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Construction of a New Electrochemical Sensor Based on MoS_2 Nanosheets Modified Graphite Screen Printed Electrode for Simultaneous Determination of Diclofenac and Morphine

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This study used a hydrothermal method to synthesize MoS_2 nanosheets (NSs). The study also utilized various analytical procedures to characterize the MoS_2 NSs. It has been found that XRD, in particular, gave information on the crystal structure of the MoS_2 NSs. These NSs have been visible with SEM. In addition, EDX has been used to scrutinize MoS_2 NSs formation. Moreover, MoS_2 NSs modified graphite screen printed electrode (MoS_2 NS_S/GSPE) has been built by dropping the MoS_2 NS_S onto GSPE for making a voltammetric sensor as well as the evaluation of the morphine voltammetric behavior. Findings showed stronger electro-catalytic oxidation of MoS_2 NS_S for morphine with a more negative potential. Consequently, the modified electrode enabled the simultaneous detection of diclofenac and morphine with the peak potential at 0.47 V and 0.27 V. Results indicated linear response in a concentration range between 0.05 and 600.0 µM (morphine) with 0.03 µM limit of detection (LOD). Finally, the modified electrode has been substantially utilized for analyzing diclofenac and morphine in the samples of diclofenac tablet, urine, and morphine ampoule with acceptable recovery and accuracy.

Keywords: Diclofenac, Graphite screen printed electrode, Morphine, MoS_2 nanosheets

INTRODUCTION

Drug analysis, which is an important branch of analytical chemistry, plays an important role in drug quality control. For example, morphine has been introduced as one of the pain medications of the family "opiate" that naturally occurs in the poppy plant. This drug applies its direct effect on the central nervous system (CNS) for relieving the intense pain in the patients, in particular, those with the surgery [1]. However, drug abuse has been reported due to its euphoric feeling, resulting in addiction [2]. In addition, in case of the use in overdose or abuse, such a drug becomes toxic. In fact, in case of the reduction of dosage following a lengthy consumption, it is possible to withdraw. Moreover, multiple very unpleasant consequences like a slow heartbeat, drowsiness, vomiting, constipation, muscle stiffness, respiratory issues, and even coma have been reported [3]. Hence, morphine concentration must be specified in the urine or blood of patients with the use of a sensitive method for the prevention of toxicity from overdose or abuse, induced by overdosing or abusing. Over the last decades, experts in the field presented multiple analytical procedures like liquid chromatography (LC) accompanied by UV detection [4], chemiluminescence [5], fluorimetry [6], gas chromatography-mass spectrometry [7], spectrometry [8], thin layer chromatography [9], immunoassay [10] as well as electrochemical methods [11-13] in order to quantitatively detecting morphine in the samples of plasma, drug, and blood.

Moreover, diclofenac has been proposed as one of the nonsteroidal anti-inflammatory drugs (NSAIDs) that are exploited for treating a wide range of diseases like rheumatoid arthritis, ankylosing spondylitis, ankylosing spondylitis, osteoarthritis, osteoarthritis, rheumatoid

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arthritis, and so forth [14,15]. Interestingly, the effectiveness of diclofenac is the same as the efficiency of several current NSAIDs. In fact, this drug, as an analgesic, enjoys a rapid onset and longer period of action. In comparison to the available NSAIDs, the body can tolerate diclofenac well, and it hardly generates gastrointestinal ulceration or other acute consequences. Therefore, it could be regarded as an NSAID of the first option utilized for treating chronic and acute, aching, and inflammatory condition [16]. Hence, establishing a selective, effective, and sensitive technique would be vital for the assessment and quantification of diclofenac in real samples. In addition, experts in the field proposed diverse analytical procedures for detecting diclofenac that involves high-performance liquid chromatography (HPLC)-mass spectrometry [17], capillary zone electrophoresis [18], thin layer chromatography [19], gas chromatography [20], spectrofluorometry [21] and electrochemical techniques [22-24].

As one of the NSAIDs, diclofenac decreases the use of morphine following the surgery in adults. Moreover, the need to use morphine following abdominal surgery can be reduced by adding a regular dose of diclofenac [25]. Therefore, a highly selective and sensitive electrochemical sensor would be crucial to simultaneously determine the mentioned drugs in the biological fluids.

Furthermore, electrochemical determination has been considered as one of the alternative methods that have been largely considered because of simplicity, more rapid responses, time-saving operations, affordable instruments, higher sensitivity as well as inexpensiveness. However, in the electrochemical analyses, the main issue is to modify electrodes, which demands choosing proper materials for the improvement of the detection function [26-29].

It is notable that SPEs have been introduced the successful sensors, which are due to their wider potential window, lower background, versatility, sensitivity, and practicality. A feasible advantage in utilizing the SPEs is that they provide a reference, working, and auxiliary electrodes in a single tool [30]. Additionally, SPEs surfaces could be modified with different nanoparticles (NPs). A majority of the modifications could enhance the surface areas and produce sensors with greater LODs and better electrocatalytic features [31].

Moreover, researchers considerably attended to the uses of the nanostructured substances to fabricate the chemically modified electrodes. Furthermore, as the NPs are in small sizes, they exhibited certain electronic and physico-chemical features that could not be shown by the bulk forms [32-35].

Other studies considered the MoS2 as one of the types of transition metal sulfide that is fabricated by stacking covalently bound S–Mo–S via the weak Van der Waals interaction. Since MoS_2 is a 2D graphene analog, it is increasingly common because of its interesting features like uncommon optical characteristics, strong mechanical features, as well as more reasonable electrical functions, reflecting the encouraging options in photovoltaics, nanoelectronics, sensing, energy storage, biology, and catalysis [36-38].

This research aimed at the provision of a simplified, fast, and sensitive procedure that could simultaneously separate the electrochemical response of diclofenac and morphine. In addition, MoS_2 NSS showed enhanced catalytic activity in comparison to the unmodified electrode. Finally, the sensor viability has been confirmed and evaluated by diclofenac and morphine detection in the real samples.

EXPERIMENTAL

Apparatus and Chemical

For this step, each electrochemical experiment has been done at room temperature (25 ± 1 °C) with the use of an Auto-lab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie: the Netherlands) as well as a computer with the General-Purpose Electrochemical System (GPES) software. Then, electro-chemical cells have been adapted to the SPEs with the use of a Drop Sens-specific connector. After that, an SPE (DropSens: DRP-110: Spain) has been applied for obtaining the Differential pulse voltammogram (DPV), chronoamperogram (CHA), and cyclic voltammograms (CVs). The SPE has been constructed with a graphite working electrode (Ø= 4 mm) and graphite and silver (Ag) have been utilized as an auxiliary electrode, and pseudo-reference. To adjust the pH of the solutions, a 691 PH meter (Metrohm) was used. It should be noted that diclofenac, morphine, as well as each reagent and chemical employed

in the research, we obtained from Merck Co. (Darmstadt: Germany) has been of analytical grade and has been utilized as received with any additional treatment.

Synthesis of MoS_2 NS_S

We synthesized pristine MoS_2 NSs and thus we used 1.6 g NH_2CSNH_2 and 1.2 g $Na_2MoO_4.2H_2O$ as the S and Mo sources. Then, 0.6 g oxalic acid and the mentioned materials have been dissolved in the deionized water (80 ml) for adjusting the value of pH to the acid context. In the next stage, the mixed liquor has been magnetically shaken for nearly thirty minutes and consequently transported into a 100 ml Teflon-lined stainless-steel autoclave. Afterward, we sealed autoclave and heating has been performed in a drying oven at 200 ℃ for 24 hours. Upon the natural cooling to room temperature, the black resultants on the inner wall of the liner have been observed. Such black products have been cleaned using an ultrasonic cleaning with the distilled water and ethanol many times in order to eliminate the impurity and finally we dried it into a vacuum at 50 °C for twelve hours for obtaining the black MoS_2 powder [39].

Modification of SPGE

Notably, the electrode has been modified prior to each of the voltammetric experiments for improving the reproducibility and sensitivity of the outputs. Moreover, SPE has been modified using the MOS_2 NS_S through the drop casting pipetting a little volume (3 µl) over the surface of the working electrode. In addition, the solvent has been evaporated at the room temperature and a MoS_2 NS_S/SPE was created. As a result, we used water to wash the MoS_2 NS_S/SPE and dry it at room temperature.

Preparation of Real Samples

According to the research design, morphine injection has been diluted 10 times with water. After that, we transferred a distinct volume of the diluted solution to a 10 ml volumetric flask and diluted it to a mark with PBS at a pH of 7.0. Then, various contents of morphine have been used to spike the diluted sample.

In the next stage, we thoroughly ground and homogenized 5 tables of diclofenac for preparing the tablet (with the label: 100 mg per tablet, Abidi: Iran) solution. Next, an adequate volume of the tablet powder has been properly dissolved in 100 ml water with the use of ultra-sonication. Following an acceptable mixing, we filtered the mixture onto an ordinary filter paper, 10 ml of which has been consequently transported to the 50-ml volumetric flask and diluted to the mark with a buffer solution of pH 7.0. Therefore, a sample of the urine has been centrifuged, purified, and finally diluted with a 0.1 M PBS at a pH of 7.0 and utilized to detect the spiked diclofenac and morphine in the sample of the urine.

RESULT AND DISCUSSION

Characterization

Analysis of morphology. In this stage, we applied SEM to prepare the microscopic structure and morphology of the as-prepared pristine MoS_2 NSs with a hydrothermal procedure. Figure 1 represents the pertinent images. As seen, the MoS_2 powder contained big, smooth flower-like

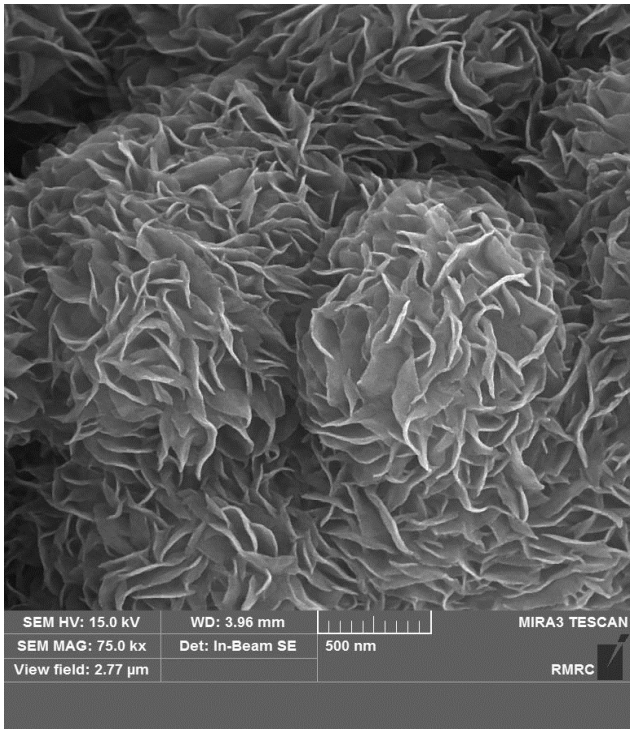

Fig. 1. The SEM image of the MoS_2 nano-sheets.

microspheres that have been created *via* multiple NSs, which have been gathered perpendicular to the spherical surfaces. Figure 1 shows that every MoS_2 micro-sphere structure had an average diameter equal to 1-1.5 µm. These nano-flowers surfaced had massive NSs with free and close aggregation. As shown, NSs expanded on the MoS_2 flower surfaces had disordered intersections and pointed towards a shared center of the sphere for forming spherical structures.
For the formation system of the micro-sphere structure, MoS_2 NSs have been largely affected by the hydro-thermal context. In fact, amorphous MoS_2 firstly evolved under 200 °C during the earlier hydro-thermal reaction time. Within the next reduction procedure from $Na_2MoO_4{\cdot}2H_2O$to MoS_2, the amorphous primary NPs could experience a free roll-up for forming the spherical structures with the dense curls over their surface for the elimination of the dangling bonds and diminishment of the total energy. These layered 2D properties of MoS_2 induced the prime structures to be aggregated into the spheres [40]. Figure 2 shows the EDX spectrum of the layers, verifying the presence of S and Mo in MoS_2 with no other impurity from the source constituents.

XRD analysis. The XRD patterns of MoS_2 powder are depicted in Fig. 3. As shown in the figure, visible diffraction peaks at 14.11, 33.19, and 58.1 have been allocated to (002), (101), and (110) planes of the hexagonal phase of the MoS_2 (JCPDS No. 37-1492). Therefore, we did not observe any impurity phase in the LOD of the instrument, reflecting the formation of a pure MoS_2 hexagonal phase. Moreover, the NSs crystalline can involve in the intensity of (002), (101) and (110) diffraction peaks.

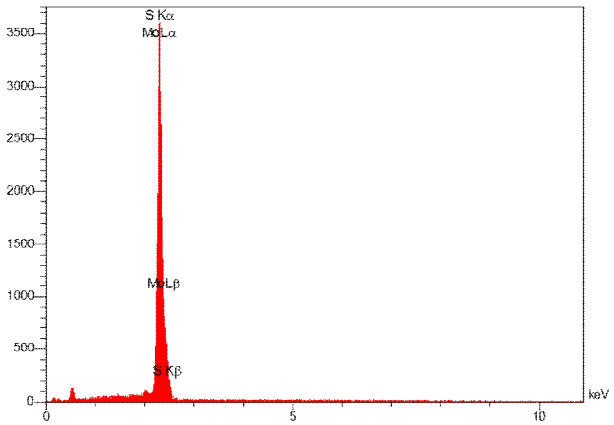

Fig. 2. The EDX spectrum of the MoS_2 nano-sheets.

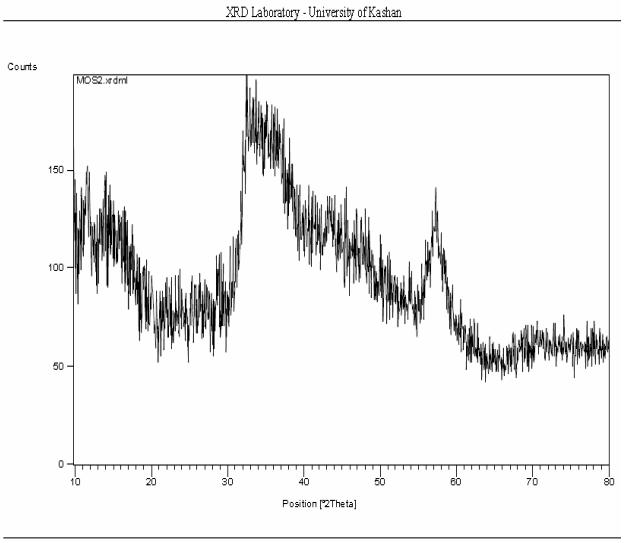

Fig. 3. The XRD pattern for the MoS_2 nano-sheets.

Electro-chemical Detection of Morphine on MoS_2 NS_S/GSPE

As we know, electrochemical behaviors of morphine depend on the value of the aqueous solution pH. Moreover, pH-value impact on morphine electro-oxidation has been determined at MOS_2 NS_S/GSPE surface with various 0.1 M PBS (pH at 2.0 to 9.0) using voltammetry. Outputs demonstrated helpfulness of the neutral condition for the electro-oxidation of morphine at the MoS_2 NS_S/GSPE surface as compared to the acidic or basic media. As a result, we chose pH at 7.0 as an optimized pH and thus additional research has been done at pH of 7.0.

Figure 4 is a representation of the cyclic voltammograms of MoS_2 NSs/SPE and bare SPE to oxidize 200.0 µM morphine. As seen, at the MoS_2 NSs/SPE and bare SPE, the potential of the oxidation peak of morphine equaled 280 and 360 V, which consequently switched to the more negative potentials. In addition, MoS_2 NSs/SPE demonstrated maximum peak current in comparison to the bare SPE. Therefore, greater current responses and shifting the anodic peak to a more negative potential reflected that MoS_2 NSs/SPE could be utilized as one of the beneficial promoters for increasing the kinetic of electro-chemical

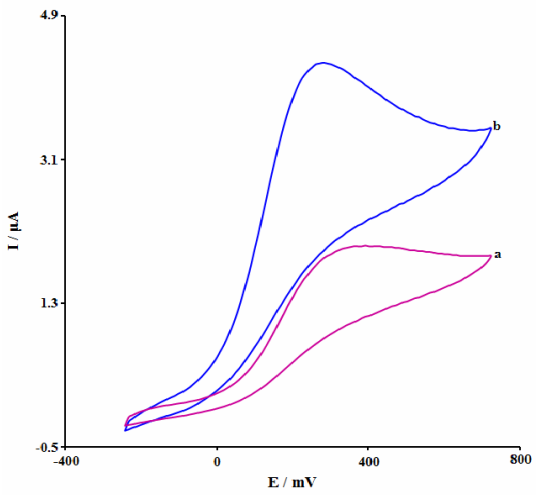

Fig. 4. The CVs of a. the bare SPE and b. the MoS_2 NS_S/SPE in the presence of 200.0 µM of morphine at pH equal to 7.0. The scan rate has been 50 mV s^{-1}.

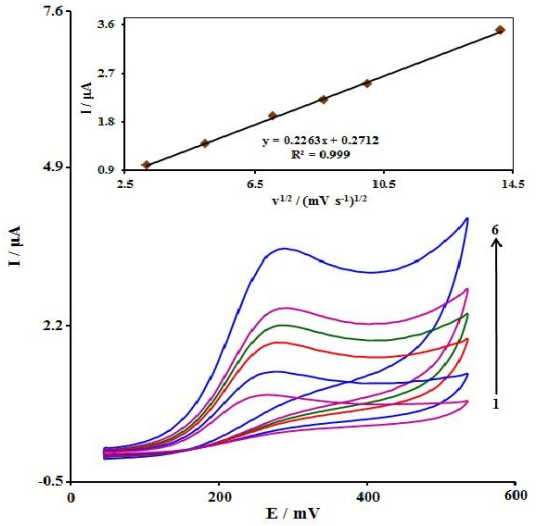

Fig. 5. CVs of MoS_2 NS_S/SPE in 0.1 M PBS (pH of 7.0) containing 70.0 µM of morphine at diverse scan rates. 1 to 6 corresponded to 10, 25, 50, 75, 100, and 200 mV s^{-1}. Inset shows changes in the anodic peak current *versus the* square root of the scan rate.

morphine oxidation procedure.

Impacts of the Scan Rate on Morphine Electro-oxidation

In the present research, we determined impacts of diverse scan rates in the ranges between 10 and 200 mV s^{-1}) on the morphine current responses (70.0 µM) on MoS_2 NS_S/SPE in PBS at pH of 7.0. Figure 5 represents the pertinent expansion spectrum. Outputs suggested the linear changes of the peak current with the square root of the scan rate ($v^{1/2}$) (Fig. 5 inset), verifying the diffusion-controlled procedure for morphine electro-oxidation at MoS_2 NS_S/SPE surface.

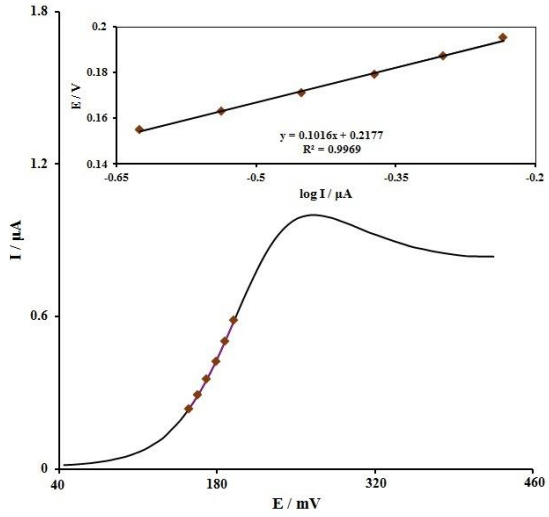

Fig. 6. LSV (at 10 mV s^{-1}) of the electrode in 0.1 M PBS (pH of 7.0) consisting of 70.0 µM morphine. As seen, the points represent data utilized in the Tafel plot and inset represents Tafel plot derived from LSV.

It should be mentioned that for obtaining data on the rate determining step, we drew the Tafel plot with the outputs extracted from the ascending part of the current-voltage curve, which has been registered at the scan rate equal to 10 mV s^{-1} (Fig. 6). Moreover, the value of the Tafel slope of 0.1016 V reflected the transfer coefficient as 0.42 for the 1-electron transfer procedure in the rate-determining step.

Chronoamperometric Measurement

According to Fig. 7, chrono-amperometric measurement of morphine at MoS_2 NS_S/SPE has been accomplished via adjusting the potential of the working electrode at 0.33 V for diverse concentrations of morphine in PBS. However, regarding an electro-active substance like morphine, which

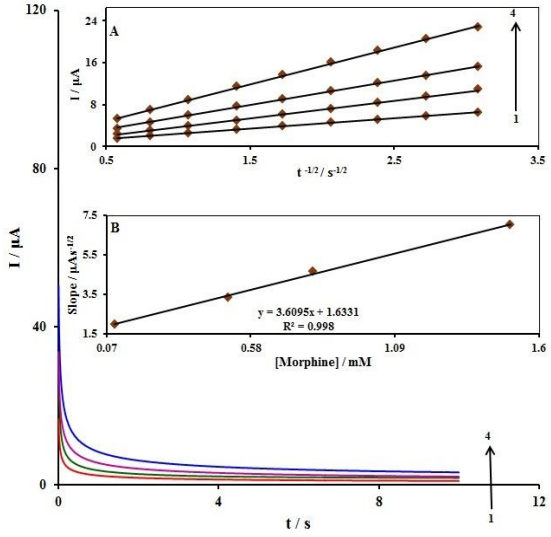

Fig. 7. Chrono-amperograms observed at MoS_2 NS_S/SPE in 0.1 M PBS (pH = 7.0) for distinct concentrations of morphine. 1 to 4 corresponded to 0.1, 0.5, 0.8, and 1.5 mM of morphine. Insets a): I *vs.* $t^{-1/2}$ plots achieved from chrono-amperograms 1-4. Inset b) The slope plot of the straight lines *versus* the concentration of morphine.

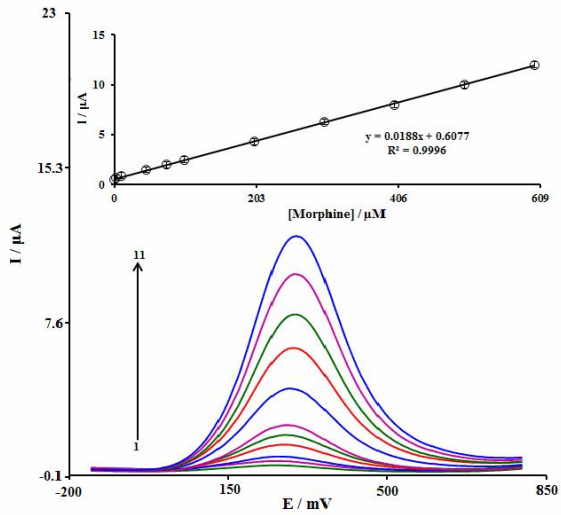

Fig. 8. DPVs obtained for MoS_2 NS_S/SPE in 0.1 M PBS (pH 7.0) consisting of distinct concentrations of morphine. 1 to 11 corresponded to 0.05, 2.5, 10.0, 45.0, 75.0, 100.0, 200.0, 300.0, 400.0, 500.0, and 600.0 µM of morphine. Inset: The peak current plot as a function of concentration of morphine in a range between 0.05 and 600.0 µM.

has a diffusion coefficient of D, Cottrell equation describes oxidation current seen to establish the electrochemical reactions at the mass transport limited conditions [41]. For this reason, we utilized the experimental plots of I *vs.* $t^{-1/2}$ that showed the best fits for distinct concentrations of morphine as shown in Fig. 7A. In the next stage, we drew slopes of the final straight lines versus the concentration of morphine (Fig. 7B). Finally, the resulting slopes and Cottrell equation have been used to determine the mean value of D, which equaled 1.1×10^{-6} cm^2 s^{-1}.

Calibration Plot and LOD

For this step, we exploited DPV for investigating MoS_2 NS_S/GSPE sensitivity with regard to the LOD for morphine at the modified GSPE (Fig. 8) (Step potential = 0.001 V, Amplitude = 0.02 V, Frequency = 10 Hz). Therefore, the peak current plot *versus* the morphine concentration linearly ranged in a concentration range between 0.05 and 600.0 µM. Moreover, morphine LOD equaled 0.03 µM. In the case of diclofenac electrocatalytic peak currents of diclofenac oxidation at the surface of MoS_2 NS_S/GSPE were linearly dependent on the diclofenac concentrations, over the range of 1.0×10^{-6}-8.0×10^{-4} M and the detection limit was obtained 5.0×10^{-7} M.

Simultaneous Determination of Diclofenac and Morphine

A major objective of the present research has been the simultaneous detection of morphine and diclofenac. Figure 9 is a representation of diverse DPVs of morphine with distinct concentrations in the presence of 150.0 µM diclofenac (Step potential = 0.001 V, Amplitude = 0.02 V, Frequency = 10 Hz). As seen, the peak current for morphine experienced a linear increase as the morphine concentrations enhanced in a range between 300.0 and 500.0 µM.

Figure 10 demonstrates the usability of the MoS_2 NS_S/SPE to simultaneously determine diclofenac and morphine. Moreover, simultaneous changes in the diclofenac and morphine concentration have been used to obtain the differential pulse voltammograms (Step potential = 0.001 V, Amplitude = 0.02 V, Frequency = 10 Hz). DPV outputs indicated 2 completely differentiated anodic peaks in accordance with diclofenac

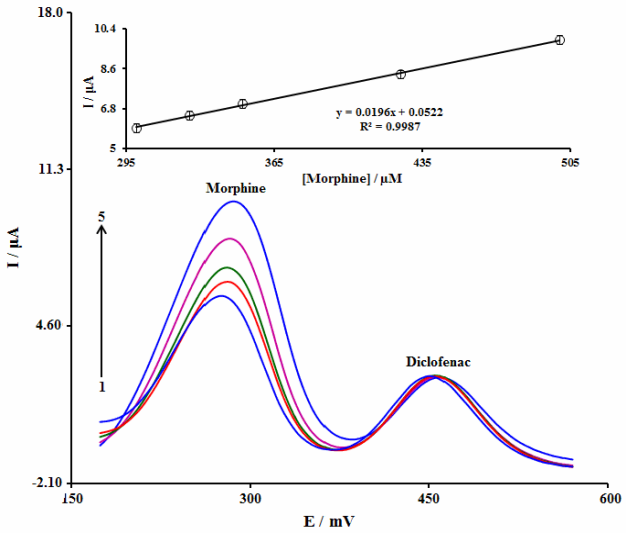

Fig. 9. DPVs observed for morphine at MoS_2 NS_S/SPE in the presence of 150.0 µM diclofenac in 0.1 M PBS (pH = 7.0). Concentration of morphine (in a range between 1 and 5): 300.0, 325.0, 350.0, 425.0, and 500.0 µM.

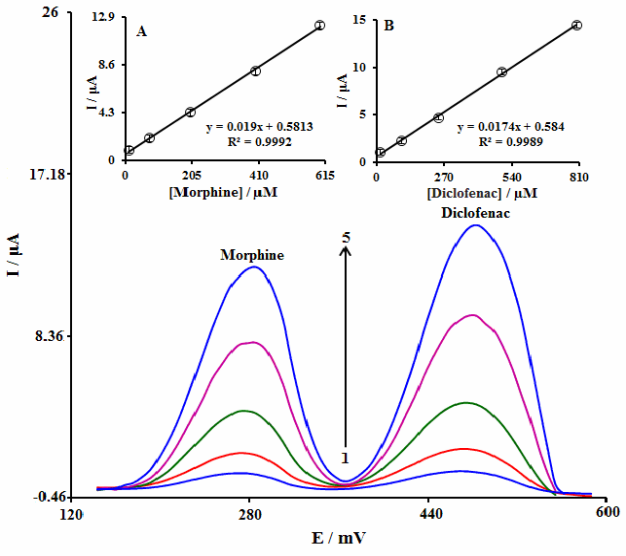

Fig. 10. DPVs observed on the MoS_2 NS_S/SPE surface in 0.1 M PBS (pH of 7.0) containing distinct Concentrations of diclofenac and morphine. Moreover, DPVs from internal to external correspond to 10.0+15.0, 75.0+100.0, 200.0+250.0, 400.0+500.0, and 600.0+800.0 µM of morphine and diclofenac, respectively. Inset a) Ip plot *vs.* the concentration of morphine and inset B) Ip plot *vs.* concentration of diclofenac.

and morphine oxidation at MoS_2 NS_S/SPE surface. In addition, results indicated approximately 0.019 µA μM^{-1} sensitivity of the modified electrode toward morphine oxidation in the presence of diclofenac that has been strongly close to the value (0.0188 µA μM^{-1}) in the absence of diclofenac. Hence, it has been probable to simultaneously have a voltammetric detection of diclofenac and morphine at the MoS_2 NS_S/SPE surface in the mixture samples with no cross interference.

MoS_2 NS_S/SPE Stability

A major feature in the current research has been considered to be the extended stability of the modified electrode. Upon the storage of MoS_2 NS_S/SPE for two weeks, just a little reduction has been seen in the peak current sensitivity with the relative standard deviation (RSD) equal to 1.6% (for 50.0 µM morphine). Such a condition reflected the acceptable stability of the modified electrode. In addition, detection reproducibility has been possible using 10 successive scans in a solution consisting of 50.0 µM morphine. Moreover, RSD-value equaled 2.3% for morphine, illustrating an acceptable reproducibility of the modified electrode.

Recovery Test for Morphine and Diclofenac in the Real Samples

In this section, we measured diclofenac and morphine concentrations in the samples of morphine ampoule, urine, as well as diclofenac tablet to test the functional utilization of the MoS_2 NS_S/SPE. Therefore, the standard addition method has been exploited for examining diclofenac and morphine recoveries in the real samples. Table 1 presents the outputs of the observed recovery and a summary of the outputs. This new method exhibited an acceptable recovery for the spiked diclofenac and morphine in the real samples, which reflected the application of such a modified electrode for determining diclofenac and morphine in diverse human fluids.

CONCLUSIONS

We made, the MoS_2 NS_S, determined their characteristics and utilized them to modify GSPE for getting

Table 1. Comparison of the Efficiency of some Electrochemical Methods in the Determination of Morphine

Electrode	Methods	Limit of detection (μM)	Linear dynamic range (μM)	Ref.
Glassy carbon	HPLC system	0.5	1.0-50.0	[40]
Glassy carbon	Amperometry	0.2	0.5-15.0	[41]
Glassy carbon	Cyclic voltammetry	0.2	4.0-100.0	[42]
Glassy carbon	Amperometry	≈100.0	90.0-1000.0	[43]
Aluminum	Amperometry	0.8	2.0-50.0	[44]
Carbon paste	DPV	0.14	0.45-450	[45]
Carbon paste	SWV	0.09	0.2-250.0	[46]
Screen printed electrode	Cyclic voltammetry	0.03	0.05-600	This work

Table 2. Diclofenac and Morphine Detection in the Samples of Diclofenac Tablet, Ampoule, and Urine. Each Concentration is Represented in μM (n = 5)

Sample	Spiked		Found		Recovery (%)		R.S.D. (%)	
	Morphine	Diclofenac	Morphine	Diclofenac	Morphine	Diclofenac	Morphine	Diclofenac
Morphine Ampoule	0	0	7.0	-	-	-	3.4	-
	2.5	5.0	9.6	4.9	101.0	98.0	2.4	3.2
	7.5	10.0	14.3	10.2	98.6	102.0	2.7	1.8
	12.5	15.0	20.0	14.9	102.5	99.3	3.1	2.4
	17.5	20.0	24.4	20.2	99.6	101.0	1.9	2.8
Diclofenac Tablet	0	0	0	11.0	-	-	-	2.9
	5.0	5.0	5.1	15.7	102.0	98.1	3.5	1.7
	10.0	10.0	9.9	21.5	99.0	102.4	2.3	3.3
	15.0	15.0	15.5	21.6	103.3	100.4	1.9	2.4
	20.0	20.0	19.5	30.8	97.5	99.4	2.7	2.6
Urine	0	0	-	-	-	-	-	-
	5.0	7.0	4.9	7.2	98.0	102.9	1.8	2.9
	7.5	12.0	7.6	11.8	101.3	98.3	3.5	1.8
	12.5	17.0	12.2	17.1	97.6	100.6	2.8	2.4
	17.5	22.0	18.1	21.8	103.4	99.1	2.3	3.3

a new electrode to be used in the electrochemical sensing. In fact, MoS_2 NS_S/SPE has an integration of the larger surface area and specific conductivity of MoS_2 NS_S with the notable electro-catalytic activities of MoS_2 NS_S and DPV has been used to exhibit their suitable sensitivity and higher selectivity for simultaneous individual determination of diclofenac and morphine with lower LOD. Moreover, MoS_2 NS_S/SPE showed greater implementation on the basis of the lengthier stability and higher reproducibility. In the end, our MoS_2 NS_S/SPE exhibited essential potential utilization to determine d for detections diclofenac and morphine in the real samples. Therefore, it has been concluded that the MoS_2 NS_S/SPE could be an encouraging electrode material for the electro-chemical bio-sensor utilizations.

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