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A Novel Flakes-Like Structure of Molybdenum Disulphide Modified Glassy Carbon Electrode for the Efficient Electrochemical Detection of Dopamine

Rajalakshmi Sakthivel[1], *S. Dhanalakshmi*[2], *Shen-Ming Chen*[1,*], *Tse-Wei Chen*[1], *V. Selvam*[2], *Sayee Kannan Ramaraj*[3], *Wen-Hui Weng*[1,4,*], , Wai-Hung Leung[5,*]

[1] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, Republic of China.
[2] Department of Chemistry, VHNSN College, Virudhunagar – 626001, Tamilnadu, India**.**
[3] PG & Research department of Chemistry, Thiagarajar College, Madurai 09, Tamilnadu, India
[4]Graduate Institute of Biochemical and Biomedical Engineering, National Taipei University of Technology, Taipei City 106, Taiwan, R.O.C.
[5]Division of Colorectal Surgery, Department of Surgery, Mackay Memorial Hospital, Taipei City 104, Taiwan, R.O.C.
[*]E-mail: smchen78@ms15.hinet.net wendywwh@ntut.edu.tw leungwh22@gmail.com

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In this present study, we have reported a novel and simple hydrothermal approach for synthesis of molybdenum disulphide (MoS_2) flakes. The synthesized material effectively utilized for the fabrication dopamine electrochemical sensor. Moreover, the successful formation of flakes-like MoS_2 was confirmed by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray (EDX) studies. The electrochemical characteristics of the flakes-like MoS_2 were studied by using cyclic voltammograms (CVs) and amperometric (*i-t*) techniques. As an electrochemical sensor, the flakes-like MoS_2 modified glassy carbon electrode (GCE) exhibited higher electrocatalytic activity in the oxidation of dopamine in terms of higher oxidation peak current and lower oxidation potential when compared with bare GCE. The flakes-like MoS_2 based electrochemical sensor has been fabricated which detect dopamine in wide linear response range (0.006 - 181 µM), good sensitivity (3.98 $\mu A \mu M^{-1} cm^{-2}$) and very low detection limit of 2 nM. Moreover, the flakes-like MoS_2 modified GCE showed good selectivity even in the presence of biologically co-interfering compounds and common metal ions.

Keywords: Flakes-like structure, MoS_2, SEM, Electrochemical sensor, Dopamine

1. INTRODUCTION

Nanostructured materials possess great interest in the field of physics, chemical and electronic devices [1]. Recently, transition metal dichalcogenides such as MX_2 (M = Mo, W, V; X = S, Se, Te) have stimulated intensive research due to their excellent semiconducting performances, unique thickness, versatile electronic and optical properties. In particular, MoS_2 is an important transition metal dichalcogenides with analogues equal to graphene, which built up of molybdenum atom sandwiched between two sulphur atoms by a weak van der Waals force [2-4]. MoS_2 have been widely investigated in various potential applications in lubricants, photoactive material, solar energy device, catalysis, photocatalysis owing to their high surface area, excellent optical, electronic, optoelectronic properties and so on [5-7]. In addition, MoS_2 demonstrates intrinsic peroxidase-like activity which makes them numerous nanozyme biological sensors applications [8]. Furthermore, MoS_2 is considered as a suitable material for transistors, semiconductor devices and spintronics due to its peculiar high on/off ratio, high charge-carrier mobility, spin-spitting nature [9]. nanosheets, plate-like, wall-like have been synthesized by utilizing the variety of synthetic routes [10]. However, to the best of our knowledge, there is no report available for the synthesis of flake-like structured MoS_2 and utilized as an electrochemical sensor for the detection of dopamine.

Dopamine (DA) is an important neurotransmitter, which plays an essential physiological role in human brain and neural system [11]. On the other hand, the DA hydrochloride salt is used for the shock treatment in heart attack, open heart surgery and some bacterial infections disease. Increasing the level of DA concentration in biological system of human body cause several diseases such as schizophrenia, Huntington's disease and Parkinson's disease [12-14]. Hence, the selective and sensitive determination of DA is more essential. Now days, various detection techniques have been used for the detection of DA, such as high performance liquid chromatography, mass spectrometry, calorimetric method, fluorescence, chemiluminescence, electrochemical methods and spectrophotometry [15-18]. Among those aforementioned methods, electrochemical determination is more suitable methods due to their high sensitivity, simplicity, low cost and fast response [19-21]. Unfortunately, the uric acid (UA) and ascorbic acid (AA) are the two main interfere with the DA detection, because UA and AA oxidation potential are similar with DA oxidization potential. In order to regulate these problems need to develop suitable electrode materials for the detection of DA.

The main objective of this work is synthesizing a flake like structured MoS_2 for the determination DA. A simple drop caste method was utilized for the fabrication of MoS_2 modified glassy carbon electrode (GCE). The prepared modified electrode is exhibited an excellent electrocatalytic activity for electrochemical oxidation DA due to the high surface area and enhanced electrical conductivity of MoS_2. Moreover, the GCE/MoS_2 modified electrode shows an excellent sensitivity and selectivity towards the detection of DA in real sample analysis.

2. EXPERIMENTAL SECTION

2.1 Materials and methods

Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), dopamine ($C_8H_{11}NO_2$) and thiourea (CH_4N_2S) and all chemicals were purchased from Sigma-Aldrich. All the chemicals were of

analytical grade and used without purification. The phosphate buffer solution (0.05 M PBS) was prepared by mixing of sodium dihydrogen phosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) and all the required solution were prepared by DI water.

The powder XRD analysis was probed by Bruker D8 Advance X-ray diffractometer (XRD) with monochromatized Cu-Kα radiation (λ=1.5418 Å). The scanning electron microscope studies were analyzed using Hitachi S-3000 H scanning electron microscope attached with HORIBA EMAX X-ACT energy dispersive X-ray spectrometer (EDX). The electrocatalytic behavior and the determination of dopamine were performed by cyclic voltammetry (CV) and amperometric (*i-t*), CHI 405a workstation (CH Instruments, USA). A conventional three-electrode system has been used for the electrocatalytic studies where the modified GCE as a working electrode (0.07 cm^2 & rotating disc glassy carbon electrode (RDGCE) 0.2 cm^2), platinum wire as a auxiliary electrode and Ag/AgCl- 3M KCl is used as a reference electrode.

2.2 Synthesis of flakes-like MoS_2

In a typical process, 0.2 mM of $(NH_4)_6Mo_7O_{24}.4H_2O$ and 0.5 mM of thiourea were dissolved in 80 mL of deionized water under vigorous stirring for 1 h. Then, the suspension was transferred into 100 mL Teflon-lined stainless steeled autoclave and heated at 160 ˚C for 8 h. After that, the resultant black colored precipitate was washed with water and acetone to remove impurities and dried at 100 ^oC for overnight.

2.3 Fabrication of flakes-like MoS_2 modified GCE

The flakes-like MoS_2 was prepared aforesaid synthesis method and the obtained black precipitate (5 mg/mL) was taken and it redispersed in de-ionized water. Before the modification, the GCE was well polished using 0.05 µm alumina slurry and washed with DI water for several times to remove the alumina particles on the polished GCE surface. Afterwards, the redispersed flakes-like MoS_2 was drop coated (optimized concentration; 8 µL) on the GCE surface and it was allowed to dry at room temperature. Finally, the dried flakes-like MoS_2 modified GCE was gently washed with DI water to remove the loosely attached molecules on the GCE surface. Finally, the MoS_2 modified GCE was used to further electrochemical studies.

3. RESULT AND DISCUSSION

3.1 Characterization of the flakes-like MoS_2

The crystallographic nature of as-prepared flakes-like MoS_2 were analyzed by X-ray diffraction analysis and shown in Fig.1. The distinctive diffraction peaks at 19.72, 29.30, 35.62 and 57.8 were assigned to the (002), (100), (102) and (110) planes of hexagonal MoS_2 [22]. There are no other significant peaks were identified which suggested that the purity of the MoS_2 flakes.

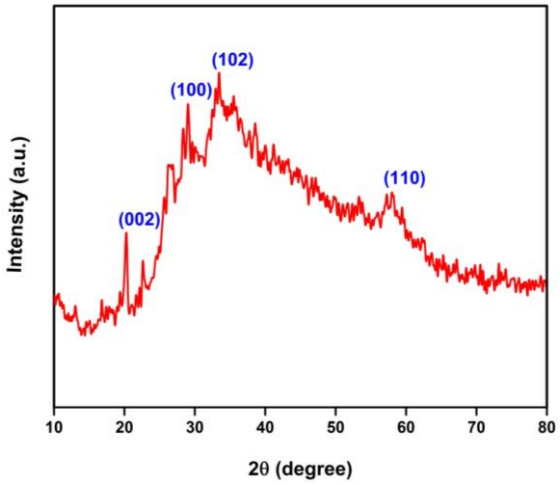


Figure 1. The XRD pattern of as-prepared flakes-like structure of MoS_2

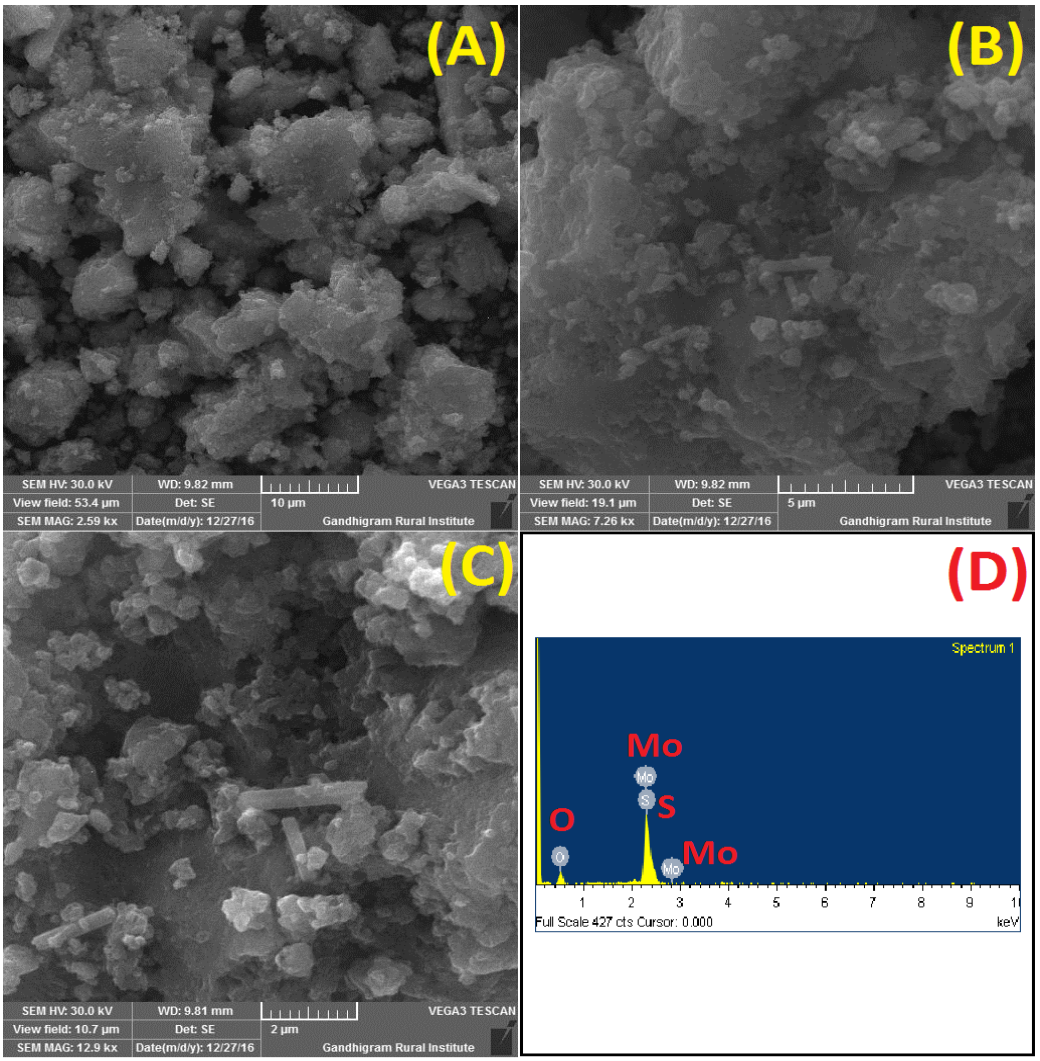


Figure 2. SEM images of flakes-like MoS_2 with different magnifications 10 µm (A), 5 µm (B), 2 µm (C) and corresponding to the EDX spectrum of MoS_2 (D).

Furthermore, the average crystalline size of the MoS_2 flakes were determined by using Scherer's equation as follows,

$$X_s = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where Xs is the size of crystalline, k is Scherer's constant, λ is X-ray wavelength, β is full width at half maximum of the high intense diffraction peak and θ is diffraction angle. The estimated grain size is to be 37 nm [49] .

The surface topography of the material was observed by scanning electron microscopy (SEM) analysis. Fig.2 (A-C) demonstrates the SEM images of as-prepared MoS_2 displays the flake-like structure with rough surfaces which randomly arranged one another. The average diameter range is to be 40-70 nm with the length of 1 µm. The elemental compositions of MoS_2 flakes were determined by energy dispersive x-ray studies (EDX) and the results are represented in Fig.2D. It revealed that, the MoS_2 flakes could consists of Mo and S elements without significant impurities.

3.2 Electrochemical behavior of dopamine at nanoflakes-like MoS_2 modified GCE

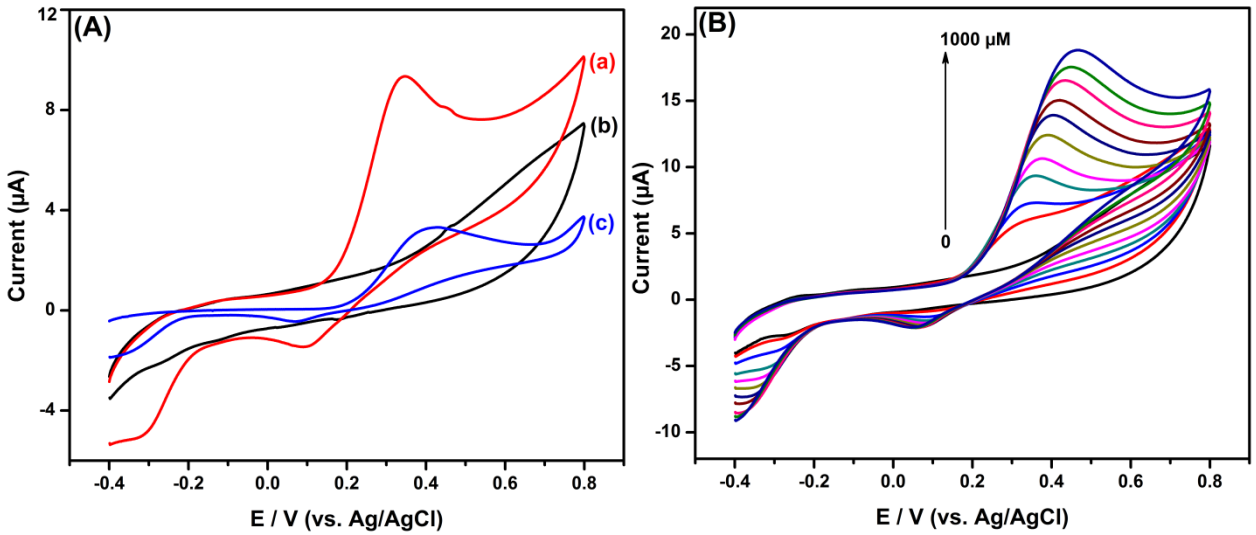
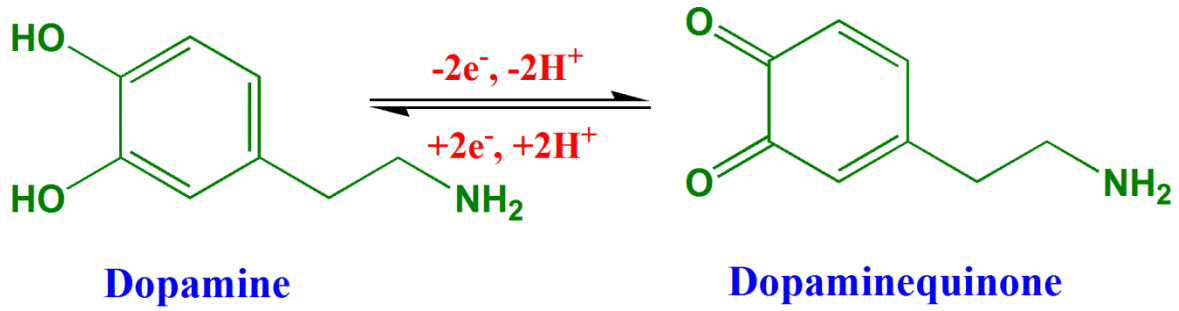


Figure 3. CVs recorded for 300 µM dopamine (absence (b) and presence (c, a)) in 0.05M PBS (pH 7.0) at (c) bare GCE, (b) flakes-like MoS_2/GCE at a scan rate 50 mVs^{-1} (A). CVs obtained for flakes-like MoS_2 modified GCE as a function of various concentrations of dopamine (0-1000 µM) (B).

The cyclic voltammograms (CVs) of various electrodes for the electrochemical oxidation of 300 µM dopamine were studied and the corresponding curves are shown in Fig.1. For unmodified GCE in the presence of 300 µM dopamine (Fig.3A (b)) in 0.05 M phosphate buffer solution (PBS) pH 7.0 at a scan rate of 50 mVs^{-1}, the oxidation of dopamine occurred at a longer positive potential (0.42 V), which is due to the slow electron transfer between electrode surface and electrolyte. At the same time, the flakes-like MoS_2 modified GCE in the presence of 300 µM dopamine (Fig.3A (a)) shows well-defined quasi-reversible redox couple with lower potential and enhanced anodic peak current. The

oxidation peak was observed at the potential of 0.34 V, which is due to the oxidation of dopamine to dopaminequinone and the reduction peak was observed at the potential of 0.09 V, which is due to the reduction of dopaminequinone to dopamine [50]. The overall electrochemical oxidation and reduction mechanism of dopamine is shown in Scheme 1. This obtained result indicates that the flakes-like MoS_2 modified GCE could be facilitate the electrocatalytic activity (oxidation) of dopamine and reduce the over-potential of dopamine electrochemical oxidation at the surface of the modified electrodes. Moreover, the absence of dopamine there is no obvious redox peak was observed at the nanoflakes-like MoS_2 modified GCE, which indicates that the flakes-like MoS_2 modified GCE effectively oxidized the DA at given potential range -0.4 to + 0.8 V. Furthermore, the obtained anodic peak current at flakes-like MoS_2 modified GCE is 2.8 fold higher and 80 mV lower potential when compared to unmodified GCE. The obtained overall results indicate that the flakes-like MoS_2 modified GCE was act as an excellent electron mediators for the electrochemical oxidation of dopamine sensor.



Scheme 1. the overall electrochemical mechanism of dopamine

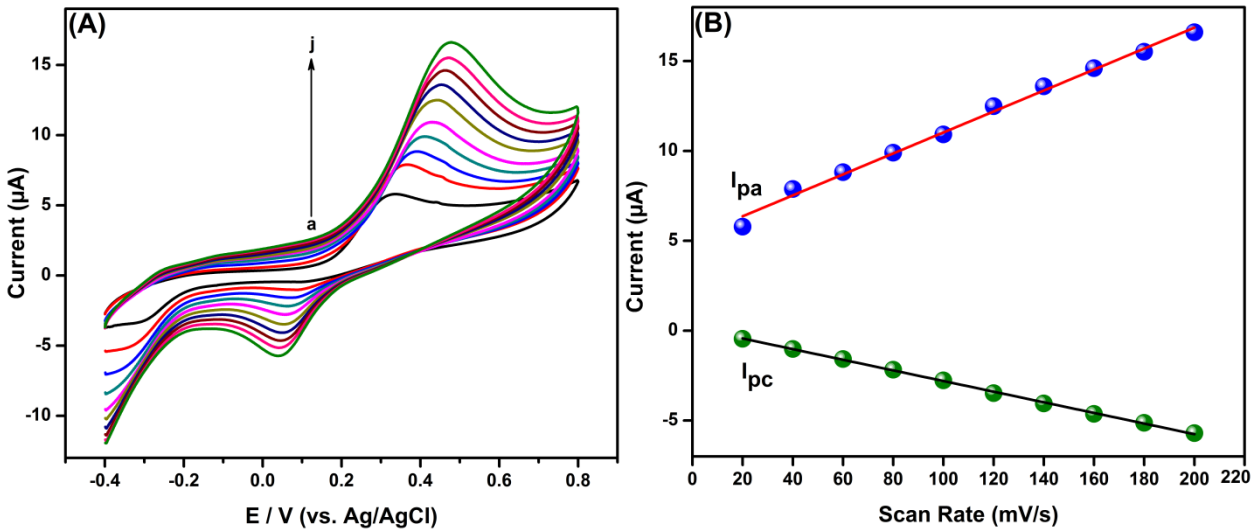


Figure 4. CVs of 300 μM dopamine for flakes-like MoS_2/GCE at various scan rates (20 - 200; a-j) (A) The plot of anodic and cathodic peak current *vs.* scan rate (B)

Furthermore, the electrocatalytic activity at flakes-like MoS_2 modified GCE for the electrochemical oxidation of dopamine was further confirmed by CVs with addition of different concentration of dopamine in 0.05 M PBS (pH 7.0) at a scan rate of 50 mVs^{-1} as it can be seen Fig.3B.

From the Fig.3B, it can be clearly seen that the increasing the concentration of dopamine from lower to higher concentrations such as 0 to 1000 µM, the anodic and cathodic peak current of dopamine was linearly increased, which indicates that the flakes-like MoS_2 modified GC electrodes had excellent electrocatalytic activity for the detection of dopamine and this excellent activity was occurred from the availability of large surface area, excess electro active sites and good electron conductivity on the MoS_2 surface, thus improve the electrocatalytic activity for the electrocatalysis of dopamine. Moreover, the electrochemical aspects such as correlation coefficient, sensitivity, linear response range and limit of detection (LOD) are discussed in elaborately in the amperometric (*i-t*) section (3.4).

3.3 The influence of scan rate and pH

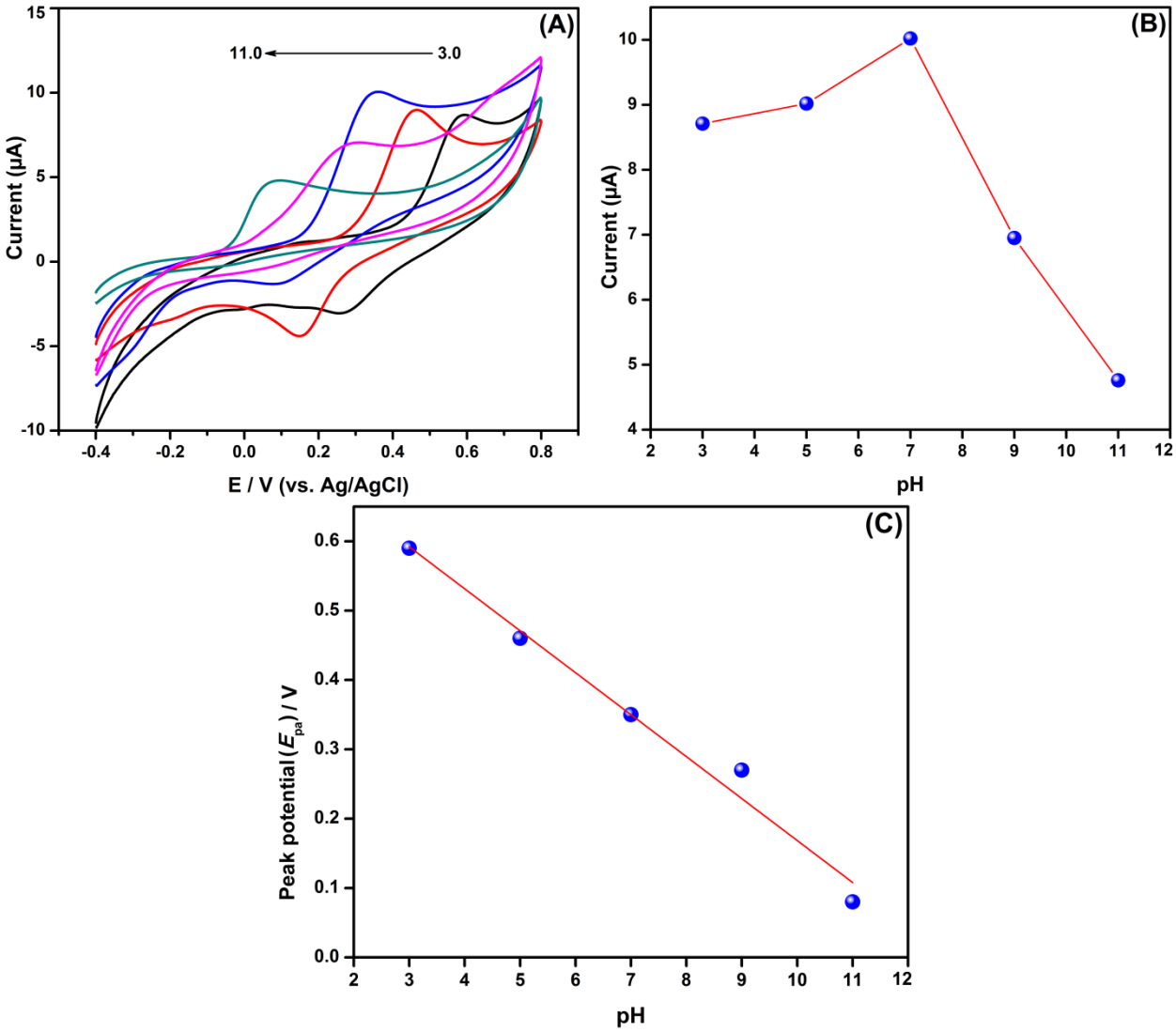


Figure 5. Effect of different pH solutions (3.0, 5.0, 7.0, 9.0 and 11.0) using flakes-like MoS_2 modified electrode containing 300 µM DA into 0.05M PBS at a scan rate of 50 mVs^{-1} (A). Calibration plot for E_{pa} vs. pH (B) and the linear plot between peak potential *vs.* pH (C).

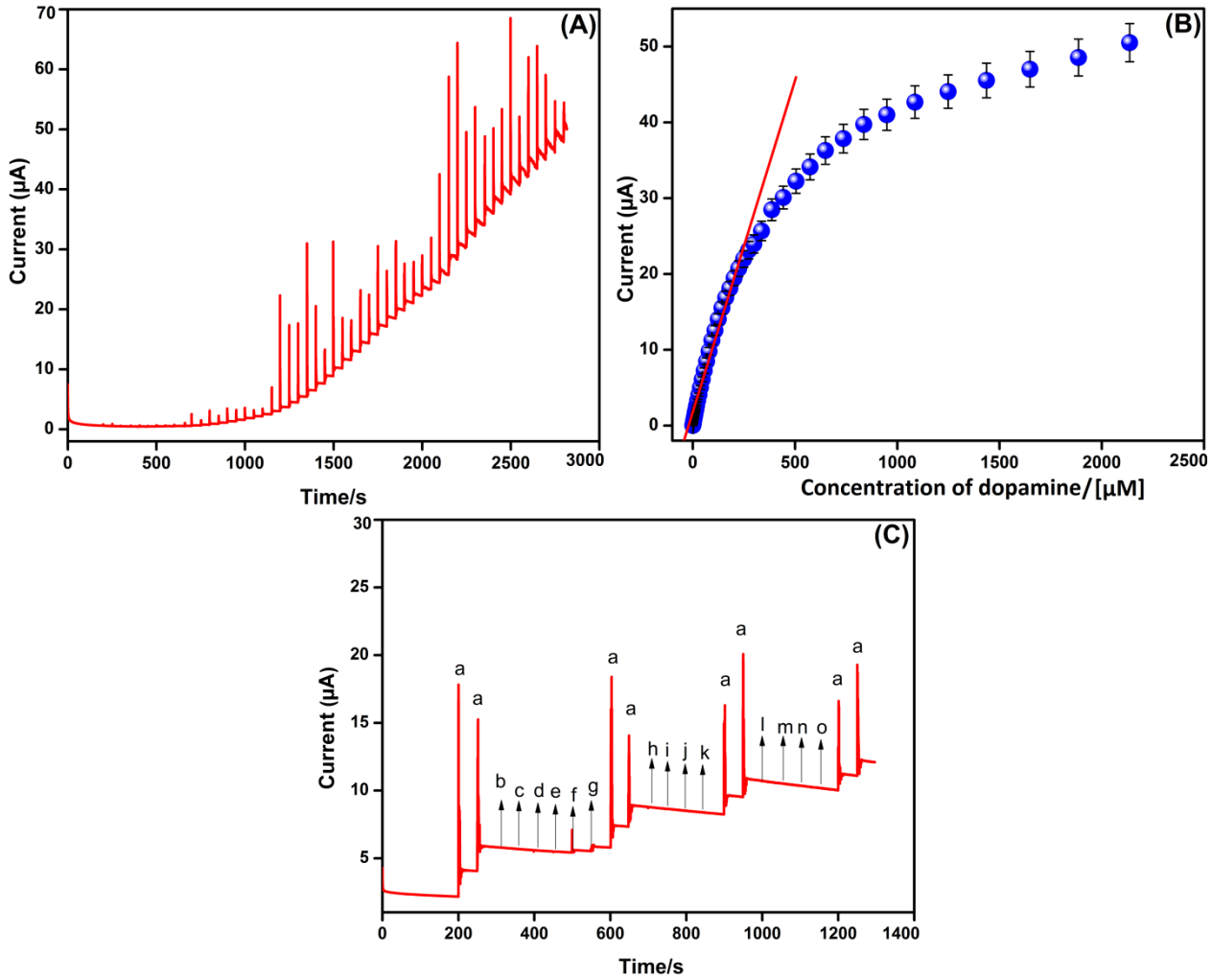


Figure 6. Amperometric (*i–t*) response obtained at flakes-like MoS_2/GCE (E_{app}= 0.35 V, rotation speed: 1200 rpm) upon successive addition of different concentrations of dopamine from 0.006 to 2136 µM into continuously stirred 0.05 M PBS (pH 7.0) (A). Concentration [dopamine] *vs.* I_{pa} (B). Amperometric (*i-t*) responses for dopamine at flakes-like MoS_2 modified RDGCE with successive additions of 12 µM dopamine (a) and 50 fold excess of glucose (b), sucrose (c), gallic acid (d), uric acid (e), catechol (f), ascorbic acid (g) and 100 fold excess of common metal ions Fe^{2+} (h), Cu^{2+} (i), Zn^{2+} (j), Co^{2+} (k), Br^- (l), Cl^- (m), I^- (n), NO_3^- (o) (C).

Fig.4A shows the CVs response of flakes-like MoS_2 modified GC electrode in the presence of 300 µM dopamine with various scan rates ranging from 20 - 200 mVs^{-1} (20-200; a-j) into 0.05 M PBS pH 7.0. It can be clearly seen that the both cathodic and anodic peak current of dopamine was gradually increases while increasing the scan rates from 20 - 200 mVs^{-1}. The linear plot was plotted between oxidation, reduction peak current vs. against the square root of scan rates (Fig.4B) with the linear regression equations of I_{pa} = 0.583 + 5.198 (µA, mV/s, R^2=0.9936); I_{pc} = -0.0296 + 0.156 (µA, mV/s, R^2=0.9992). The obtained results indicates that the electrochemical oxidation process of dopamine at flakes-like MoS_2 as an adsorption controlled electron transfer process rather than a diffusion-controlled at these scan rates [23,53].

The pH study is very important parameters for the electrochemical studies because the electrochemical response, peak shape, peak potential of the dopamine oxidation should be changed in

change in pH value. In order to investigate the different pH studies (pH= 3.0, 5.0, 7.0, 9.0, and 11.0) in the presence of 300 µM dopamine at the scan rate of 50 mVs^{-1} on the flakes-like MoS_2 modified GCE using CVs as shown in Fig.5 (A-C). The oxidation peak current of dopamine was increases with increasing the pH value from 3.0 to 7.0 and the oxidation peak current of dopamine was decreased while increasing the pH value above 7.0, the maximum oxidation peak current was observed at pH 7.0 (Fig.5B). Hence, we have chose pH 7.0 as a favorable electrolyte for the further electrochemical measurements of dopamine detection. Moreover, the increasing the pH value from lower to higher the peak potential also shifted to more positive potential which suggest that the protons are involved in the electrochemical oxidation process [51]. In addition, we also studied the linear relationship between oxidation peak potential and respect to the various pH values from pH 3.0 - 11.0. From the Fig.5C, it can be clearly seen that the oxidation peak potential has a linear relationship with pH 3.0 to 11.0; obviously suggesting that the electrocatalytic activity of dopamine at the flakes-like MoS_2 modified GCE is a pH dependent reaction. From the linear plot of Fig.5C, the calculated slope value is 60 mV/pH at 25 ^oC. According to the Nernst equation, the calculated slope is equal to the theoretical value of -59 mV/pH, suggesting equal number of protons and electrons are involved in the electrochemical oxidation process of dopamine [52].

3.4 Amperometric determination of dopamine at flakes-like MoS_2 modified GCE

Fig.6A reveals the amperometric (*i-t*) response of flakes-like MoS_2 modified RDGC electrode at 0.35 V upon consecutive addition of dopamine from lower to higher concentration of 0.006 to 2136 µM. The oxidation current changes monitored and reached steady state current quickly when dopamine is added into the 0.05 M PBS (pH 7.0). The response time is less than 5 s, which indicates that the flakes-like MoS_2 modified RDGC electrode had excellent electrocatalytic activity. Fig.6B exhibits the calibration plot (the calibration plot is derived from Fig.6A) of the response of the flakes-like MoS_2 modified RDGC electrode, it shows that the modified electrode has a wide linear response to dopamine ranging from 0.006 to 181 µM and the sensitivity of 3.985 $\mu A \mu M^{-1} cm^{-2}$ with the linear regression equation of I (µA) = 0.1074x + 0.35 dopamine (µM); correlation coefficient of R^2 =0.9903. From the calibration plot, the limit of detection is calculated to be 0.002 µM. The obtained analytical parameters such as limit of detection, linear response range and sensitivity of the flakes like MoS_2 modified RDGC electrode are summarized in Table.1. The lower LOD and linear response range was obtained as compared with other chemically modified dopamine sensor as reported in previously, indicating that the flakes-like MoS_2 modified RDGC electrode might be very effective for the detection of dopamine sensor.

The selectivity is also one of important study for the newly developed electrochemical sensor/ electrochemical biosensor. In order to evaluate the selectivity of the dopamine sensor at the flakes-like MoS_2 modified RDGCE by using anmpromtric (*i-t*) technique. The common interfering species such as 50 fold excess concentration of biological compounds; glucose (b), sucrose (c), gallic acid (d), uric acid (e), catechol (f), ascorbic acid (g), and 100 fold excess concentrations of some common metal cations and anions; Fe^{2+} (h), Cu^{2+} (i), Zn^{2+} (j), Co^{2+} (k), Br^- (l), Cl^- (m), I^- (n), NO_3^- (o), and 12 µM

dopamine (a) which are selected for the interference studies (Fig.6C). The interfering species such as common metal ions and biological compounds does not affected the oxidation signals of dopamine produced at the flakes-like MoS_2 modified RDGCE. However, the same oxidation current signals was observed even in the presence of aforementioned interfering compounds, suggesting that the prepared flakes-like MoS_2 modified RDGCE had excellent selectivity and it could be used for the real sample analysis for the dopamine sensor.

Table 1. Comparison of analytical performance of flakes-like MoS_2 with previously reported other chemically modified electrode for the detection of dopamine.

Nano material modified GCE	Detection Method	LOD (μM)	Linear range (μM)	Ref.
Graphene	DPV	2.64	4-100	24
Graphene-LDH	SWV	0.3	1-199	25
Cu_2O/Graphene	CV	0.01	0.1-10	26
Pd/NPs	DPV	NA	8-88	27
Au-NPs/Polyaniline	Amperometry	0.8	3-115	28
RGO-Pd-NPs	LSV	0.2333	1-150	29
Pyrolytic Graphite	DPV	0.02	0.05-30	30
NiHCF/Graphite Wax/Nafion	FIA	0.49	1.5-1200	31
Graphite nanosheet/Nafion	DPV	0.02	0.5-10	32
Oxidized GCE	CV	-	1.97-9.88	33
Pretreated GCE	CV	0.03	0.1-9	34
Electrochemically pretreated Graphite/Nafion	LSV	0.02	0.5-70	35
GNF electrode	DPV	1.5	1.5-27.5	36
Nanostructured Au	Amperometry	0.026	0.2-600	37
AuNPs/PANI	Amperometry	0.8	3-115	38
Au/PE/PS/BBD	CV	0.8	5-100	39
GO	DPV	0.27	1-15	40
Graphene/AuNPs	DPV	1.86	5-1000	41
Pt@Au/MWCNT	Amperometry	0.08	Upto120	42
Au Nanowire	Amperometry	0.4	0.4-250	43
AuNPs/β-CD/GR	DPV	0.15	0.5-150	44
GO-MWCNT/MnO_2/AuNPs	Amperometry	0.17	0.5-2500	45
Fe_3O_4@GNS/Nafion	DPV	0.007	0.02-130	46
AuNPs@PS/RGO	DPV	0.005	0.05-20	47
GA-RGO/AuNPs	DPV	0.0026	0.01-100.3	48
Flakes-like MoS_2	Amperomtry	0.002	0.006 -181	This work

3.5 Stability, reproducibility and repeatability

The CVs were chosen for the stability, reproducibility and repeatability studies. For the storage stability studies, the flakes-like MoS_2 modified GCE in presence of 200 μM dopamine have been taken and the anodic peak current was monitored periodically (one week). Only a small (5%) anodic peak current response was decreased from its original peak current response after one week, which suggests

good storage stability of the electrode. For the reproducibility studies, we chose 3 independent flakes-like MoS_2 modified GCE for the detection of dopamine with relative standard deviation (RSD) of 3.58 %, indicating good reproducibility. The repeatability studies were carried out in a single GC electrode modified with flakes-like MoS_2 for 5 consecutive measurements with RSD of 2.89 %, revealed its appreciable repeatability.

5. CONCLUSIONS

In conclusion, the flakes-like structured MoS_2 was successfully synthesized by simple hydrothermal treatment. The prepared materials were characterized and confirmed by XRD and EDX analysis also the surface morphology of MoS_2 was analyzed by SEM. Moreover, the synthesized flakes-like MoS_2 material was effectively used for the fabrication of dopamine sensor. The flakes-like MoS_2 modified GCE showed admirable electrocatalytic activity towards the detection of dopamine .The electrochemical biosensor exhibits quick response, wide linear ranges, low detection limit and it exhibited excellent anti-interference ability, good repeatability, reproducibility and storage stability. The obtained overall results revealed that the flakes-like MoS_2 could be used as a promising active electrode material for the detection of dopamine.

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