hasan, J. Iqbal, A. Islam, M. A. Islam, A. M. Asiri and M. M. Rahman, *Microchem. J.*, 2020, 154, 104585.
- 62 R. D. Crapnell and C. E. Banks, Electroanalytical overview: The electroanalytical detection of theophylline, *Talanta Open*, 2021, 00037.
- 63 E. Bahrami, R. Amini and S. Vardak, *J. Alloys Compd.*, 2021, **855**, 157292.
- 64 A. K. Keyan, C. L. Yu, R. Rajakumaran, S. Sakthinathan, C. F. Wu, S. Vinothini, S. M. Chen and T. W. Chiu, *Microchem. J.*, 2021, **160**, 105694.
- 65 H. Guan, B. Liu, D. Gong, B. Peng, B. Han and N. Zhang, *Microchem. J.*, 2021, **164**, 105943.
- 66 H. Li, K. Zhou, J. Cao, Q. Wei, C. T. Lin, S. E. Pei, L. Ma, N. Hu, Y. Guo, Z. Deng and Z. Yu, *Carbon*, 2021, 171, 16–28.
- 67 P. R. Kasturi, T. K. Aparna, A. L. Arokiyanathan, S. Lakshmipathi, R. Sivasubramanian, Y. S. Lee and R. K. Selvan, *Mater. Chem. Phys.*, 2021, 260, 124094.
- 68 Z. Huang, L. Zhang, P. Cao, N. Wang and M. Lin, *Ionics*, 2021, 27(3), 1339–1345.
- 69 A. Kannan, S. Manojkumar and S. Radhakrishnan, *Electro-analysis*, 2021, 33, 1–11.
- 70 H. Li, Y. Guo, S. Zeng, Q. Wei, P. E. Sharel, R. Zhu, J. Cao, L. Ma,
   K. Zhou and L. Meng, *J. Mater. Sci.*, 2021, 56(7), 4700–4715.
- 71 G. Singh, A. Kushwaha and M. Sharma, *J. Electroanal. Chem.*, 2021, **880**, 114889.