

Article

Electrochemical Sensing of H_2O_2 by Employing a Flexible Fe_3O_4 /Graphene/Carbon Cloth as Working Electrode

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Abstract: We report the synthesis of Fe_3O_4 /graphene (Fe_3O_4 /Gr) nanocomposite for highly selective and highly sensitive peroxide sensor application. The nanocomposites were produced by a modified co-precipitation method. Further, structural, chemical, and morphological characterization of the Fe_3O_4 /Gr was investigated by standard characterization techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and high-resolution TEM (HRTEM), Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS). The average crystal size of Fe_3O_4 nanoparticles was calculated as 14.5 nm. Moreover, nanocomposite (Fe_3O_4 /Gr) was employed to fabricate the flexible electrode using polymeric carbon fiber cloth or carbon cloth (pCFC or CC) as support. The electrochemical performance of as-fabricated Fe_3O_4 /Gr/CC was evaluated toward H_2O_2 with excellent electrocatalytic activity. It was found that Fe_3O_4 /Gr/CC-based electrodes show a good linear range, high sensitivity, and a low detection limit for H_2O_2 detection. The linear range for the optimized sensor was found to be in the range of 10–110 μM and limit of detection was calculated as 4.79 μM with a sensitivity of 0.037 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$. The cost-effective materials used in this work as compared to noble metals provide satisfactory results. As well as showing high stability, the proposed biosensor is also highly reproducible.

Keywords: co-precipitation; Fe_3O_4 /Graphene; flexible carbon fiber cloth; electrochemical; peroxide sensor



Citation: Sobahi, N.; Imran, M.; Khan, M.E.; Mohammad, A.; Alam, M.M.; Yoon, T.; Mehedi, I.M.; Hussain, M.A.; Abdulaal, M.J.; Jiman, A.A. Electrochemical Sensing of H_2O_2 by Employing a Flexible Fe_3O_4 /Graphene/Carbon Cloth as Working Electrode. *Materials* **2023**, *16*, 2770. <https://doi.org/10.3390/ma16072770>

Academic Editor: Alexander N. Obraztsov

Received: 20 January 2023

Revised: 14 March 2023

Accepted: 15 March 2023

Published: 30 March 2023



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1. Introduction

Nanocomposites (NCs) are used in many applications including adsorption and photodegradation of dyes [1–3], pharmaceuticals [4,5], as well as in computers and electronics [6,7], sensors [8,9], heat transfer [10,11], energy storage, renewable energy and supercapacitors [12–14]. NCs are also explored in several applications, such as, drug delivery [15,16], hyperthermia [17,18], tissue engineering [19,20], biosensing [21–23], energy conversion, and microwave adsorption [24,25]. The NCs are considered as nanomatrix for two or more nanoscale materials which present better performance as compared to their individual counterparts [26]. NCs materials have advantageous and unique properties owing to their boosted physical and chemical properties, high surface area, greater electron transfers ability, and exclusive optical properties [27,28].

Recently, NCs developed using carbon cloth aligned with different nanoparticles for various electrochemical applications. Carbon fiber cloth or/carbon cloth (CFC or/CC) is an

alternative to the conventional glassy carbon electrode, screen printed, and carbon paste which are used to fabricate working electrodes in electrochemical-based techniques [29]. The carbon fiber cloth (CFC) is usually made of the polyacrylonitrile-based carbon fiber with high conductivity, excellent flexibility and high porosity with adjustable size property [29,30]. The CC is employed in various electrochemical-based techniques such as fuel cells, supercapacitors, and sensors and biosensors applications [31–33].

Khorablou et al. [30] modified carbon cloth with Au nanoparticles and polythiophene for the detection of methadone. The prepared flexible NCs bear excellent sensitivity and selectivity toward methadone. Similarly, Liu et al. [34] have prepared Cu-coordinated molecularly imprinted polymers (Cu-MIP) and flexible carbon-cloth-supported Ag nanoparticles. The prepared materials were used as working electrodes for detection of perphenazine. The sensor provides satisfactory results with high sensitivity, good selectivity, and promising reproducibility and anti-interference ability. Ahmed et al. [35] proposed a histamine electrochemical biosensor based on a MIP, fabricated using Au inverse opal electrode. To improve the electrical characteristics of substrate, 3,4-ethylenedioxythiophene (EDOT) was electropolymerized on a scaffold of Au electrode. The biosensor exhibited high selectivity, good stability with a limit of detection (LOD) of 1.07 nM, and a linear response from 50 nM–500 μ M. Moreover, Xu et al. [36] have proposed an electrochemical enzyme-free biosensor for glucose detection using conductive Ni/Co bimetal metal oxide framework (MOF) which was grown on carbon cloth using facile hydrothermal method. The proposed flexible sensor exhibits a low detection limit of 100 nM (S/N = 3), excellent linearity range of 0.3 μ M–2.312 mM, high sensitivity of 3250 μ A mM^{−1} cm^{−2}, and a fast response time of 2 s under optimized conditions.

Among the most important sensors, the hydrogen peroxide (H₂O₂) sensor is in high demand and studied by various researchers. The precise H₂O₂ detection is of important concern due to its involvement in many fields, such as, chemical, biological, pharmaceuticals, clinical, environmental, and food processing industry. Therefore, it is necessary to have a H₂O₂ sensor with high sensitivity, good reproducibility, fast response, and high stability [37,38]. The sensor based on Fe₃O₄ shows excellent stability and electro-catalytic action against a different type of sample [37]. Zhang et al. designed the electrochemical sensor from the nanoparticles of iron oxide-polymer for the detection of H₂O₂. Cao et al. employed the co-precipitation method for the preparation of iron oxide NPs and characterized them by several techniques (EDX, SEM, and XRD). Fe₃O₄ NPs-based electrode materials showed a good response against the detection of H₂O₂. For the detection of H₂O₂, high sensitivity and good limit of detection were found [38]. Lin et al. have used the Fe₃O₄ and iron oxide/chitosan-based sensor for the detection of H₂O₂ in buffer solution. The electro-catalytic performance was measured by cyclic voltammetry at low voltage and also checks the response of H₂O₂ with the help of improved glassy carbon (GC) electrode with Fe₃O₄. The improved electrode of iron oxide/chitosan revealed good sensitivity and high stability with a considerable limit of detection [39].

In another study, Cao et al. used a co-precipitation method for the fabrication of NCs of ferric oxide-ferrous oxide and analyzed by different techniques (EDX, TEM, SEM, and XRD). The prepared Fe₃O₄-Fe₂O₃ is used as an electrode for the detection of hydrogen peroxide and finds a LOD of 200 μ M in 10 mM buffer solution at pH 7 [40]. Ates et al. fabricated NCs materials from biochar (BC) and Fe₃O₄ (Fe) and pasted them on the glassy carbon for the detection of H₂O₂. For sensing H₂O₂ in the real sample, the detection limit was arranged between 0.5 mM and 10 mM. From the results of reproducibility and sensitivity, it is clearly shown that Fe₃O₄-biochar is a good sensing material for the detection of H₂O₂ [41]. Cui et al. have also used the co-precipitation method for the fabrication of NCs of cobalt-doped iron oxide and characterized it by several techniques (SEM, XRD, and EDX). The SEM results show the spinal shape NPs forms of Co-doped Fe₃O₄ and LOD of H₂O₂ were found at 10 mM with a pH of 7 [42]. Sun et al. employed dumbbell-shaped Pt- and Pd-doped iron oxide NPs for the detection of H₂O₂ in buffer solution. Different impurities of Pt and Pd in Fe₃O₄ were used for H₂O₂ sensing and found the LOD of 5 $\times$ 10^{−9} M and analyzed that

NPs of Pd-Pt-Fe₃O₄ are excellent for the detection of H₂O₂ in the real sample as well as in the biomedical field [43]. Xu et al. employed the dual mode sensor (colorimetric sensor and electrochemical sensor) for the detection of H₂O₂ in the linear range from 1.0 µM to 120 µM. They prepared the NCs of iron oxide-molybdenum disulfide-gold (Fe₃O₄-MoS₂-Au). The limit of detection from electrochemical (EC) and colorimetric sensing was 0.08 µM and 0.109 µM, respectively [44].

Iron oxide NPs, despite their large surface area, tend to aggregate due to large magnetic dipole interaction. Therefore, iron oxide NPs-based sensors show poor sensing performance [45]. Iron oxide nanoparticles (NPs) with carbon-based compounds result in excellent biosensor applications. Due to the unique electrochemical properties of various nano allotropes of carbon reinforced with Fe₃O₄ NPs, they show better performance for the detection of H₂O₂. Zhao et al. [46] have demonstrated a real sample H₂O₂ sensor based on 3D graphene (Gr)-supported Fe₃O₄ quantum dots. H₂O₂ released from living cells is in very small quantities so it is a huge challenge to detect in situ detection of H₂O₂. The Fe₃O₄/3DGr NCs was found to be very efficient in situ detection with an outstanding reproducibility and very high sensitivity and selectivity of 274.15 mA M⁻¹ cm⁻². The sensor also revealed LOD of ~78 nM and a fast response time of 2.8 s. In a similar study, Yousefinejad et al. [47] have proposed a novel NCs for the detection of H₂O₂ in nanomolar range. The proposed NCs comprise carbon dots and iron oxide (Fe₃O₄) NPs. The LOD for hydrogen peroxide was determined to be 1.0 × 10⁻⁹ M and linear range was found to be from 1.0 × 10⁻⁸ M to 1.0 × 10⁻³ M.

Cai et al. have prepared the ternary NCs materials of GO (graphene oxide, Fe₃O₄ and PG (pristine graphene) and analyzed by transmission electron microscope (TEM) which clears that the NPs of Fe₃O₄ are arranged on the sheets of PG and GO. They employed this sensor for the detection of H₂O₂ and dopamine and found the LOD of 90 nM for hydrogen peroxide and 180 nM for dopamine [48]. Zhao et al. have synthesized a sensor by spraying the particles of platinum on NCs of Fe₃O₄/rGO and checked the electrochemical performance peroxide sensing. This sensor is very fast and sensitive for the detection of H₂O₂ and also very stable and compatible as compared to the other reported sensors. The limit of detection was 1.58 × 10⁻⁶ M, sensitivity was 6.9 µA mM⁻¹ [49]. Cai et al. also made the ternary materials of GO (graphene oxide), PG (pristine graphene), and Fe₃O₄ by co-precipitation method and checked by SEM and XPS. With the help of SEM, it concludes that the ternary compound of GO, PE, and Fe₃O₄ has outstanding performance for the detection of dopamine as compared to the binary compound of Go and Fe₃O₄. The finding limit of detection by this sensor was about 370 nM [50]. Hence, carbonaceous materials provide an excellent platform for biosensors due to their excellent thermal conductivity, high charge mobility and extraordinary electrochemical catalytic activity and shielding properties [51]. However, there is not much literature available on Fe₃O₄/Gr NCs for H₂O₂ sensing. Therefore, due to the unique chemical structure and electronic properties of NCs materials, it is required to explore such NCs prepared by different methods for H₂O₂ sensing.

To further explore the sensing abilities of Fe₃O₄/Gr NC, we have successfully synthesized these NCs via chemical co-precipitation method. The electrochemical performance of bare electrodes, Fe₃O₄/CC and Fe₃O₄/Gr NCs, was analyzed. All sensing parameters such as, LOD, sensitivity, selectivity, stability, and reproducibility were performed. Fe₃O₄/Gr/CC shows the better sensing ability such as high selectivity and high reproducibility toward H₂O₂. Moreover, Fe₃O₄/Gr/CC NCs-based flexible electrodes show a good linear range and a low detection limit for H₂O₂ detection.

2. Experimental

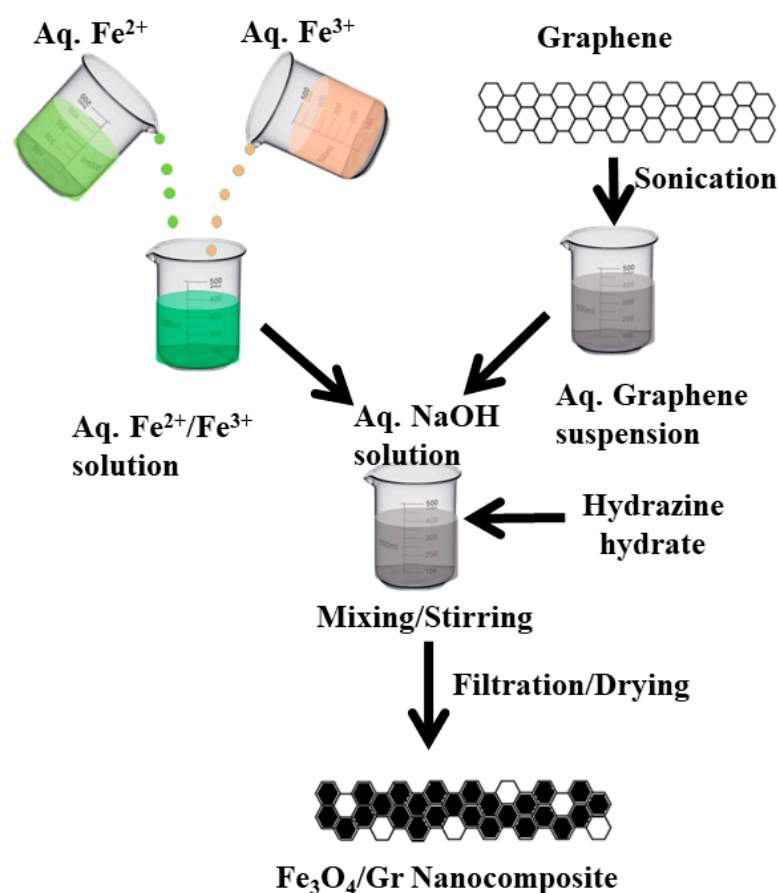
2.1. Materials Used in Synthesis

To obtain Fe³⁺/Fe²⁺ ions we have used 99.9% pure ferric chloride hexahydrate and ferrous sulfate heptahydrate salt which was procured from Sigma-Aldrich (St. Louis, MO, USA). Graphene nanopowder was purchased from Iljin Nano Tech, Seoul, Republic of

Korea. HCl (35%) and H_2O_2 were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Polymeric carbon fiber cloth was purchased from AvCarb Material Solutions (Lowell, MA, USA) and polymeric carbon fiber cloth (pCFC or CC) with a thickness of 356 microns and basis weight of 132 g/m^2 , grade of HCB with a plain weave construction.

2.2. Synthesis of Nanocomposite

Nanocomposite was synthesized by conventional chemical co-precipitation method. First, in a separate beaker, both salts of iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) were taken in 1:2 ratios and dissolved in distilled water to obtain a clear aqueous solution. Second, ultrasonic treatment was given to as-received graphene powder in distilled water for 3 h and solid graphene sample was collected from aqueous solution using a centrifuge at $3000 \times g$ RPM. Both samples of iron oxide were transferred into the aqua treated graphene suspension and the mixtures were stirred for 30 min. A 2M NaOH aqueous solution was added into the mixture drop by drop with continuous stirring until the whole solution turns into black precipitates. Additionally, 10 mL of hydrazine hydrate was added to the solution to stop the oxidation of graphene into graphene oxide during NCs preparation. The precipitates obtained from nanocomposite were washed several times by using distilled water and dried in an oven at $70\text{--}80^\circ\text{C}$ for 4–5 h. A schematic representation of $\text{Fe}_3\text{O}_4/\text{Gr}$ NCs fabrication is illustrated in Scheme 1.



Scheme 1. Schematic representation for the fabrication of $\text{Fe}_3\text{O}_4/\text{Gr}$.

2.3. Characterization

The investigation of nanocomposite was done by X-ray diffraction using Cu $\text{K}\alpha$ radiation ($\lambda = 1.54156 \text{ \AA}$) with D8A α S advanced X-ray diffractometer to obtain phase and crystallite size. Particle size and morphology were observed by scanning electron microscopy (FESEM, JEOL, JSM-7600F, Tokyo, Japan). The chemical bonding characteristics

were explored using Fourier transform infrared (FTIR) spectroscopy (ATR-FT-IR model Nicolet IS 10). For TEM images, a transmission electron microscope (TEM/HRTEM, JEOL, JEM-2100F) was used and operated at 120 kV for nanocomposite samples. A X-ray photoelectron spectroscopy was carried out by ESCALAB250 equipment outfitted with an Al K X-ray source.

2.4. Electrode Fabrication Process

For the fabrication of working electrodes, the surface of the CC is washed with ethanol/water under sonication and dried at room temperature. The 100 mg powder of each material (GO, Gr, and $\text{Fe}_3\text{O}_4/\text{Gr}$) is dispersed individually in the 1 mL of Nafion solution (binder) in order to generate a well dispersed slurry. The prepared slurry was dropped carefully onto the CC ($1\text{ cm} \times 2\text{ cm}$) with a marked area of 1 cm^2 and dried at room temperature. The fabricated electrodes were denoted as GO/CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ and results were compared with bare CC. The fabricated flexible electrodes such as GO/CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ were used as the working electrodes for the electrochemical measurements. The electrochemical tests were carried out on a potentiostat (VersaSTAT 3, Princeton Research, Princeton, NJ, USA) with a standard three electrode system. The Ag/AgCl was used as a reference electrode (filled with 3.0 M KCl) and a platinum gauge as a counter electrode.

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

From the XRD patterns, a significant peak of graphene was observed at two theta angles of 26.49° corresponding to the (002) plane of graphene [52], as represented in Figure 1a. The rest of the peaks are related to iron oxide which were observed at 30.19° , 35.55° , 43.18° , 53.63° , 57.11° , 62.82° , and 74.42° corresponding to (220), (311), (400), (422), (511), (440), and (622) crystal planes respectively. The iron oxide peaks intensity and relevant angles match with the JCPDS card no. 01-082-1553 which assures the cubic spinel structure and crystalline nature of the powder nanocomposite sample [53]. The crystal size was calculated using Scherrer equation which was found to be 14.5 nm.

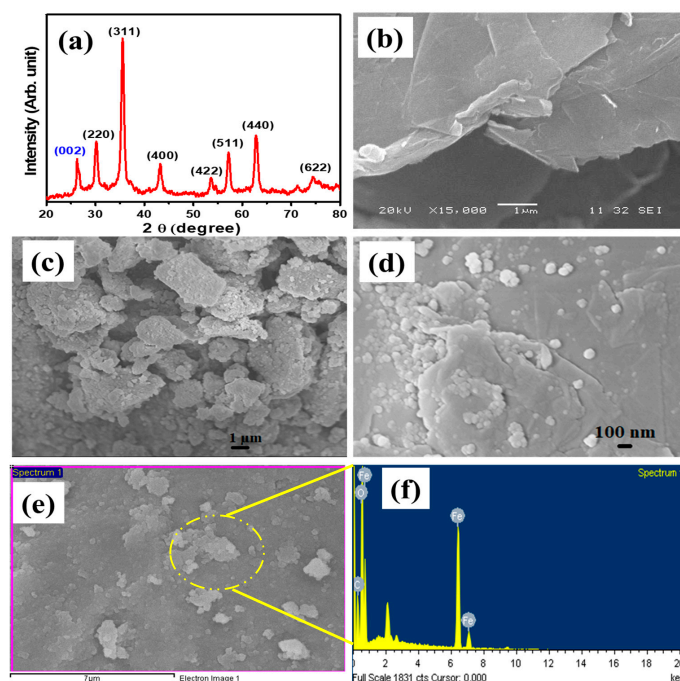


Figure 1. (a) XRD pattern of $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposite, (b) SEM image of graphene, (c,d) SEM image of $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposite, (e,f) SEM image and EDS analysis.

3.2. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

The morphology of graphene and $\text{Fe}_3\text{O}_4/\text{Gr}$ NCs was studied and represented in Figure 1. The Figure 1b shows the SEM image of graphene. The SEM image was taken with a magnification of 15,000 times under an electron beam accelerated with a 20 kV. The image shows multiple graphene sheets spread over each other. At the edge, many aggregates of graphene sheets with multi thick layers are visible. There may be some functional groups found attached on the surface of graphene sheets. It may be due to the fact that during the synthesis process some functional groups such as ($-\text{OH}$ and $-\text{COOH}$) still get attached and they can tune the electronic and chemical properties of graphene [54]. The SEM image in Figure 1c shows that at low magnification, several nanosheets of graphene can be seen decorated with Fe_3O_4 NPs. The spherical shape of Fe_3O_4 NPs in the form of clusters is grafted onto the nanosheets of graphene. Further analysis shows the random distribution of various clusters of Fe_3O_4 NPs on the graphene (Figure 1d). The nanospheres of iron oxide are spread on the surface of graphene sheets individually and most of the particles are aggregated. These clusters are helpful during electrochemical reactions by providing a more reactive site and extending the link of the Fe_3O_4 nanospheres with the analytes [55]. Additionally, SEM image, FTIR and RAMAN spectra are presented in Figure 2.

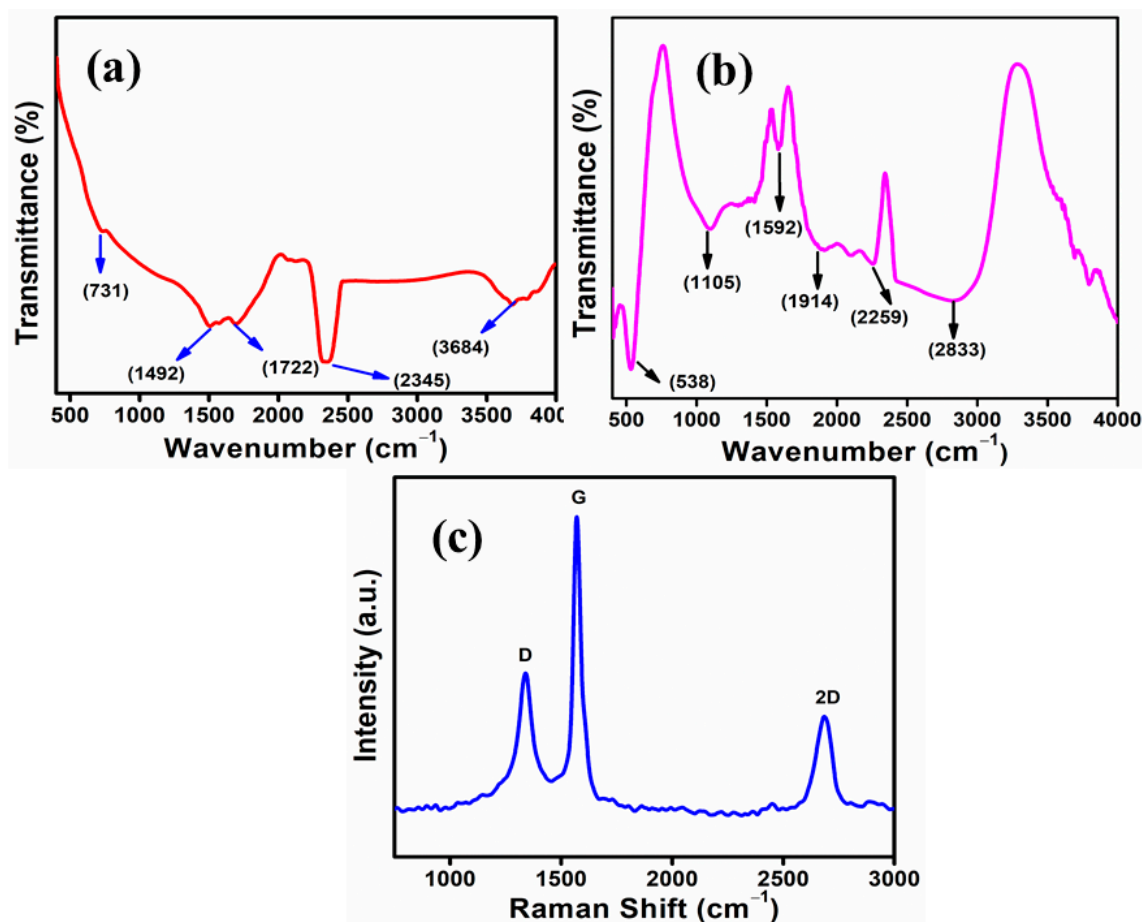


Figure 2. (a) FTIR spectra of graphene, (b) FTIR spectra of $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposite, and (c) RAMAN spectra of graphene.

The standard method for measuring the elemental make-up and composition of materials in the scanning or transmission electron microscope (SEM/TEM) is energy dispersive X-ray spectrometry (EDXS). EDS is typically used in place of the frequently abbreviated EDXS. An elemental breakdown of the $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposite is shown in the energy-dispersive

X-ray spectra (Figure 1d,e). It thus validates the formation of Fe₃O₄/Gr nanocomposite. The elemental composition for Fe, O, and C atoms was obtained and presented in Table 1.

Table 1. Elemental composition of Fe₃O₄/Gr nanocomposite from SEM-EDX analysis.

Element	Weight (%)	Atomic (%)
C K	14.98	31.44
O K	26.85	42.30
Fe K	58.17	26.26
Total	99.9	99.9

3.3. Fourier Transform Infrared Spectroscopy (FTIR)

NCs of iron oxide and graphene were analyzed using FTIR to identify their chemical structure. Figure 2a presents the FTIR spectra of graphene where certain peaks are visible due to the attached functional group. However, peaks at 731 cm^{−1}, 1492 cm^{−1}, and 1722 cm^{−1} appeared with weak intensity which are attributed to the C=C bending, C-H bending, and C=O stretching, respectively [56–58]. The other strong peak is observed at 2345 cm^{−1} which is attributed to the O=C=O and another band appears at 3684 cm^{−1} which is attributed to O-H stretching. However, these bands are due to the partial oxidation of graphene-to-graphene oxide [59]. But most of the peaks which are due to partial oxidation of graphene, vanished in Fe₃O₄/Gr nanocomposite. In Figure 2b, the FTIR spectrum displays the peaks of nanocomposites (Fe₃O₄/Graphene) at different wavenumbers. Absorption peak of Fe₃O₄/graphene nanocomposites is observed at 538 cm^{−1}, 1105 cm^{−1}, 1592 cm^{−1}, 2259 cm^{−1}, and 2833 cm^{−1}. First peak appeared at 538 cm^{−1} denoted the stretching vibration mode of Fe-O [53,60]. Two broad absorption peaks appear at 2833 cm^{−1} due to the stretching of C-H mode [61] and at 1105 cm^{−1} represents the stretching vibration of C=C mode [53,62] while another peak appear at 1592 cm^{−1} also denoted the stretching vibration mode of C=C [53,63,64]. The peak observed at 2259 cm^{−1} specifying the stretch vibration mode of C≡C [65]. Thus, corresponding peaks are related to the FTIR spectra of Fe₃O₄/Gr NCs and differ from the peaks of Gr/GO used as precursor in the synthesis of NCs.

3.4. RAMAN Spectroscopy

Figure 2c presents the RAMAN spectroscopy of graphene. RAMAN analysis is a helpful technique which provides eminence features. The peak intensities, positions, and shapes of the curve give useful information in graphene and related materials [66]. From Figure 2c, we observe three different peaks appearing at 1338 cm^{−1}, 1571 cm^{−1}, and 2688 cm^{−1}. The bands appearing at 1338 cm^{−1} and 2688 cm^{−1} are assigned to the D band and 2D band respectively. The band appears at 1571 cm^{−1} is assigned to the G band. The Id/Ig ratio was found to be less than 1 which shows that graphene has less defects [66,67]. The intensity of the 2D band is observed to be less than D and G band which explains that the graphene used in this study is the multilayer graphene (MLG) [66,67].

3.5. TEM and HRTEM Analysis

Figure 3 represents the TEM and HRTEM images of the Fe₃O₄/Gr matrix which analyzes the particle size and morphology of iron oxide nanoparticles. Figure 3a shows the spherical shaped Fe₃O₄ nanoparticles decorated on the graphene sheets ranging from 5–10 nm in size. Figure 3b demonstrates the Fe₃O₄ nanoparticles encircled at a point, presented in yellow color while at other points a rectangle is marked which represents the graphene sheets. Figure 3c, d is the enlargement of the point which is marked for Fe₃O₄ and graphene sheets respectively. The interplanar lattice space calculated for the Fe₃O₄ nanoparticles was found to be 0.25 nm while for graphene sheets it was calculated 0.34 nm.

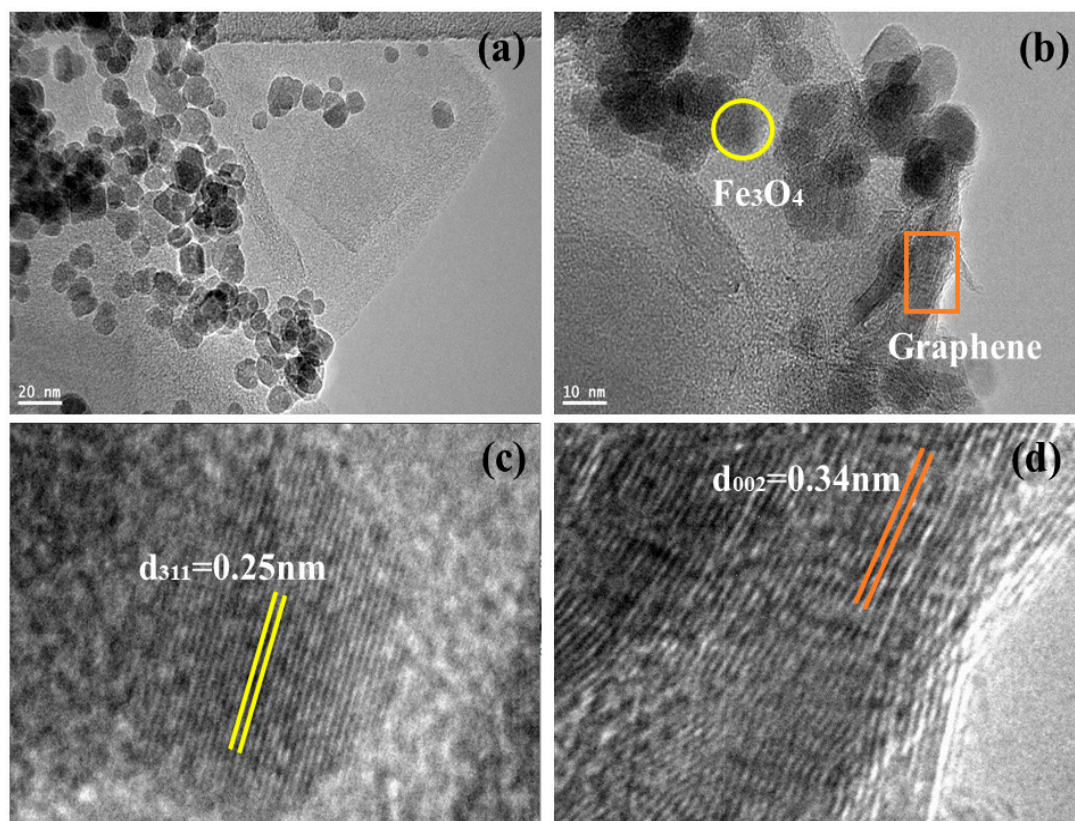


Figure 3. (a) TEM image of $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposite, (b–d) HRTEM images of nanocomposites showing Fe_3O_4 nanoparticles presented in circle shape (yellow color) corresponding to (311) plane with 0.25 nm interplanar lattice spacing (c) and rectangular shape shows the graphene (orange color) corresponds to (002) plane with 0.34 nm interplanar lattice spacing, presented in (d).

3.6. X-ray Photoelectron Spectroscopy (XPS)

XPS survey scan of $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposites is shown in Figure 4a. The presence of peaks related to carbon, oxygen, and iron in the prepared material of $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposites confirms the nanocomposite synthesis. Figure 4b shows that there are 2p core levels of iron, such as, $\text{Fe } 2p_{1/2}$ with binding energy of 723.9 eV and $\text{Fe } 2p_{3/2}$ with binding energy of 710 eV. In Fe_3O_4 , Fe exists in two states i.e., Fe^{2+} and Fe^{3+} , so the peak observed at 710.2 eV (red color) corresponds to Fe^{2+} states and the peak observed at 712.6 eV (cyan color) corresponds to Fe^{3+} in $\text{Fe } 2p_{3/2}$. Moreover, at 718 eV (green color), a satellite peak was observed, indicating that there is partial oxidation of Fe_3O_4 to Fe_2O_3 [68,69]. Figure 4c, d shows the spectrum of 1s core level of oxygen and carbon, respectively. In Figure 4c the peak of the oxygen atom appears at 530.2 eV (red color) attributed to the Fe-O bond and at 531.2 eV (green color) attributed to O-H bonds. The scan of C 1s core level spectrum is shown in Figure 4d. The peak in C 1s is obtained at 284.7 eV (red color) corresponding to $\text{C}=\text{C}$ sp^2 carbon atom and at 285.3 eV (green color) attributed to $\text{C}-\text{C}$ sp^3 atom. Moreover, the peak appearing at 287.5 eV (blue color) corresponds to C-O bonds which may be due to the functionalized group attached on graphene [70–72]. The XPS data also show that no reaction takes place between graphene nanosheets and iron oxide nanoparticles [11].

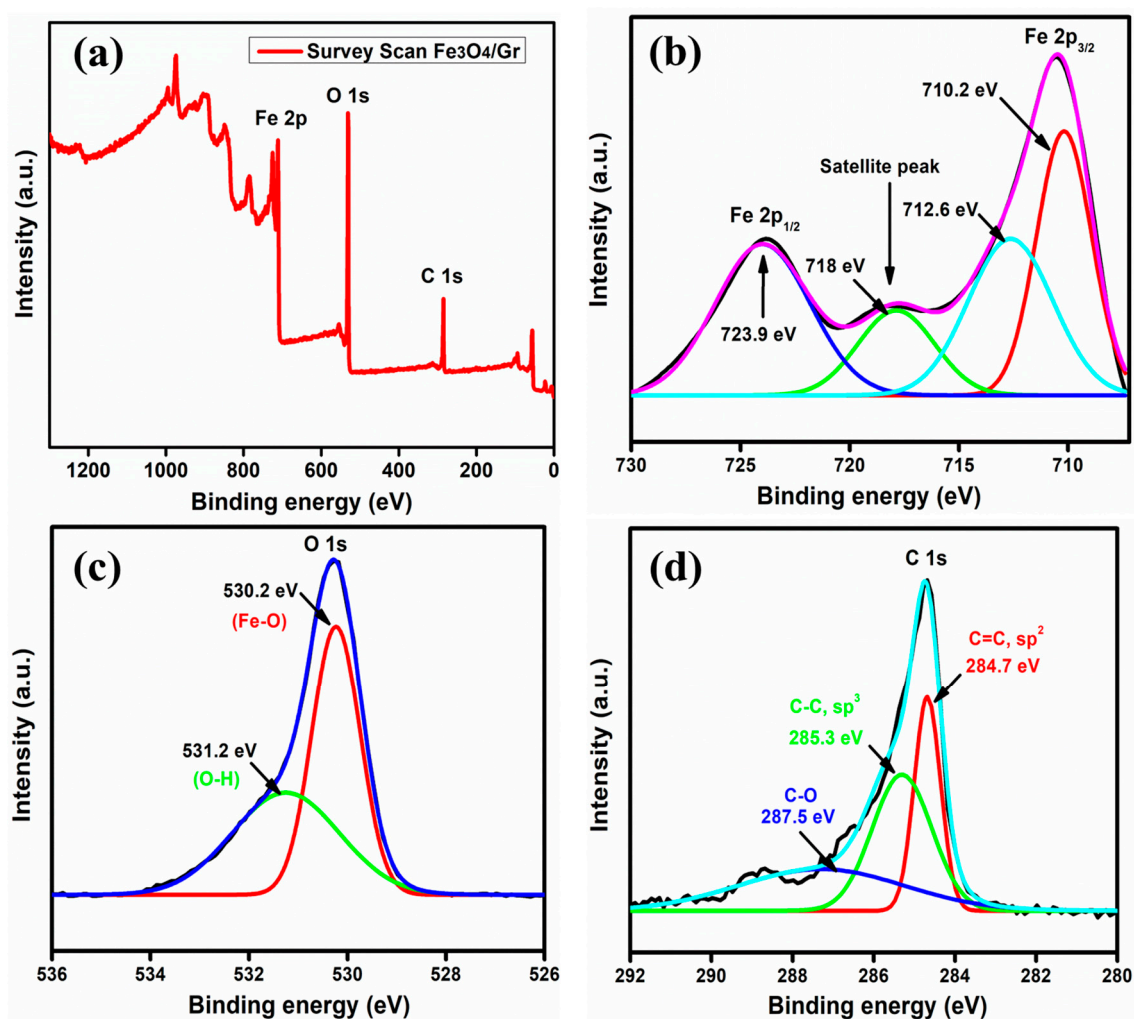
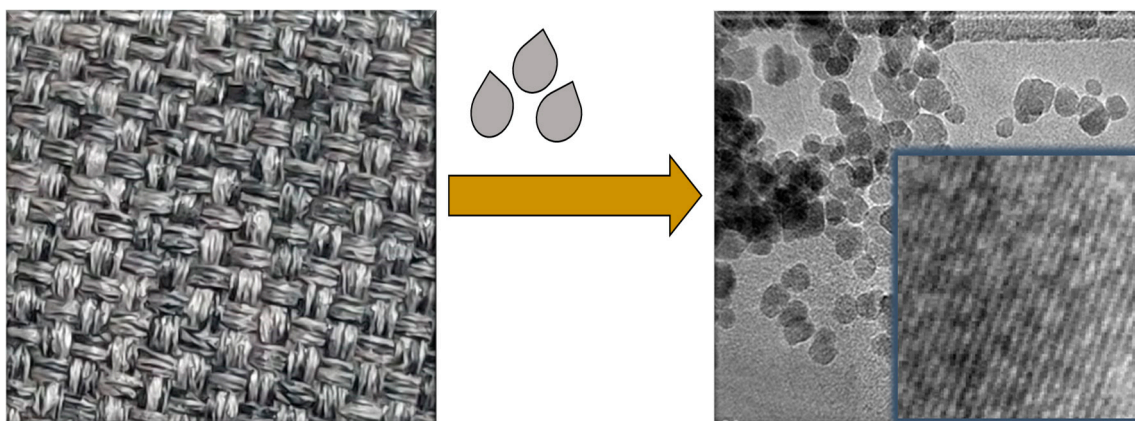


Figure 4. XPS spectra of $\text{Fe}_3\text{O}_4/\text{Gr}$ nanocomposite. (a) Survey scan, (b) $\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$, (c) O 1s, and (d) C 1s spectra.

4. Fabrication of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ and Electrochemical Performances

4.1. Fabrication of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ and Sensing toward H_2O_2

At room temperature, the fabrication of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ flexible electrode was carried out and the schematic representation is shown in Scheme 2 and the detailed process is described in Section 2.4.



Scheme 2. Schematic representation for the fabrication of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$.

On a computer-controlled three-electrode system, the electrochemical sensing experiments of all the fabricated electrodes (GO/CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$) were performed and results were compared with bare CC. The fabricated electrodes were employed as working electrodes, while a platinum and Ag/AgCl electrode served as the counter and reference electrode, respectively. Using cyclic voltammetry (CV), the testing of each electrode in phosphate buffer solution (PBS) was performed (Figure 5a). The fabricated electrodes (GO/CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$) were tested in 0.1 M PBS (PH = 7.0) at a scan rate of 0.08 V s^{-1} , the electrochemical behaviors of GO/CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ were examined, and results were compared with CC (Figure 5a). The electrocatalytic properties of the GO/CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ were examined in the 0.1 M PBS (pH = 7.0) at a scan rate of 0.08 V s^{-1} using cyclic voltammogram (CV). Figure 5a represents the current response of each electrode in PBS and shows pCC has negligible current response. Other electrodes have displayed higher current response. This not only confirms the successful modification of CC's surface, but also shows the credibility of each electrode for electrochemical performance. This higher electrocatalytic property of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ may be ascribed to the good electrocatalytic properties of the $\text{Fe}_3\text{O}_4/\text{Gr}$. Furthermore, the charge kinetics of the $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$, GO/CC, Gr/CC, and CC were explored in 0.1 M PBS (pH = 7.0) using electrochemical impedance spectroscopy (EIS) as shown in Figure 5b. From Figure 5b, we observe that a wide semicircle was observed for GO/CC and Gr/CC (Figure 5b), thus large charge-transfer resistance can be expected. However, CC and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ displayed a low semicircle as compared to GO/CC and Gr/CC, thus would have smaller charge-transfer resistance (Figure 5b). The low-frequency portions of the EIS plot with smaller semicircles of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ have better conducting properties with the diffusion-controlled process and demonstrated better electrocatalytic properties.

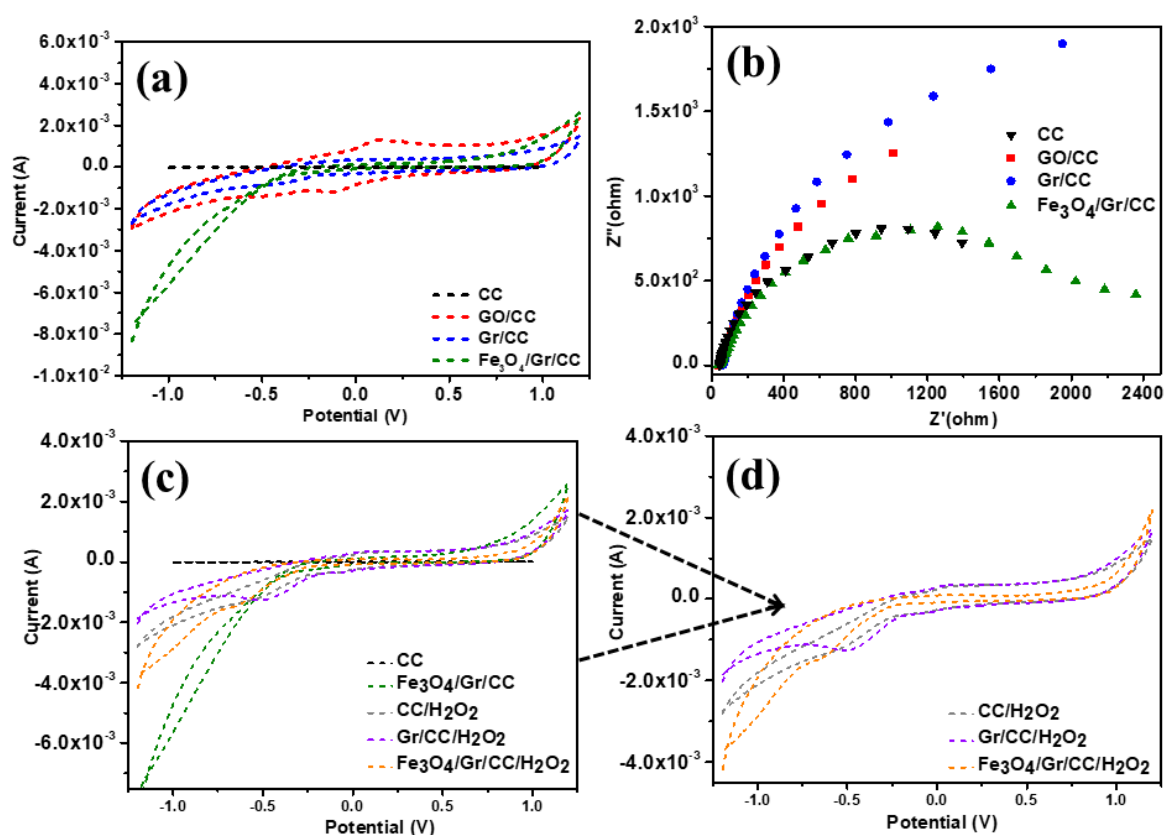


Figure 5. Electrochemical test of fabricated electrodes, (a) CV and (b) EIS of CC, GO/CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ in 0.1 M PBS (pH = 7.0), (c) comparative CVs of CC, Gr/CC, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ in 0.1 M PBS (pH = 7.0) with and without H_2O_2 at a scan rate of 0.08 V s^{-1} (d) CVs of CC, Gr/CC, $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ with H_2O_2 in 0.1M PBS, pH=7.0 (CC/ H_2O_2 , Gr/CC/ H_2O_2 , $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}/\text{H}_2\text{O}_2$).

Additionally, we looked into the electrochemical capabilities of the $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ for sensing of H_2O_2 (Figure 5c). Figure 5c displays the CV curves of the $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ and CC in 0.1 M PBS with a pH of 7.0 and a scan rate of 0.08 V s^{-1} . For the bare CC, a poor current response was observed. For the $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$, an improved current response toward the detection of H_2O_2 that may arise due to the reduction/oxidation was observed. This high current response originated due to the good electrocatalytic properties of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$. Moreover, we have observed good current response for Gr/CC and CC toward H_2O_2 . Figure 5d provides the enlargement image of Figure 5c where CV curves for $\text{CC}/\text{H}_2\text{O}_2$, $\text{Gr}/\text{CC}/\text{H}_2\text{O}_2$, and $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}/\text{H}_2\text{O}_2$ are compared.

Using CV, it was also investigated how different H_2O_2 concentrations affected the electrochemical performance of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ (Figure 6a). With a scan rate of 0.08 V s^{-1} , we were able to get various CV curves of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ in the presence of varying concentrations of H_2O_2 from $10 \mu\text{M}$ to $110 \mu\text{M}$ (Figure 6a,b). The observations obviously demonstrated that the current response for reduction has increased at each addition of H_2O_2 . The calibration plot for linearity check between the peak current response and concentration of H_2O_2 revealed that this improved current response was linear (Figure 6c). The linear equation was observed as $y = -3.70091\text{E}^{-5}x - 0.00122$, and $R^2 = 0.995$.

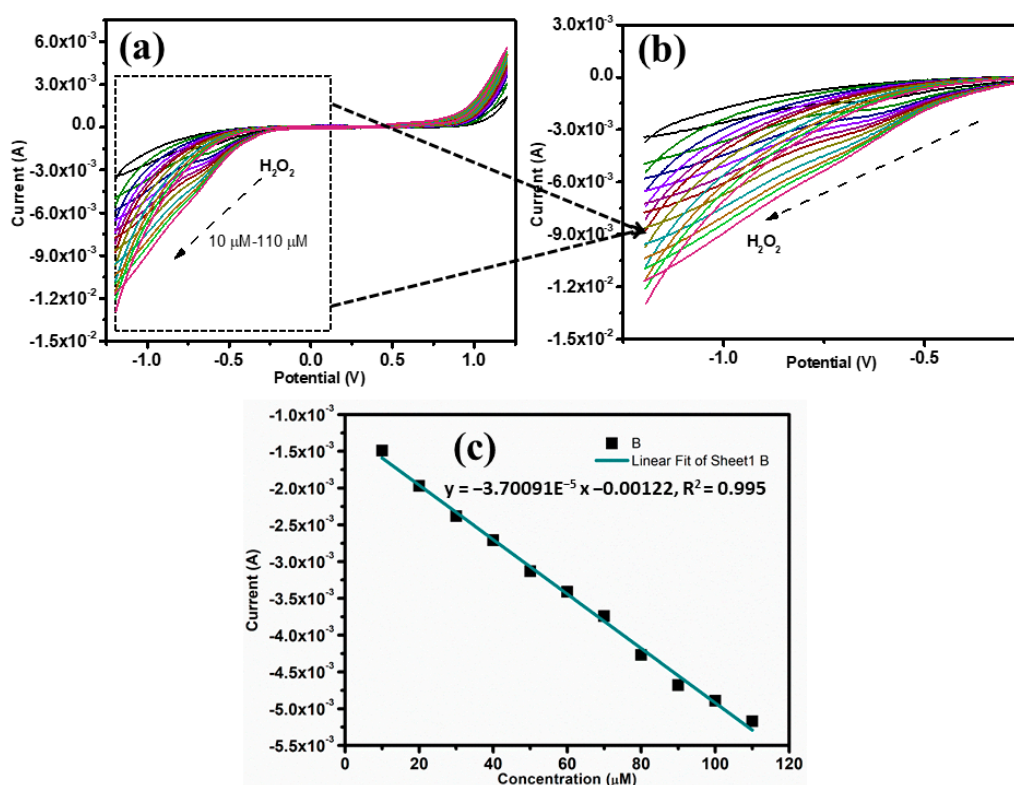


Figure 6. (a) CVs shows electrochemical performance with different H_2O_2 concentrations in 0.1 M PBS (pH = 7.0) at a scan rate of 0.08 V s^{-1} ; (b) enlargement of 5a which show the linearity of the sensing performance of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$; and (c) a calibration plot for varying concentrations versus peak current.

Additionally, we have also looked at the effects of various scan speeds on the $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ toward H_2O_2 for the electrocatalytic reduction H_2O_2 for sensing application (Figure 7). Figure 7 displays the CVs of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ that were obtained at various applied scan speeds of $20\text{--}210 \text{ mVs}^{-1}$ in 0.1 M PBS (pH 7.0) containing initial concentration of H_2O_2 . We noticed that as the scan rate increased from 20 to 210 mVs^{-1} , the peak current response at the reduction side increases as the scan speed increases. The obtained results show the responses of peak current at 20 to 210 mVs^{-1} and a linear plot can be obtained. This plot further provides the information that indicates the linear increase in the response

of the peak current and suggests the process is diffusion controlled for the sensing of H_2O_2 [73].

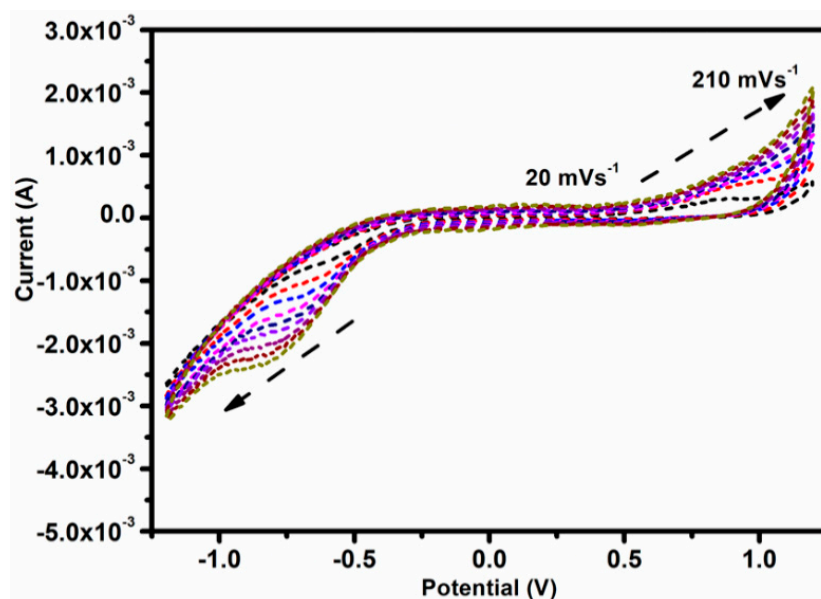


Figure 7. CVs of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ obtained at various applied scan speeds of 20–210 mVs^{-1} in 0.1 M PBS (pH 7.0).

4.2. Limit of Detection and Sensitivity of Flexible Sensor

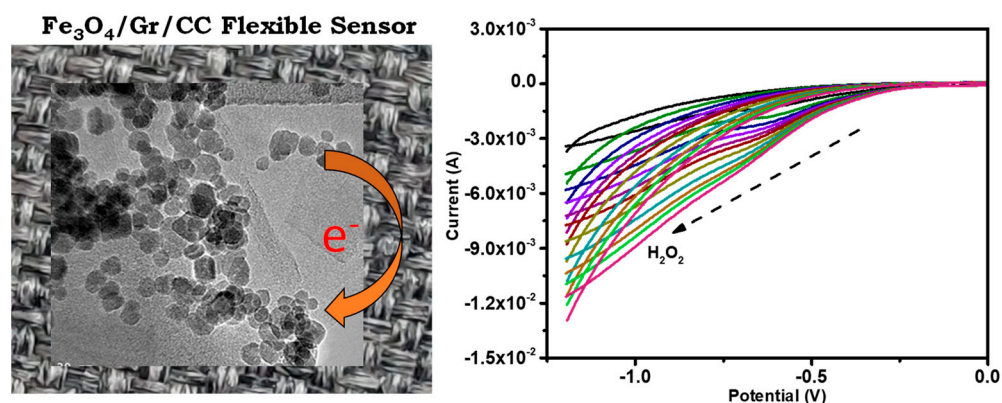
The limit of detection (LOD) and sensitivity of fabricated $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ sensors can be estimated using the previous method reported [74,75]. For this, we used Equations (1) and (2), which were mentioned below, to find out the LOD and sensitivity of the $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ for the sensing of H_2O_2 :

$$\text{Limit of detection (LOD)} = 3.3 (\sigma/S) \quad (1)$$

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

where σ = standard error, and S = slope.

The sensitivity, LOD, and linear range of the $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ toward H_2O_2 using an electrochemical approach were recorded as $0.037 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$, $4.79 \mu\text{M}$, and $10\text{--}110 \mu\text{M}$ respectively, and the plausible mechanism can be seen in Scheme 3. Scheme 3 shows the micrographic images which show the transformation of H_2O_2 to $\text{H}_2\text{O} + \text{O}_2$ with the electrochemical cyclic voltammetry graph. The graph shows the gradual changes in the detection slope of H_2O_2 . The reduction/oxidation takes place at the surfaces of an electrode ($\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ electrode) and helps in the detection of H_2O_2 (Scheme 3). The reduction of H_2O_2 carried out by $\text{Fe}_3\text{O}_4/\text{Gr}$ NC via electron transfer leads to the formation of hydroxyl ions (OH^-), and after combining produced water and oxygen molecules [75].



Scheme 3. Schematic for the mechanism towards the detection of H_2O_2 on $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$.

4.3. Test of Analytical Parameters (Selectivity, Repeatability, Reproducibility, and Stability) for $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ as Flexible Sensor

One of the most essential analytical parameters for sensors is selectivity. Several bodies, including glucose (Glu), uric acid (UA), ascorbic acid (AA), dopamine (DA), nitrophenol (NP), chlorophenol (CP), nitrophenol (NP), and sodium chloride (NaCl) were applied to test the anti-interference performance of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$, as shown in Figure 8a. There was no noticeable current change after the addition of interfering species, and the current response to the addition of H_2O_2 was unaffected, confirming the exceptional selectivity. Further, CV curves were used to test the repeatability of the modified electrode ($\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$) in order to evaluate the accuracy of the sensor. The results were repeatable, with a relative standard deviation (RSD) of 3.27% (four repeated runs at single electrode) (Figure 8b).

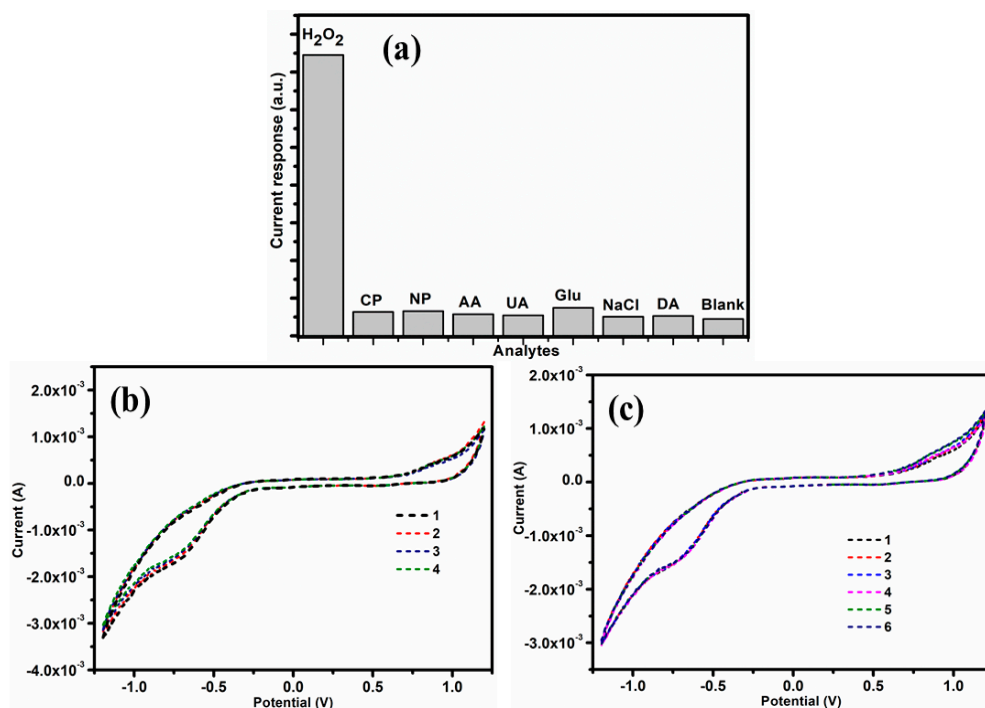


Figure 8. (a) Selectivity test of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ with various interference, (b) repeatability, and (c) reproducibility test.

The reproducibility of $\text{Fe}_3\text{O}_4/\text{Gr}/\text{CC}$ sensor was tested by fabricating six independent electrodes and RSD of current responses for the sensing of H_2O_2 was revealed to be 3.04%. (Figure 8c). A stability was also assessed by evaluating the current response toward H_2O_2 for 10 days with the retention of 93.01–94.7% of its initial current response and advising

good stability. Thus, the presented sensor has acceptable selectivity, reproducibility, and stability.

In comparison with fabricated electrodes consisting of graphene, CNTs, MOFs, noble metals, and metal oxides, we presented a rather economical sensing platform (Table 2). The CC is a suitable, cost-effective substrate with flexible properties, good conductivity, and tunable size, in contrast to certain typical electrodes [30]. Designing a sensing platform based on the CC with variable sizes results in fast analyte adsorption because of its synergistic and structural features. We can see from Table 2 that low detection limit was obtained using Fe₃O₄/Gr/CC for the H₂O₂ detection with a good linear range. The noble metal-containing electrodes such as Ag NPs/SnO₂/GCE, AgNPs/PQ11/graphene, and Pt NPs/UiO-66/GCE were even found comparable in terms of LOD (Table 2). The graphene-MWCNT/GCE, rGO-Fe₂O₃-GCE, CuGa₂O₄/GCE shows either narrow LOW or comparable as compared to Fe₃O₄/Gr/CC. As a result, we have a sensor with good LOD, adaptable characteristics, and a low cost.

Table 2. Comparison of sensing performance of some reported peroxide sensors with the present work.

Electrode	Linear Range	LOD/Sensitivity	Reference
graphene-MWCNT/GCE	0.02–2.1 mM (R ² = 0.997)	9.4 µM; 32.91 µA mM ^{−1} cm ^{−2}	[76]
Pt NPs/UiO-66/GCE	5 µM to 14.75 mM	3.06 µM; 75.33 µA mM ^{−1} cm ^{−2}	[77]
rGO-Fe ₂ O ₃ -GCE	0.05 to 9.0 mmol L ^{−1} (R ² = 0.995)	6.0 µM; —	[78]
Ag NPs/SnO ₂ /GCE	0.01 to 35.0 mM	5 µM; —	[79]
CuGa ₂ O ₄ /GCE	5–200 µM (R ² = 0.999)	5 µM; —	[80]
AgNPs/PQ11/graphene	100 µM–40 mM (R ² = 0.996)	28 µM; 56.6 µA mM ^{−1} cm ^{−2}	[81]
Fc-GNs/GCE	0.05–4.75 mM (R ² = 0.997) and 5.75–14.75 mM (R ² = 0.997)	4.15 µM —	[82]
Fe ₃ O ₄ /Gr/CC	10–110 µM (R ² = 0.996)	4.79 µM; 0.037 µA µM ^{−1} cm ^{−2}	This work

5. Conclusions

The simplistic and facile fabrication of a new type of flexible Fe₃O₄/Gr/CC was achieved by the co-precipitation method. This modified carbon cloth-based electrode exhibited excellent physical and electrochemical properties. When a carbon fiber cloth-based electrode was used as a flexible electrochemical sensor for H₂O₂ determination, the modified electrode demonstrated high sensitivity, a wide linear range, and a low detection limit. The results show the high sensitivity of 0.037 µA µM^{−1} cm^{−2} with a limit of detection of 4.79 µM and linearity range was measured from 10 µM to 110 µM. The sensor also revealed good reproducibility and high selectivity. It is expected that the flexible and freestanding Fe₃O₄/Gr/CC will provide a modular approach for materials to be manufactured in the future due to its ease of preparation, compatibility with in vivo work, and availability in many potential applications.

Author Contributions: N.S.: methodology/supervision/resources/editing. M.I.: curation/resources, data/writing—original draft, investigation/writing—original draft. M.E.K.: data/writing—original draft, data curation, conceptualization/validation. A.M.: data curation, conceptualization/validation. M.M.A.: writing—original draft, investigation/writing—original draft, data curation, conceptualization/validation. T.Y.: resources/editing. I.M.M.: review and editing. M.A.H.: review and editing. M.J.A.: review and editing. A.A.J.: review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research work was funded by Institutional Fund Projects under grant no. (IFPRC-049-135-2020). Therefore, authors gratefully acknowledge technical and financial support from the Ministry of Education and King Abdulaziz University, Jeddah, Saudi Arabia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available from the corresponding authors upon reasonable request.

Acknowledgments: This research work was funded by Institutional Fund Projects under grant no. (IFPRC-049-135-2020). Therefore, authors gratefully acknowledge technical and financial support from the Ministry of Education and King Abdulaziz University, Jeddah, Saudi Arabia.

Conflicts of Interest: The authors declare that there is no conflict of interest.

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