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RESEARCH PAPER

One pot green synthesis of novel rGO@ZnO nanocomposite and fabrication of electrochemical sensor for ascorbic acid using screen-printed electrode

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ABSTRACT

Developing a novel sensor for analysing ascorbic acid present in food items and nutraceuticals is been very important research topic for materials scientists, medicine and food researchers. In the present work, we demonstrate the detection of an ascorbic acid (AA) by using an electrochemical sensor made from novel rGO@ZnO nanocomposite. We synthesized ZnO-nanoparticle-decorated reduced graphene oxide composite (rGO@ZnO) using a one-pot hazard free green-hydrothermal method. Multi characterization techniques like X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy and Raman spectroscopy, were precisely used to understand the structure and properties of the rGO@ZnO nanohybrid. Finally, the synthesized rGO@ZnO nanohybrids were utilized to fabricate low cost screen printed electrode (SPE) electrochemical sensor for highly sensitive detection of ascorbic acid (AA). The observed electrochemical sensing results indicate wide linearity from 0.1 mmol to 1.5 mmol with good repeatability and reproducibility. The results confirm that the synthesized novel rGO@ZnO nanohybrids exhibit excellent electrocatalytic activity towards AA with high stability and sensitivity.

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INTRODUCTION

Ascorbic acid (AA), also called vitamin C or ascorbate, an outstanding reducing agent, it is known for its high antioxidant activity [1]. It helps in the removal of highly toxic reactive oxygen species and free radicals, formed in cell metabolism, which causes tissue damage and diseases[2]. Owing to its outstanding biological and medical importance, there is a continued effort to develop a simple, rapid and highly sensitive analytical technique for the repetitive determination of AA. Several techniques have been used for the analysis of ascorbic acid, such as electrophoresis[3], fluorescence[4], chemiluminescence [5], UV spectroscopy[6], liquid chromatography[7, 8],electrochemical methods[9-11]. Among them, electrochemical technique is considered to be the most reliable, promising, and low cost analysis method with high sensitivity and simplicity. Electrochemical biosensors are the best choice

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when rapid and on-site results are needed in medical diagnostics, environmental monitoring, food safety, waste water treatment, biomedical research and life sciences discovery research among many others[12, 13].

The detection of AA at bare conventional electrodes in electrochemical technique, generally foul the electrodes due to the strong adsorption of 2,3-diketogluconic acid formed by irreversible oxidation reaction of AA[14]. Therefore, for the design and development of long lasting electrochemical sensors, the bare electrodes have to be suitably modified using nanomaterials, which are able to provide the redox active site for effective sensing bio-molecule. So, the development of novel nanomaterials, to solve the above issues of electrode is at most urgent and has become a challenging research problem[15]. In-line with, several type of nanomaterials, such as Titanate nanowires[16], silver and carbon nanoparticles[17], $Ni(OH)_2$/AuNP/SPE [17], Cobalt-Coated Si Nanowire Electrodes[18], CuO/Pt nanocomposites [19], ZrO_2/rGO [20], have been used for the modification of conventional electrodes. Li Fu et al have developed RGO–ZnO-modified GCE for electrochemical sensing of uric acid [21]. Using costly (Pd/PEDOT) nanocomposite, Fengxing Jiang et al have modified glassy carbon electrode (GCE) for the detection of hydrogen peroxide(H_2O_2).[22] Unfortunately, due to their scarcity, high cost, sensitivity, detection limit, selectivity, linear responses in narrow concentration ranges, and less stability, developing a nanomaterial elelctrocatalyst to address these issues is still a great challenge for materials researchers. To address these issues, we have made sincere effort to develop low cost, highly sensitive and stable nanocomposite consisting of rGO@ZnO for the first time as electrochemical sensing platform for ascorbic acid.

Graphene, a zero-bandgap atomic scale thick carbon sheet, exhibiting an incredible electron mobility (200000 $cm^2\ V^{-1}\ s^{-1}$), large surface area (2630 m^2/g), excellent thermal conductivity (5300 $Wm^{-1}\ K^{-1}$), high mechanical strength, chemical stability and electric conductivity[23] has been more attractive nanomaterial in the field of material science, electrochemistry and biomedical field [24, 25]. This has been extensively and successfully used as active electro catalyst in biosensing[26], super-capacitors[27],fuel cells[28], solar cells[29] and Lithium-ion batteries [30].

Very interestingly, the nanohybrids or nanocomposites of graphene and rGO with inorganic nanomaterials exhibit synergetic electrochemical performances[31]. Various attempts were made to develop inorganic nano materials decorated graphene or rGO hybrid materials for the detection of different analytes. Along with a low detection limit and reasonable sensitivity, the rGO nanohybrid sensor is expected to exhibit a very low detection potential and anti-interference. For the selective detection of AA in Vitamin C tablets, Liu et al have developed NiO/graphene composite modified GCE, which displayed high catalytic activity due to the combined effect of highly conductive graphene and NiO electrocatalytic activity[32]. In another work, for electrochemical detection of AA in spiked serum samples, Au nanoplates-decorated graphene hybrid nanomaterial (rGO/Au) have also been used[33]. Inspired by the synergetic effect of rGO@inorganic nano hybrids for electrochemical sensing of AA, many have developed sensors based on AgNP/rGO/GCE[34], Au@Pd-rGO/GCE[14], rGO-CNT/ITO[35], MoS_2/rGO/GCE [36]. rGO-SnO_2/GCE[37], TiO_2-rGO/GCE[38], and Fe_3O_4/rGO/GCE [39]. The RGO–ZnO/GCE biosensor, developed by Xuan Zhang et al, exhibit satisfying results AA, DA and UA in real plasma and urine samples with very good reproducibility and stability[40].

One of the most researched inorganic metal-oxide, ZnO is known to be bio-friendly, non-toxic, thermally stable, and electrochemically active. Varius nanostructures with the combination of ZnO, have been widely used in the development of N_2H_4 sensor, and glucose and H_2O_2 biosensors[41]. Xiaojing Si et al have fabricated ZnO/GR/GCE to determine ofloxacin[42]. Qizhao Wang et al have developed ZnO nanorods and graphene nanosheets on ITO glass for electrochemical sensing of uric acid in the presence of ascorbic acid[43]. For the electrochemical detection of dopamine (DA) in the presence of ascorbic acid (AA) and serotonin (SE), Omolola E.Fayemi et al have used Polyaniline (PANI)- ZnO nanocomposites coating on GCE[44]. Junwei Ding et al have also developed ZnO-rGO nanocomposites for an electrochemical N_2H_4 sensor using costly GCE[45].

It is very important to note that most of the reported work, utilized GCE or ITO electrode, which are costlier than our screen printer carbon electrode (SPEs). To the best our knowledge, we are the first to develop rGO@ZnO/SPE nano

hybrid working electrode, using rGO@ZnO, prepared by one pot hydrothermal method, for electrochemical sensing of ascorbic acid. The highlight of the present work is that the rGO@ZnO nancomposite material is synthesized by hazard free green method using water as a solvent. The green synthesis has received great attention in recent years due to its capability to design alternative, safer, energy efficient, and less toxic routes towards synthesis.[46] Our work describes systematic preparation procedure for rGO@ ZnO nano hybrid, fabrication of rGO@ZnO/SPE electrode and electrochemical analysis of ascorbic acid. The prepared nanohybrid is systematically characterized by XRD, FESEM, Raman and FTIR analytical techniques. The fabricated electrode is successfully used for sensing ascorbic acid.

MATERIALS AND METHODS

Graphene Oxide (GO) is purchased from TATA steel India, and zinc nitrate ($Zn(NO_3)_2.6H_2O$), Potassium Chloride (KCl) and L-Ascorbic acid ($C_6H_8O_6$) from MERCK, India, were used without further purification.

Instrumentation

The purity, and the crystallographic information of rGO@ZnOnanocomposite was thoroughly characterized using PANalytical powder X-ray diffractometer with CuKα radiation (λ=1.5418 Å) in the 2ϑ range 10-80°. The FESEM images of the of rGO@ZnO nanocomposite was recorded by Using Ultra high resolution scanning electron microscope (ULTRA 55, GEMINI technology)equipped with EDS at CeNSE, IISc Bengaluru. Raman spectroscopy (New XploRA™ PLUS V1.2 Multiline, HORIBA JOBIN YVON), Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum 1000), were used for the detailed structural characterization of rGO@ZnO nanocomposite. Electrochemical experiments were carried out using Biologic SP150 electrochemical workstation. A three-electrode system was used where standard silver/silver chloride (Ag/AgCl) electrode serves as reference electrode, platinum wire as the counter electrode and rGO@ZnO nanocomposite as working electrode.

Synthesis of the hetero-structured rGO@ZnO nanocomposite

Among the various developed methodologies, hydrothermal technique is one of the promising methods to produce pure and well defined nanostructures with rich functional properties [47]. The rGO@ZnO nanocomposite was prepared by one pot hydrothermal method. In a typical experiment 0.7370g of $Zn(NO_3)_26H_2O$ and 0.25g GO was dispersed using 35ml of distilled water taken in 50 ml Teflon lined container. The reaction container, Teflon lined container is placed in an air tight stainless steel autoclave and then it is kept in the hot air oven maintained at 120 °C for 10h. After hydrothermal treatment, in order to remove impurities, the product was washed with deionized water flowed by acetone three times each, and further it was dried at 80 °C for 1h. The hydrothermal synthesis of rGO@ZnO is represented in Fig. 1(a). The instantaneous reduction GO to rGO via hydrothermal conditions is been proved by many researchers. The experimental results of these published work is supporting the observation made in our experiment. [48, 49]

Fabrication of the rGO@ZnO/SPE-electrode

To fabricate the working electrode, 0.02g of the rGO@ZnO was dispersed in 1 ml of deionized water and then subjected for sonication for 40 min to get a homogenous dispersion. Prior to the surface functionalization with nanocomposite, the SPE substrate was cleaned with ethanol and double distilled water, and dried at room temperature. The 20µL of the resulted homogenous dispersion was coated on cleaned and dried SPE. Then, the fabricated electrode was heated in INFRA-RED light for about 30 minutes to evaporate the solvents. Finally, the dried rGO@ZnO/SPE was used for sensing ascorbic acid. Fig. 1(b) represents the typical image of SPE used for electrochemical sensing of ascorbic acid. It consists of graphite working electrode (3 mm geometric surface area), a Ag/AgCl reference electrode and a graphite auxiliary electrode.

Ascorbic acid solution preparation

0.098g of ascorbic acid powder is dissolved using 50ml of distilled water is a volumetric flask. For nanocomposite testing, a solution consisting of 8ml of 7 pH phosphate buffer solution and 2ml of 0.1M KCl (electrolyte) was used. The chemical structure of ascorbic acid and the possible electro catalytic oxidation reaction on the surface fabricated rGO@ZnO/SPE, working electrode during sensing studies is represented in Fig. 1(C).

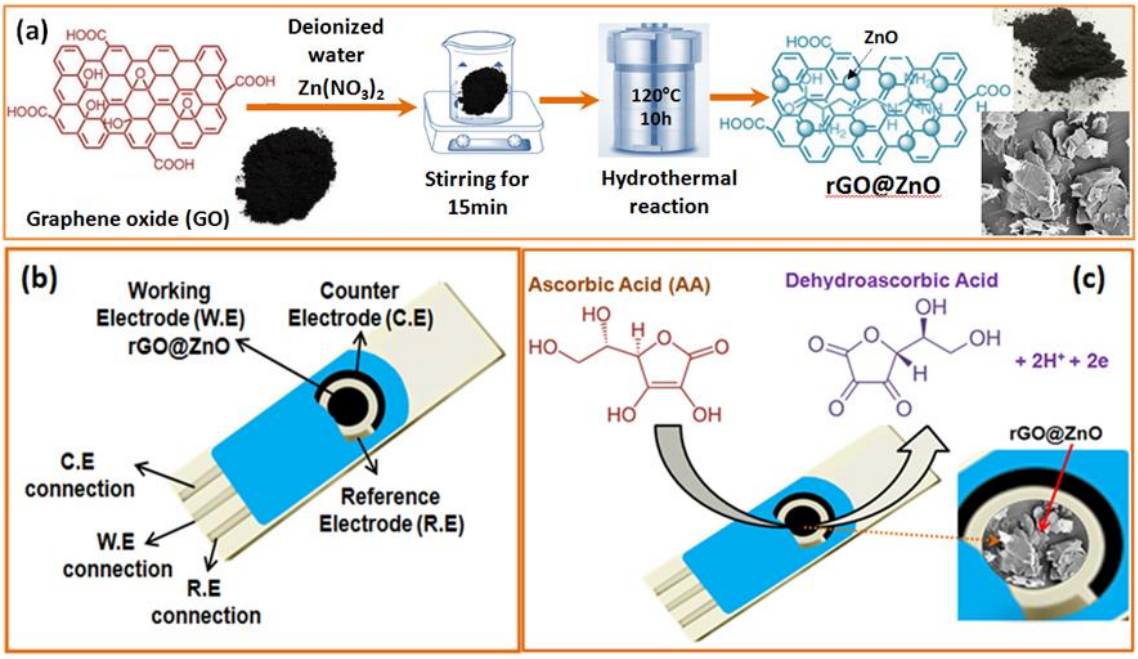

Fig. 1. Schematic diagram of (a) the hydrothermal synthesis of rGO@ZnO nanocomposite (b) Design of screen printed electrode and (c) Mechanism of electrochemical oxidation reaction during sensing of AA by rGO@ZnO/SPE.

RESULTS AND DISCUSSION

XRD analysis

The XRD patterns of the as-prepared rGO@ZnO are shown in Fig. 2(a). The characteristic peaks of rGO, such as a broad peak at 2θ=25°, matching to (002) plane of rGO, (JCPDS 75-2078) is evident for complete conversion of GO into rGO. The XRD spectrum of rGO@ZnO hybrid depicts peaks at 31.53°, 34.23°, 36.25°, 47.52°, 56.6°, 62.83°, 66.37°, 68.05°, 69.06° and 76.97° which correspond to the (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202) crystalline planes of ZnO, respectively. This confirms the wurtzite structure of ZnO (JCPDS No.36–1451)[47]. No other reflection peaks, except rGO and ZnO peaks, in the XRD pattern, reveals the absence of impurity phases. Moreover the appearance of intense peaks of rGO and ZnO, strongly confirms the successful formation of hybrid nanocomposite[50].

Raman studies

The Raman spectrum is an essential and versatile tool to study the crystallization, structural disorder and defects in micro and nanostructures[51]. The vibrational properties of the synthesized rGO@ZnO nanocomposite are investigated by Raman spectra. Fig. 2b presents the Raman spectra of rGO@ZnO, showed two predominant peaks at the wavenumber of 1350 cm^{-1} and 1594cm^{-1}, which corresponds to the well-documented D and G bands, respectively. The presence of sp^2 hybridized carbon structure in rGO is clearly supported by the G-band observed at 1594 cm^{-1}, whereas, localized vibrational modes, D-band at 1318 cm^{-1} confirms the oxygen functionalities. The degree of structural disorder in the samples, which is proportional to the I_D/I_G value, can be analyzed by correlating the intensity ratio (I_D/I_G). For pure rGO, the intensity ratio of D to G peak (I_D/I_G) is expected to be one[52]. However, the I_D/I_G ratio of our rGO@ZnO product is equal to 0.996, which is close to 1, confirms lower defects and disorders. This is the evidence for the reduction of GO to rGO during hydrothermal synthesis. The last peak at 2698cm^{-1} (2D) is related to the number of graphene layers. Raman spectra are considered as "finger-prints" of rGO. The Raman spectrum of our sample is very well similar with the previous reports on rGO@ZnO [53, 54].The basic phonon modes of hexagonal ZnO are expected to be at 100, 385, 440 and 585 cm^{-1}, which represents to the E_{2L}, A_1(TO), E_{2H} and A_1(LO)/E_1(LO), respectively. The wide peak around 500cm^{-1}peak belonging to the ZnO hexagonal crystals[53]. E_{2H} mode at 437cm^{-1}, involves the oxygen motion, sensitive to

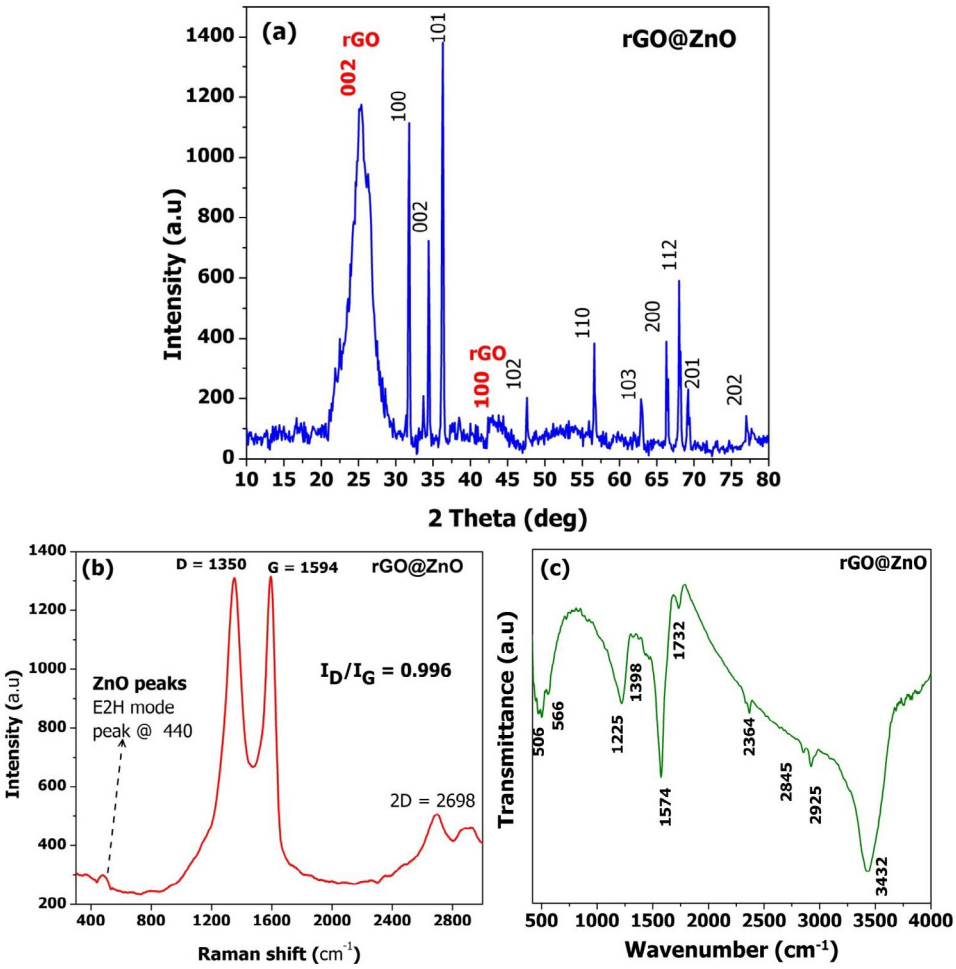

Fig. 2. (a) XRD pattern (b) Raman spectra and (c) FT-IR spectra of rGO@ZnO nanocomposite.

internal stress and is characteristic of hexagonal wurtzite structure of ZnO nanostructures. The E_{2H} mode has a huge reduction in the intensity of ZnO in rGO@ZnO nanocomposites due to breakdown of translational crystal symmetry by the incorporation of rGO as well as defects. All Raman signals corresponding to rGO and ZnO could clearly be clearly observed in the rGO@ZnO nanocomposite.

FT-IR studies

FT-IR spectroscopy was used to analyze the functional groups of rGO such as hydroxyl, epoxy, carbonyl and carboxyl groups (–OH, -C-O, -OOH, and C=O) and ZnO, the resultant spectra is shown in Fig. 2c. In the FT-IR spectrum, the broad peak at 3432cm^{-1} can be assigned to hydroxyl (O–H) stretching vibrations of –COOH functional groups and adsorbed H_2O moisture. The absorptions around peak 1621 cm^{-1} corresponds to O–H vibration of epoxide groups and skeletal vibration of aromatic rings[55]. The peaks at 2925 and 2845 cm^{-1} can be ascribed to C-H vibrations. The strong peak at 1574 cm^{-1} is due to C=C vibrations. It is clearly noticed that, the intensity of the peaks of C=O and C-O(epoxy) functional group a1732 cm^{-1}, 1398 cm^{-1}, and 1225 cm^{-1} are less intense, indicating reduction of GO to rGO[45, 56]. The stretching modes of Zn–O the strong peak is found between 400 and 500 cm^{-1} [57]. Expectedly, intensities of C-O, O-H and C=O stretching vibration peaks in rGO@ZnO hybrids is found to decrease as compared to those in GO, which is obvious for composites. [58].

SEM and EDS analysis

The morphology and microstructure of the rGO@ZnO nano composite was investigated

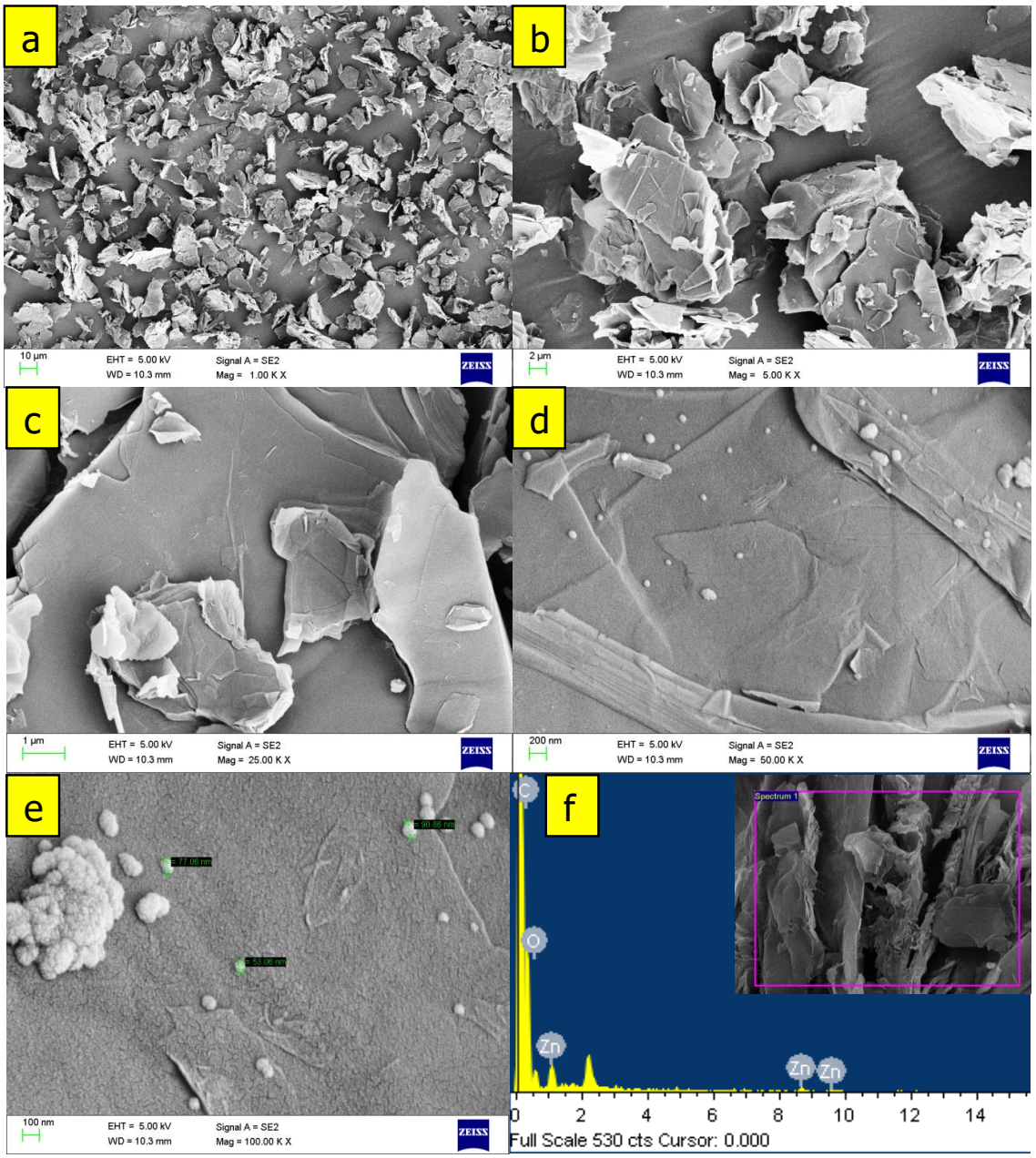

Fig. 3. (a–e) Low- to high-magnification FESEM image and (f) Corresponding EDS element mappings of the rGO@ZnO nanocomposite.

using FESEM, as shown in Fig. 3. It can be clearly seen in Fig. 3(a) that the rGO@ZnO nano composite appears to be more uniform in terms of microstructure, which has major impact on electrochemical sensing mechanism. The uniform microstructure helps is effective sensing, due to uniformly distributed active sites in the nanocomposite powder. Highly magnified FESEM images Fig. 3(b-e) clearly confirm the graphene sheets embedded on each other along with ZnO nano particles. The size of aggregated ZnO nanoparticles distributed on graphene sheets is found to be 20-60nm. The composition of rGO@ ZnO nano composite is further confirmed by EDS analysis, corresponding image is shown in Fig. 3(f). The EDS spectra confirms the presence of all the expected elements such as 'C', 'O', and Zn, with no other elements.

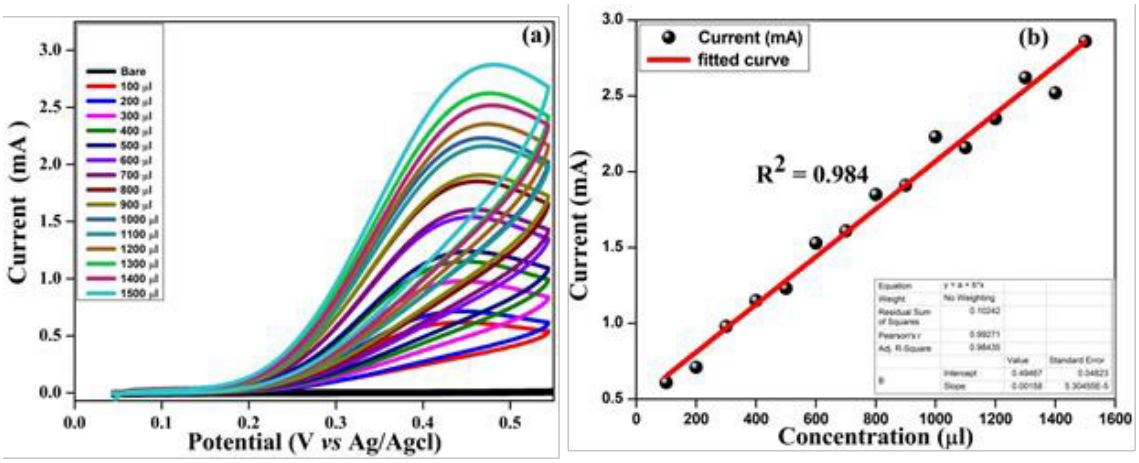

Fig. 4. (a) Cyclic voltammetry curves of the rGO@ZnO nanocomposite modified SPE and (b) (b) plot of the peak current *vs* concentration of AA.

Electrochemical sensing

The electrochemical behavior of rGO@ZnO nano composite modified SPE towards ascorbic acid was studied in phosphate buffer of pH = 7.0 using cyclic voltammetry. The observed results were shown in Fig. 4a. No oxidation peak appeared in presence of ascorbic acid for bare SPE indicating the no sensitivity. Whereas, the rGO@ZnO nano composite modified SPE shows an oxidation peak at around 0.42 V demonstrating the ability to sense ascorbic acid. Further, the sensitivity of the rGO@ZnO nano composite modified SPE towards ascorbic acid concentration has been tested. The results shown in Fig. 4b indicate as the concentration of ascorbic acid increases, the oxidation peak current increases linearly with R^2 =0.984. Further, the proposed rGO@ZnO nano composite modified SPE exhibits wide linearity from 0.1 mmol to 1.5 mmol. Thus, this proposed rGO@ZnO nano composite electrochemical sensor could be used for the detection of ascorbic acid from the real samples.

CONCLUSION

In summary, we fabricated rGO@ZnO hybrid nanocomposite via one pot hydrothermal method, and used for developing of electrochemical biosensor rGO@ZnO/SPE for detection of ascorbic acid (AA). The better electrochemical activities of the fabricated non-enzymatic electrochemical AA sensor are due to active nanohybrid of rGO@ZnO. The large numbers of active functional groups of graphene nanosheets are making it an ideal active material for electrochemical sensor. On the other hand, the ZnO nanoparticle could act as active sites of rGO nanosheets. These above two reasons make the synthesized rGO@ZnO nanohybrids potential electrode materials for fabricating AA sensor. The rGO@ZnO sensor shows wide linearity with good repeatability and reproducibility. These findings would be beneficial to develop advanced electrode materials for novel electrochemical biosensors.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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