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Fabrication of Sulfur-Doped Reduced Graphene Oxide Modified Glassy Carbon Electrode (S@rGO/GCE) Based Acetaminophen Sensor

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Abstract: In the past few years, the design and fabrication of highly sensitive and selective electrochemical sensors have received enormous attention from electrochemists. Acetaminophen is an important drug that is used as an antipyretic and analgesic drug throughout the world. It is important to monitor the accurate amount of acetaminophen. Herein, we have prepared sulfur-doped reduced graphene oxide (S@rGO) using simple strategies. The morphological feature of the S@rGO was characterized by using scanning electron microscopy whereas phase purity and formation of S@rGO were authenticated by X-ray diffraction. Further, the glassy carbon electrode was modified using S@rGO as an electrode modifier and employed as an acetaminophen sensor (S@rGO/GCE). This modified sensor (S@rGO/GCE) demonstrates a reasonable detection limit of 0.07 μM and a sensitivity of 0.957 μA/μMcm^2.

Keywords: S@rGO; acetaminophen; electrochemical sensor; differential pulse voltammetry

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1. Introduction

Acetaminophen is one of the most widely used antipyretic and analgesic drugs in the world [1–3]. Acetaminophen is commonly used to alleviate joint pain, headaches instigated by influenza, migraine, and mild pains [4–7]. Acetaminophen has the potential to control the preparation and discharge of central prostaglandins by tuning the body temperature [8]. In general, regular doses of acetaminophen have been considered harmless for the human body [9]. However, continuing or extreme use of acetaminophen can influence the human body [10,11]. The extreme use of acetaminophen can cause leukemia and liver damage, and in some cases, it can also cause malfunctions in the central nervous system of the human body. Due to the excessive production of acetaminophen, it is usually discharged into the environment as industrial effluent [12]. This release of acetaminophen as industrial effluent can pollute the environment [13–15]. Thus, it is important to develop a facile and efficient technique for the determination of acetaminophen. In this regard, conventional techniques including capillary electrophoresis, liquid chromatography, chemiluminescence, and fluorescence spectrum are widely used for the determination of acetaminophen [6–11]. Conventional methods and techniques are widely used as efficient detection techniques for the sensing of acetaminophen; however, conventional techniques have some serious limitations including larger equipment, expensive determination, and complex pretreatment [5]. Thus, it can be said that conventional techniques are not appropriate for the rapid/quick detection of acetaminophen in a routine analysis [16]. In the last few years,

the electrochemical method-based sensing platform has received enormous attention and a rapid surge in the development of electrochemical sensors has been seen [17–22]. The electrochemical sensing platform has many advantages including fast response, high sensitivity, good selectivity, cheapness, simplicity, and stability [23–26]. The acetaminophen can be easily oxidized electrochemically, therefore, acetaminophen can be easily detected by employing electrochemical methods [5]. In the present scenario, the design and fabrication of an acetaminophen sensor has drawn tremendous interest from electrochemists working on the development of electrochemical sensors for the determination of biomolecules or hazardous compounds. The detection of acetaminophen on bare electrodes such as glassy carbon electrodes (GCE) is kinetically slow [5]. In this regard, researchers have explored a variety of electrode materials to improve the sensing ability of the bare GCE by modifying the active surface of bare GCE with electrochemically active electrode materials [12–16]. The design and fabrication of an acetaminophen sensor with excellent activity and selectivity is vital to accurately detect and quantify the acetaminophen.

Due to their great chemical stability, electrical conductivity, high surface area, mechanical qualities, and optical features, carbon-based materials such as graphene oxide (GO), carbon nanotubes (CNT), graphene quantum dots, or reduced graphene oxide (rGO) are now the materials of interest [27–30]. In the past years, rGO has been extensively used in a variety of applications including electrochemical sensors, dye-sensitized solar cells, energy storage, perovskite solar cells, batteries, adsorption, wastewater treatment, and catalysis [31]. rGO plays a crucial role and has been proven as a potential candidate for electrochemical applications because of its low-cost and rich functional groups [28]. Previous reports also demonstrated that heteroatom doping can effectively improve the electrochemical behavior of rGO by tailoring its structure and functionalities [32]. The doping with heteroatoms to the rGO matrix may also create defects, tailoring band structure and tuning surface active sites.

In the present study, we have prepared sulfur-doped rGO (S@rGO) using a benign approach. Further, the acetaminophen sensor was developed by modifying the GCE with S@rGO as electrode material. So far, no research article is available on the utilization of S@rGO/GCE as an acetaminophen sensor using the DPV technique. This is the first research study that demonstrated the use of a S@rGO/GCE acetaminophen sensor.

2. Experimental Section

Graphite powder was bought from Merck. Uric acid, glucose, cholesterol, phenol, NaCl, and dopamine were bought from TCI and Sigma. We bought acetaminophen from Sigma. We bought phosphate-buffer saline (PBS) solutions from SRL. Sodium sulfide and other solvents and materials were bought from Fischer Scientific and used as received.

2.1. Synthesis of S@rGO

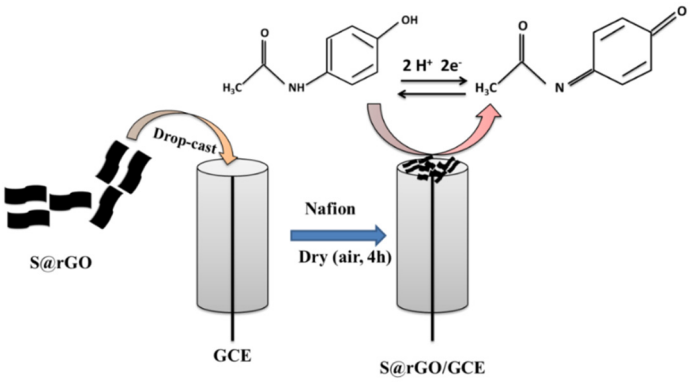
In the first step, graphene oxide (GO) was prepared using Hummer's method with some modifications [24]. Further, 30 mg of GO was dispersed in 50 mL of distilled water. In further experiments, 0.5 M sodium sulfide (Na_2S) was added to the GO dispersion and sonicated for 20 min. The reaction mixture was then transferred to a stainless steel autoclave (100 mL capacity, Teflon-lined cup) and heated at 200 °C for 6 hours before being naturally cooled to room temperature. The S@rGO was collected by centrifugation and dried at 70 °C overnight. All CV and DPV investigations were performed on CH instruments with three-electrode assembly.

2.2. Characterization

X-ray diffraction (XRD) patterns, scanning electron microscopic (SEM) images, and energy-dispersive X-ray spectroscopic (EDX) spectra of the prepared S@rGO were obtained on Rigaku (Tokyo, Japan), Xray diffractometer, Hitachi S-4800, and Horiba Instruments (Kyoto, Japan), respectively. Raman spectra were obtained on Horiba Scientific Instrument (laser wavelength = 532 nm; grating = 1800 gr/mm).

2.3. Preparation of Acetaminophen Sensor

Electrode material (3.5 mg/2 mL) ink was prepared by dispersing S@rGO in ethanol (0.1% nafion) via ultrasonication. The 9.5 µL of the prepared ink was deposited onto the bare GCE (3 mm in diameter) and dried for 4 h in air (Scheme 1). This modified electrode has been adopted as a working electrode whereas platinum and silver/silver chloride electrodes were used as counter and reference electrodes, respectively. All the electrochemical studies were performed on CH Instruments.



Scheme 1. A schematic illustration depicts the construction and operation of S@rGO/GCE.

3. Results and Discussion

3.1. Materials Characterization

Initially, we used the XRD technique to confirm the formation of GO by recording an XRD diffractogram in the 2-theta range of 5–50°. The XRD diffractogram of the obtained GO has been depicted in Figure 1. The XRD of GO exhibits the presence of a strong diffraction peak for (001) diffraction plane. This diffraction plane of (001) confirms the successful conversion of graphite to GO via Hummers' method. Further, the XRD diffractogram of the S@rGO was also obtained in the 2-theta range of 5–50°. The XRD of the S@rGO has been presented in Figure 1.

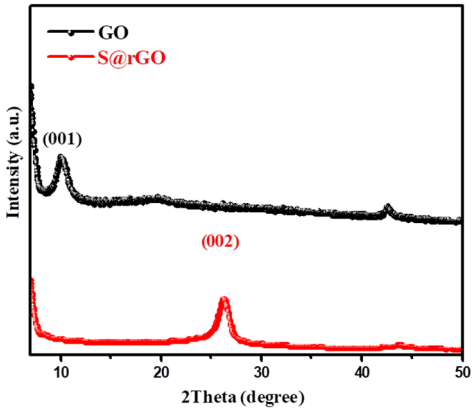


Figure 1. XRD of GO (black data) and S@rGO (red data).

The XRD pattern of the S@rGO indicated the presence of a strong diffraction peak related to the (002) diffraction plane. The disappearance of (001) and the appearance of (002) diffraction plane in the XRD pattern of S@rGO confirm the conversion of GO to S@rGO. It is clear that S@rGO has been prepared successfully. The Raman spectrum of the GO and S@rGO was also obtained which is presented in Figure S1. The Raman spectrum of GO showed the D and G bands (Figure S1). The presence of the G band with relatively higher intensity suggested the presence of graphitic nature in the prepared GO. The Raman spectrum of S@rGO also showed D and G bands with a low intensity of G band

which indicated the conversion of GO to S@rGO (Figure S1). Further, we also studied the morphological characteristics of the prepared GO and S@rGO using the SEM technique. The obtained SEM images of the prepared GO are presented in Figure 2a–c. The SEM results showed the presence of sheet-like morphological features which is a well-known characteristic of the GO (Figure 2a–c). On the other side, SEM images of the S@rGO are presented in Figure 2d–f. The SEM investigations exhibit that S@rGO is comprised of a sheet-like surface (Figure 2d–f).

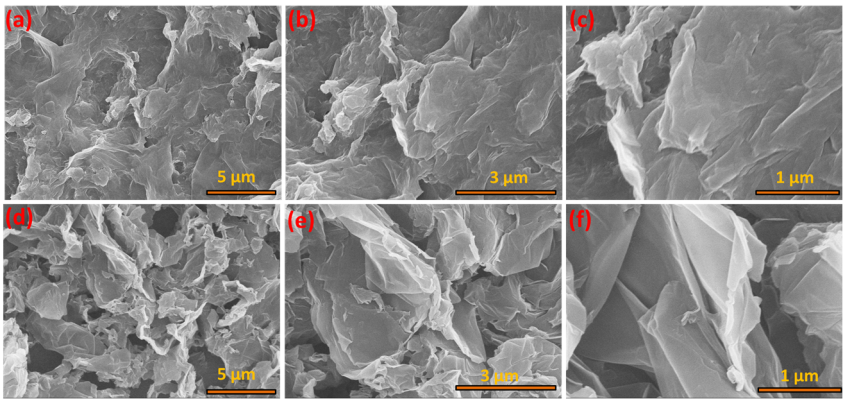


Figure 2. SEM images of GO (**a**–**c**) and S@rGO (**d**–**f**).

The determination of elemental composition is of great importance to verify the prepared materials. In this regard, we have adopted the EDX technique to verify the formation of S@rGO. The EDX results of the GO and S@rGO are presented in Figure 3a–d. The EDX spectrum of the GO showed the presence of C and O elements (Figure 3b).

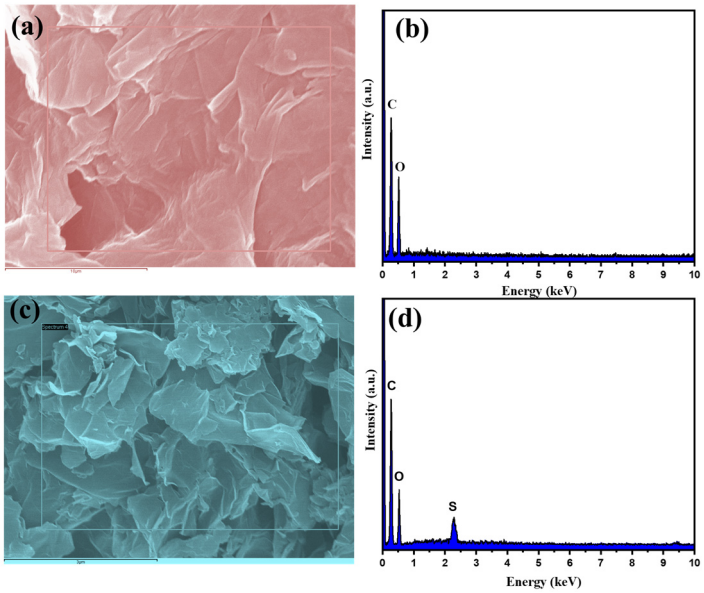


Figure 3. EDX image (**a**) and spectrum (**b**) of GO. EDX image (**c**) and spectrum (**d**) of S@rGO.

The prepared S@rGO's EDX spectrum revealed the existence of C, O, and S elements (Figure 3d). The EDX results verified that S was successfully introduced to the rGO.

3.2. Electrochemical Performance

Cyclic voltammetry (CV) was used to investigate the electrochemical activity of the GCE and S@rGO/GCE. The CV patterns of GCE and S@rGO/GCE were obtained in 0.1 M PBS at pH 7.0 with an applied scan rate of 50 mV/s (Figure 4b). The obtained

findings demonstrated that S@rGO/GCE has a considerably greater current response when compared to the GCE (Figure S1). In further examinations, the CV pattern of the GCE and S@rGO/GCE were obtained in presence of 91 µM acetaminophen in 0.1 M PBS (pH = 7.0; scan rate = 50 mV/s) (Figure 4a). The GCE demonstrates poor current response which indicated that GCE has poor electrochemical activity towards the sensing of acetaminophen. The S@rGO/GCE exhibits an improved current response for the determination of acetaminophen (Figure 4a). This suggested that the modified S@rGO/GCE has good electrochemical properties which enabled and fasten the electron transportation during electrochemical reaction for the sensing of acetaminophen (Figure 4a). Therefore, S@rGO modified (S@rGO/GCE) electrode was used as an acetaminophen sensor for further electrochemical studies using CV. The good electro-catalytic properties of the S@rGO/GCE towards the detection of acetaminophen can be attributed to the presence of defects on the S@rGO surface and functional groups. The pH of the analyte solution may influence the electrochemical sensing performance of the sensor. In this regard, we studied the effect of different pHs on the electrochemical sensing performance of the S@rGO/GCE using the CV approach. The observations showed that S@rGO/GCE has high electro-catalytic activity in PBS of pH 7.0 (Figure S2).

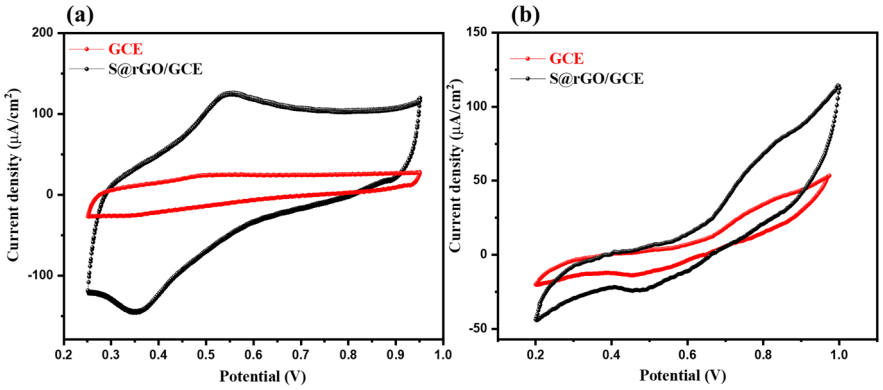


Figure 4. CV patterns of GCE and S@rGO/GCE in 91 µM (**a**) and 0 µM (**b**) acetaminophen in 0.1 M PBS of PH 7.0; scan rate = 50 mV/s.

The concentration of acetaminophen may influence the current response of the S@rGO/GCE. Hence, we obtained the CV patterns of the S@rGO/GCE in various concentrations of acetaminophen (0.05 µM, 3 µM, 9 µM, 19 µM, 28 µM, 39 µM, 50 µM, 67 µM, and 91 µM) in 0.1 M PBS of pH 7.0 (fixed scan rate = 50 mV/s) (Figure 5a). The CV studies of S@rGO/GCE in various concentrations of acetaminophen showed that current response increases with increasing concentration of acetaminophen (Figure 5a).

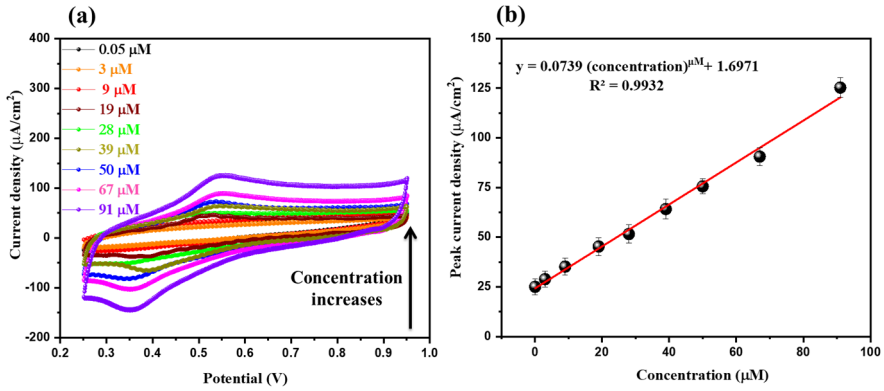


Figure 5. CV patterns (**a**) of S@rGO/GCE in various concentrations of acetaminophen (0.05, 3, 9, 19, 28, 39, 50, 67, 91 µM) in 0.1 M PBS of pH 7.0 (fixed scan rate = 50 mV/s). Calibration curve between peak current density response and acetaminophen concentration (**b**).

The calibration curve between peak current response and concentration of the acetaminophen was plotted (Figure 5b). The calibration plot indicated that the current response increases linearly with respect to the concentration of acetaminophen (Figure 5b). The scan rate can significantly change the current response of the S@rGO/GCE in a fixed concentration of acetaminophen. We also obtained CV patterns of the S@rGO/GCE in the fixed concentration of acetaminophen (91 μM) in 0.1 M PBS (pH = 7.0) at various applied scan rates (50–500 mV/s). Figure 6a shows the observed CV patterns of the S@rGO/GCE at various applied scan speeds (50–500 mV/s) in the fixed concentration of acetaminophen (91 μM) in 0.1 M PBS (pH = 7.0). The data amply shown that the S@rGO/present GCE's responsiveness grows as the applied scan rate increases (Figure 6a). The calibration curve between the scan rate and the S@rGO/current density GCE's response was shown. The calibration curve, shown in Figure 6b, suggests that the current response rises linearly as the applied scan rate increases (Figure 6b).

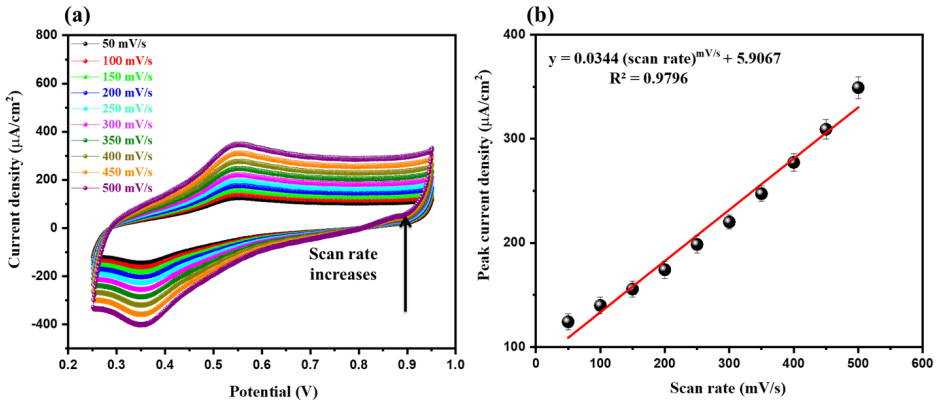


Figure 6. CV patterns (**a**) of S@rGO/GCE in a fixed concentration of acetaminophen (91 μM) in 0.1 M PBS (pH = 7.0) at various applied scan rates (50–500 mV/s). Calibration curve between peak current density responses versus scan rate (**b**).

Compared to CV or linear sweep voltammetry, differential pulse voltammetry (DPV) has emerged as a more prominent approach in recent years (LSV). In order to determine acetaminophen, we have also explored the DPV method. The DPV patterns of the GCE and S@rGO/GCE were recorded in the presence of 125 μM acetaminophen in 0.1 M PBS (pH = 7.0; scan rate = 50 mV/s).

Figure 7 displays the DPV patterns of the GCE and S@rGO/GCE that were obtained in the presence of 125 μM acetaminophen in 0.1 M PBS (pH = 7.0; scan rate = 50 mV/s). The observations suggested that GCE has a poor current response which was related to the poor electrochemical activity of the GCE (Figure 7). On the other side, S@rGO/GCE showed an enhanced current response towards the detection of acetaminophen compared to GCE (Figure 7).

This improved current response for S@rGO/GCE was related to the presence of S@rGO on the GCE surface, which verified the effective modification of GCE with S@rGO. Therefore, we have selected S@rGO/GCE as an acetaminophen sensor for further DPV studies. Similar to CV studies, we also obtained DPV patterns of the S@rGO/GCE in various concentrations (0.05 μM, 3.5 μM, 6.5 μM, 10.5 μM, 25.5 μM, 40 μM, 50.5 μM, 62 μM, 75.5 μM, 95.5 μM, and 125 μM) of acetaminophen in 0.1 M PBS of pH 7.0 at a scan rate of 50 mV/s and obtained results are shown in Figure 8a.

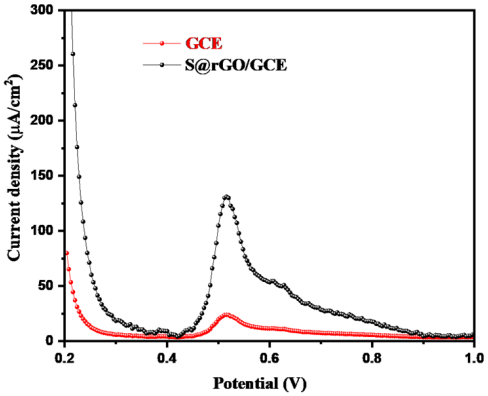


Figure 7. DPV pattern of GCE and S@rGO/GCE in presence of 125 μM acetaminophen in 0.1 M PBS (pH = 7.0; scan rate = 50 mV/s).

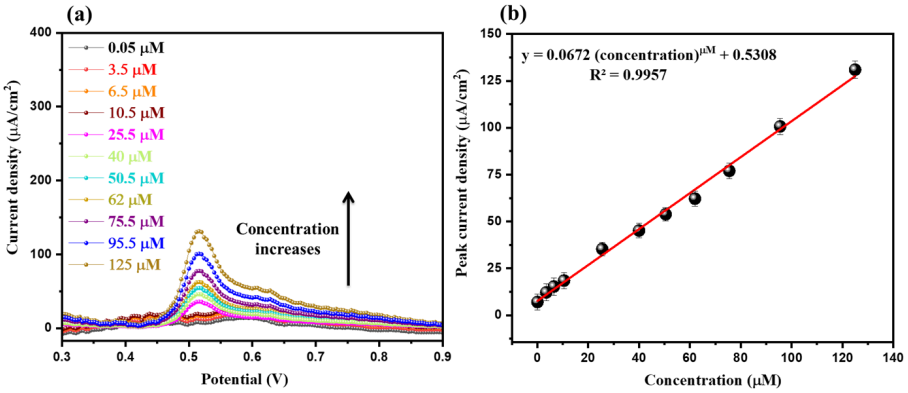


Figure 8. DPV patterns (**a**) of S@rGO/GCE in various concentrations (0.05 μM, 3.5 μM, 6.5 μM, 10.5 μM, 25.5 μM, 40 μM, 50.5 μM, 62 μM, 75.5 μM, 95.5 μM, and 125 μM) of acetaminophen in 0.1 M PBS of pH 7.0 at a scan rate of 50 mV/s. (**b**) Calibration curve between peak current density response versus acetaminophen concentration.

A similar trend was observed for DPV studies. The DPV patterns of the S@rGO/GCE exhibit that the current response for S@rGO/GCE increases with respect to the concentration of the acetaminophen (Figure 8a). The calibration plot indicated that the current response linearly increases with increasing concentration of the acetaminophen (Figure 8b). The different concentration of acetaminophen was used for DPV studies compared to the CV. This is because DPV with these concentrations (used for acetaminophen detection via the DPV method) showed good linearity in the current response.

In Scheme 1, the most likely mechanism for acetaminophen detection is depicted.

Sensitivity and detection limit (LoD) measurements were used to assess the electrochemical performance of the S@rGO/GCE. The following equations, which are shown below, were used to calculate the LoD and sensitivity of the S@rGO/GCE for acetaminophen sensing,

$$\text{LoD} = 3.3 * (\sigma/S) \quad (1)$$

$$\text{Sensitivity} = S/\text{area of the electrode} \quad (2)$$

(Herein, σ is the standard deviation/error; S = slope; and area of the electrode was 0.07 cm^2)

The calculated LoD and sensitivity of the S@rGO/GCE for acetaminophen sensing are presented in Table 1.

Table 1. Comparison of LoD, linear range, and sensitivity of S@rGO/GCE with recent reports [12,13, 33–38].

Material	LoD (μM)	Sensitivity (μA/μMcm^2)	References
NiO/CuO/rGO	1.33	0.618	[33]
Luteolin/f-MWCNTs	0.78	0.061	[34]
NiO	0.13	0.091	[12]
NiO/MWCNTs/MEFPE	0.5	-	[13]
Electrochemically activated GCE	0.28	-	[35]
C60 modified glassy carbon electrode (GCE)	50	-	[36]
Screen printed electrode modified Poly (3,4-ethylenedioxythiophene)	1.39	-	[37]
Nanoclay modified graphite	3.71	-	[38]
S@rGO/GCE	0.07	0.957	This work

The development of many acetaminophen sensors employing diverse electrode materials occurred in earlier years. In this connection, Liu et al. [33] prepared nickel oxide/copper oxide/reduced graphene oxide (NiO/CuO/rGO) composite using simple strategies. Further, the authors used this prepared composite as electrode material and investigated its electrochemical properties towards the detection of acetaminophen. The employed sensor showed an LoD of 1.33 μM and a sensitivity of 0.618 μA/μMcm^2. In another report [34], a luteolin/functionalized multi-walled carbon nanotube (f-MWCNTs) was explored as an acetaminophen sensor which exhibits LoD of 0.78 μM and sensitivity of 0.061 μA/μMcm^2. In other research work, a NiO-based acetaminophen sensor showed LoD of 0.23 μM and a sensitivity of 0.091 μA/μMcm^2 [12]. Shahmiri et al. [13] employed NiO/MWCNTs/MEFPE as an acetaminophen sensor which demonstrates the LoD of 0.5 μM. Awad et al. [35] used electrochemically active GCE as an acetaminophen sensor and reported an interesting LoD of 0.28 μM. Goyal et al. [36] employed a C60 modified glassy carbon electrode (GCE) as an acetaminophen sensor and obtained an LoD of 50 μM. Su et al. [37] used screen-printed electrode modified poly (3,4-ethylenedioxythiophene) as an acetaminophen sensor and reported a good LoD of 1.39 μM. Patil et al. [38] prepared a nanoclay modified graphite-based acetaminophen sensor and obtained an LoD of 3.71 μM. The obtained electrochemical performance for S@rGO/GCE was found to be reasonable with previous reports [Table 1].

The primary characteristic for practical application and objectives is the selectivity of electrochemical sensing. Studying how the S@rGO/GCE is selective for acetaminophen will be extremely important in this context. Thus, we also recorded DPV patterns of the S@rGO/GCE in the presence of 100 μM acetaminophen and 100 μM acetaminophen + interfering species (uric acid, glucose, cholesterol, phenol, NaCl, and dopamine) at a scan rate of 50 mV/s.

The obtained DPV patterns of the S@rGO/GCE in the presence of 100 μM acetaminophen and 100 μM acetaminophen + 500 μM interfering species (uric acid, glucose, cholesterol, phenol, NaCl, and dopamine) at a scan rate of 50 mV/s are provided in Figure 9.

The observations indicated that the presence of interfering molecules with acetaminophen does not alter the current response of the S@rGO/GCE. This revealed that S@rGO/GCE has good selectivity for the detection of acetaminophen. The consecutive 50 DPV cycles of the S@rGO/GCE were also run in the presence of 100 μM acetaminophen in 0.1 M PBS of pH 7.0 (scan rate = 50 mV/s). Figure 10 shows the first, 25th, and 50th DPV cycles of the S@rGO/GCE in the presence of 100 μM acetaminophen in 0.1 M PBS at a pH of 7.0 (scan rate = 50 mV/s). After 50 cycles, the acquired DPV data revealed no appreciable changes in the current response of the S@rGO/GCE in the presence of 100 μM. This indicated reasonably good repeatability and stability up to 50 cycles. The storage

stability of the S@rGO/GCE was also checked in presence of 100 µM acetaminophen in 0.1 M PBS (pH = 7.0; scan rate = 50 mV/s). The obtained results showed that S@rGO/GCE retained decent electro-catalytic activity after 15 days (Figure S3).

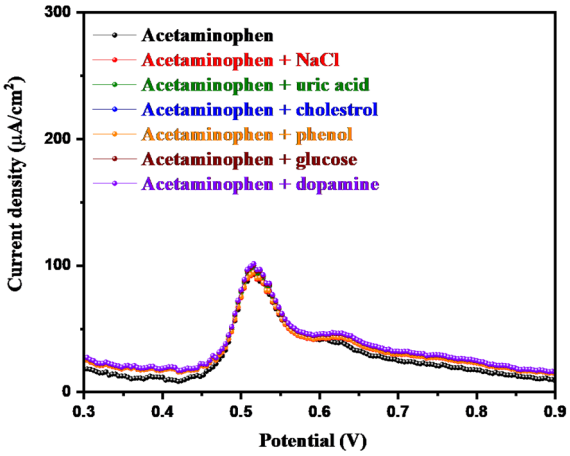


Figure 9. DPV pattern of S@rGO/GCE in presence of 100 µM acetaminophen and 100 µM acetaminophen + interfering species in 0.1 M PBS (pH = 7.0; scan rate = 50 mV/s).

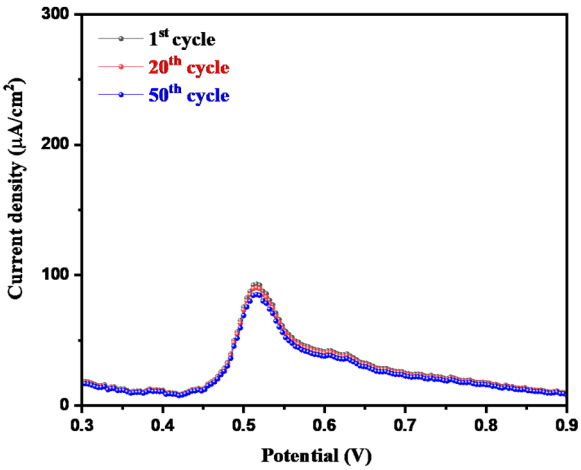


Figure 10. DPV patterns (1st, 25th, and 50th) of S@rGO/GCE in presence of 100 µM acetaminophen in 0.1 M PBS (pH = 7.0; scan rate = 50 mV/s).

4. Conclusions

It can be concluded that sulfur-doped reduced graphene oxide (S@rGO) has been synthesized by utilizing simple strategies. The synthesis of S@rGO with high phase purity was verified by the physiochemical characterization, which included X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Furthermore, the acetaminophen sensor was developed using the drop-cast method. Cyclic voltammetry and differential pulse voltammetry was used to study the electrochemical behavior of the fabricated S@rGO/GCE. The S@rGO-modified GCE exhibited a reasonable detection limit and sensitivity. Moreover, S@rGO-modified GCE showed good selective nature for the sensing of acetaminophen in the presence of various interfering compounds using differential pulse voltammetry. The S@rGO-modified GCE also shows good stability and repeatability.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics10120218/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

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