Electrochemical detection of ofloxacin with MoS$_2$/RGO composite sensor

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Abstract. This work presents the development and utilization of a MoS$_2$/RGO nanocomposite sensor for the quantification of ofloxacin. The fabrication of this sensor is based on the combination of graphite oxide and MoS$_2$ as fundamental components. The special shape ordered atomic arrangement, and flatness of the MoS$_2$/RGO nanocomposite have made the sensor more sensitive and able to detect smaller amounts of the target substance. Cyclic voltammetry was employed in the sensing investigation, where the relationship between current and potential was explored using a modified glassy carbon electrode. The data explicitly demonstrates that MoS$_2$/RGO exhibits a substantially higher peak current (22.0–33.9 µA) and considerably lower overpotential (0.27–0.12 V) compared to MoS$_2$ alone. This translates to a significant enhancement in sensitivity (89.89 A/cm²) and detection limit (18.89 µM) for MoS$_2$/RGO. These remarkable improvements are attributed to the nanocomposite's facilitated charge transfer, increased specific surface area, and superior conductivity.

1 Introduction

Every year, pharmaceutical medications are used for a variety of goals, including human and wildlife health improvement and the diagnosis, prevention, cure, and treatment of disorders. Because of the long-lasting impacts that pharmaceuticals have on both human and animal health, there are concerns about environmental pollution associated with the increasing usage of these therapies. Public health concerns about pharmaceutical medications' enduring presence in the environment are raised by their increased use. Antibiotics are of special significance in the field of pharmaceuticals because, even at modest dosages, they have the ability to cause bacterial resistance, which presents serious long-term health risks to both humans and animals. Antibiotics are metabolized by organisms after consumption[1]. Nonetheless, significant amounts of the parent molecule are released into sewage and wastewater treatment systems as metabolites or in their unprocessed form. Furthermore, it has been shown that substances with pharmaceutical origins frequently remain in wastewater without degrading naturally[2]. Although no specific regulations currently govern the amount of antibiotics permitted in drinking and surface waters, both the World Health Organization and the European Union advocate for their sparing and judicious use, recognizing the potential consequences of widespread antibiotic contamination[3]. One prominent type of synthetic, broad-spectrum antibacterial drugs that works against both Gram-positive and Gram-negative bacteria is called a fluoroquinolone; these drugs work by preventing the
bacterial DNA from unwinding and replicating[4]. Ofloxacin, also known as 10-(4-methyl-1-piperazinyl)-9-fluoro-2,3-dihydro-3-methyl7H-pyrido-7-oxo[1,2,3-de]Six-carboxylic acid 1,4-benzoaxacine Orally administered as white crystalline powder, hemihydrate is a second-generation[5] synthetic antibiotic belonging to the fluoroquinolone class. The observed peripheral activity against Gram-negative bacteria following DNA gyrase activation in Gram-positive bacteria suggests broad-spectrum antibacterial potential[6]. From prostatitis to pneumonia, the versatile antibiotic ofloxacin tackles a vast range of bacterial infections in humans and animals, even extending its reach to aquatic breeding and veterinary medicine. On the other hand, careless or overuse of ofloxacin may increase bacterial resistance and tensile strength, leading to a range of adverse consequences such as tendon injury and potentially irreversible peripheral neuropathy[7]. There is a direct need of developing newer methods for the estimation of ofloxacin. However a lot of methods like chemiluminescence[8], spectrofluorimetry[9,10] and high-performance liquid chromatography (HPLC)[8] for antibiotic estimation but, these methods also possess certain disadvantages like need of expensive equipments, costly chemicals, with elevated analytical costs. For accurate detection of ofloxacin, it is crucial to find a technique with superior selectivity and sensitivity. One approach with potential is the utilization of chemically altered electrodes, which can overcome the restrictions posed by conventional methods by capitalizing on ofloxacin's intrinsic electroactivity. Despite numerous studies examining electrochemical detection of ofloxacin, further research is necessary to achieve heightened detection levels. Achieving optimal detection performance can be accomplished by appropriately selecting electrode materials. Ofloxacin determination has been achieved with various voltammetric techniques. However, there has been no mention of MoS$_2$/RGO composite film for electrochemical determination of Ofloxacin to the best of our knowledge.

2 Experimental details

2.1 Synthesis of MoS$_2$/RGO nanocomposite

MoS$_2$/RGO nanocomposite was prepared using already reported in our laboratory[11]. A single-pot hydrothermal synthesis technique was used to create the MoS$_2$/RGO nanocomposite. To put it briefly, 50 milliliters of distilled water were mixed with 800 mg of ammonium molybdate tetrahydrate, 2.0 g of L-cysteine, and 80 mg of graphene oxide (GO). After sonication, the mixture was placed in a Teflon-lined autoclave and heated in a muffle furnace for twenty-four hours at 200 °C. After being cleaned with ethanol, the resultant black powder was dried in an oven at 70 °C until it had the consistency of fine powder. The detailed characterization has already been published elsewhere[11].

2.2 Preparation of electrodes for electrochemical detection of Ofloxacin

There were two steps involved in the manufacture of the electrodes. Initially, 0.05 and 0.3 µM alumina slurry were used in succession to polish the glassy carbon electrode (diameter = 3 mm). To remove any remaining alumina, it was then ultrasonicated for five minutes in a 1:1 solution of deionized water and ethanol. Before moving on to the next step, the electrode was dried in an oven set to 60 °C. MoS$_2$/RGO nanocomposites were mounted on the polished
glassy carbon electrode surface (3.14 mm²) in the next phase. Using a micropipette, a carefully measured 5 µL aliquot of the nanocomposite slurry was applied to create the electrode. A small quantity of a 5% nafion solution was then added. Lastly, the modified glassy carbon electrode was dried in a heating oven at 60°C for 4-6 hours in a nitrogen environment to prevent oxidation of the electrode material and guarantee a homogeneous coating throughout the entire electrode surface. Ag/AgCl (saturated KCl) was used as the reference electrode, Pt wire as the counter electrode, and the MoS₂/RGO modified glassy carbon electrode as the working electrode for the electrochemical tests. All electrochemical studies were conducted using a pH 5 0.1 M BR buffer solution.

3 Results and Discussion

3.1 Electrochemical characterization of MoS₂/RGO modified glassy carbon electrode.

Using 10 mM Fe(II)/Fe(III) in 0.1 M KCl as the supporting electrolyte, a unique redox procedure was used to evaluate the electrochemical characteristics of MoS₂/RGO. As shown in Fig. 1(a), cyclic voltammetry was used to demonstrate the usual electrochemical behaviour of bare glassy carbon electrode (GCE) and MoS₂/RGO-modified GCE in a 10 mM Fe(II)/Fe(III) solution with 0.1 M KCl and a scan rate of 50 mV/s. Between two distinct redox peaks, a peak-to-peak distance (Ep) of 83 mV was found. The peak current of MoS₂/RGO/GCE was notably higher than that of bare GCE, indicating that the modification with MoS₂/RGO had improved conductivity. Cyclic voltammetry for MoS₂/RGO/GCE at different scan rates is shown in Fig. 1(a). The redox peak current rose in step with the scan rate, rising from 0.02 V/s to 0.2 V/s. A diffusion-controlled mechanism is implied by the linear relationship that has been seen between the anodic and cathodic peak currents and the square root of the scan rate[12].

Fig. 1. (a) CV scan with multiple scan rate and (b) current vs Scan number.

3.2 Electrocatalytic oxidation of Ofloxacin
Using cyclic voltammetry in 0.1 M BR buffer with a pH of 5, the electrocatalytic oxidation of ofloxacin was examined to evaluate the suitability of the MoS$_2$/RGO nanocomposite for electrochemical sensing. In the absence of Ofloxacin, no oxidation peak was detected, whereas the presence of 20 µM Ofloxacin revealed an oxidation peak at approximately 1.1 V. The current signal is not affected by the modified thin films on the bare glassy carbon electrode (GCE), which is an observation that emphasizes the better electro catalytic activity of RGO/MoS2 for the oxidation of ofloxacin[13].

![Typical CV Curves of the RGO/MoS2 modified GCE at a scan rate of 50mVs$^{-1}$ in 0.1 M BR Buffer solution (pH = 5) with 20µM Ofloxacin present (red) and absent (black).](image)

**Fig 2.** Typical CV Curves of the RGO/MoS2 modified GCE at a scan rate of 50mVs$^{-1}$ in 0.1 M BR Buffer solution (pH = 5) with 20µM Ofloxacin present (red) and absent (black).

### 3.3 Determination of Ofloxacin Using Differential Pulse Voltammetry (DPV) and amperometry

In contrast to cyclic voltammetry, differential pulse voltammetry (DPV) exhibits a lower limit of detection (LOD), increased sensitivity, and superior resolution. Figure 3 presents the DPV results for different concentrations of ofloxacin in 0.1 M BR Buffer. The subsequent equation demonstrates a linear relationship between the peak current (Ip) and ofloxacin concentration within the range of 1-1000 µM.

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I_{pa}(\mu A) = 0.086 \times (\mu M) + 5.635 \quad (R^2 = 0.9960).
\]

By applying the formula $3\sigma/b$—where $b$ is the calibration curve's slope (sensitivity) and $\sigma$ is the blank's standard deviation—it was possible to estimate the detection limit, which was 18.89 µM[14].
The MoS$_2$/RGO nanocomposite-modified electrode demonstrated improved current responsiveness in cyclic voltammetry and was employed as an amperometric sensor for the low-concentration detection of oofloxacin. A clear linear relationship between the oxidation peak current and oofloxacin concentration can be shown in Fig. 3(b). As can be seen in Fig. 3(b), the response current increases quickly over time, initially increasing gradually before abruptly changing. This pattern corresponds to the increasing dosage of Ofloxacin administered over time. The prompt electrochemical oxidation of ofloxacin at the MoS$_2$/RGO@GCE surface is evidenced by the swift transition of the current to a steady state. The current response shows a linear increase with each added unit of hydrazine, covering a considerable linear range from 10 μM to 7.7 mM. The exceptional conductivity and catalytic activity stemming from the RGO and MoS$_2$ combination play a pivotal role in enhancing the detection process. The comparison emphasizes the wider linear detection range of the developed sensor, ensuring a specific level of measurement precision. The nanosensor, constructed with the MoS$_2$/RGO composite material, demonstrates remarkable sensitivity, successfully detecting ofloxacin concentrations as low as 18.89 μM[15].

Fig. 3. (a) DPV analysis of oofloxacin (b) LOD curve for oofloxacin.

4 Conclusion

In conclusion, microwave irradiation has been used to conveniently and affordably synthesize crystalline MoS$_2$/RGO nanocomposite. To explore its morphological and structural features, the as-synthesised nanocomposite was characterized using a variety of techniques. The characterization results demonstrated that MoS$_2$/RGO nanocomposites with MoS$_2$ ornamented on the RGO layers was manufactured and was well-defined and structured. Moreover, the as-produced nanocomposite was used to alter a glassy carbon electrode that functioned as a reliable electron mediator for the ofloxacin electrochemical detection. The 89.89 Amp/cm$^2$ sensitivity and 18.89 μM detection limit of the manufactured levofloxacin electrochemical sensor have been determined. Thus, the research presented here showed how effectively produced MoS$_2$/RGO nanocomposite may be used to create a highly sensitive ofloxacin sensor with a relatively low detection limit.
References

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