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Fabrication of Reduced Graphene Oxide Paper Doped with Zinc Oxide Nanoparticles as Flexible Electrode Material

Elif ERÇARIKCI[1], Murat ALANYALIOĞLU[*2]

Abstract

The conventional electrodes like glassy carbon electrode and graphite are restricted for large-scale electrochemical production and in-vivo applications. Therefore, flexible electrodes are beginning to replace with such electrodes. This work reports a simple preparation of flexible paper-like electrode material (FPEM) including reduced graphene oxide (rGO) and zinc oxide nanoparticles (ZnONPs) for possible electrochemical applications. For this purpose, graphene oxide dispersion was interacted with ZnONPs, filtered under vacuum effect through a membrane, peeled off the membrane and then reduced by hydrothermal reduction process. This FPEM was performed as working electrode for some redox processes and results revealed that rGO/ZnONPs paper allows a large potential region in acidic, basic, and neutral media for electrochemical processes.

Keywords: Reduced graphene oxide, zinc oxide nanoparticles, flexible electrode

1. INTRODUCTION

Electrochemical applications are performed on electrically conductive, inert and stable materials such as glassy carbon electrode, graphite, and noble metals. However, these conventional electrodes are not suitable for large-scale electrochemical production, in-vivo and in-situ applications due to fragile, solid, and inflexible character. In recent years, flexible paper-like electrode materials (FPEMs) have been developed using graphene skeleton by different fabrication routes such as vacuum filtration [1,2], mold-casting [3], and printing [4].

Up to now, many electrochemical applications e.g. supercapacitors [5,6], electrochemical sensors [1,2,7,8], Li-ion batteries [9] have been successfully executed using graphene-based FPEMs. For more intensive electrode applications, stability, flexibility, and potential region of FPEMs need to be further improved. To prepare graphene-based FPEMs, usually graphene oxide (GO) flakes are used as main material and converted to reduced graphene oxide (rGO) structure to increase the electrical conductivity. The rGO based paper is generally

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doped with different substances like metal nanoparticles [1], metal oxide nanoparticles [5,6], polymers [8], and dyes [2,7] to adjust the conductivity and functionality. Zinc oxide (ZnO), a semiconductor substance with a direct bandgap of 3.37 eV [10-13], is a useful material for the electrode designation because of electrochemical stability, basic and economic synthesis.

This work reports the fabrication of graphene based paper-like electrode doped with zinc oxide nanoparticles (ZnONPs) using vacuum-filtration method. Characterization results revealed that ZnONPs were successfully inserted to rGO paper structure and cyclic voltammetry (CV) experiments illustrated that this paper-like material provides a flexible character and a large electrode potential region in a large pH scale.

2. EXPERIMENTAL SECTION

All of the synthesis procedures and experiments were performed in aqueous media using ultrapure water and the reagents were of analytical grade. Synthesis of GO sheets were achieved using modified Hummers method as described in our previous publications [2,7,14], in which high degree chemical oxidation of graphite resulted in formation of one-atom thick GO layers.

To prepare ZnONPs, 5 mL of 1.0 M KOH solution was added to 25 mL of diethylene glycol while stirring. A 10 mL of 0.4 M $Zn(NO_3)_2.6H_2O$ solution and 0.59 g of hexadecyl trimethylammonium bromide solution was added and stirred for 10 min. This dispersion was placed into a suitable autoclave and heated at 180 °C for 3 h. The produced ZnONPs were filtered, rinsed and dried [10].

A 100 mL of 1.0 mg mL^{-1} GO dispersion was prepared, 20 mg of ZnO-NPs was added and ultrasonic treatment was applied for 1 h to supply adsorption of ZnONPs onto GO sheets. This suspension was placed to a membrane-filtration system under vacuum effect, and then peeled from membrane to obtain freestanding GO/ZnONPs paper-like material. To improve the electrical conductivity of this paper, hydrothermal reduction was performed by sealing into ultrapure water and heating at 180 °C for 4 h in autoclave system. This paper-like material was quoted as RZOP. We have also prepared another paper-like material without addition of ZnONPs and labeled it as RGP.

CV experiments were applied with three-electrode Gamry potentiostat system using RZOP or RGP as the working electrodes. A Pt wire and an Ag/AgCl (sat. KCl) were served as counter and reference electrode, respectively. Morphological characterization of the materials was executed using Zeiss brand scanning electron microscopy (SEM) and Hitachi brand transmission electron microscopy (TEM) systems. Optical analyses of the samples were acquired by Shimadzu UV-Vis. spectrophotometer. Crystallographic information of the paper-like materials was collected using Rigaku brand powder X-ray diffraction instrument. Raman spectra of the papers were provided with WITech micro-Raman system.

3. RESULTS AND DISCUSSION

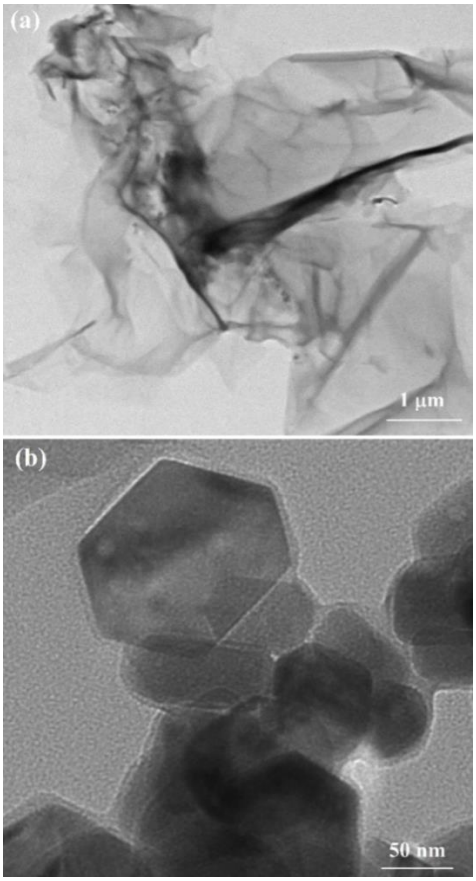

Figure 1 TEM images of GO layers (a) and ZnONPs (b)

To produce a flexible graphene-based FPEM, the quality of GO layers needs to be investigated. It is clearly seen in Fig. 1.a that GO layers are so transparent and they show as large as 10 μm sheets. GO layers demonstrate characteristic wrinkled organization because of the strong one-atom thick structure and flexibility [15]. Fig. 1.b demonstrates TEM image of ZnONPs in which particle size ranges between 20 and 150 nm with a hexagonal shape and crystalline view.

To verify the attachment of ZnONPs to GO flakes, optical analysis was performed using spectrophotometric techniques. Fig. 2 illustrates UV-Vis. region absorption behavior of GO, ZnONPs, and GO/ZnONPs dispersions. GO dispersion displays a maximum at 232 nm and a shoulder at 304 nm, which are consistent with π-π and n-π transitions, respectively [14,16]. ZnONPs include two separated bands at 269 and 372 nm, which comply with previous works [12,14]. The presence of all of these observed bands at the composite dispersion verify the effective adsorption of ZnONPs to GO flakes successfully.

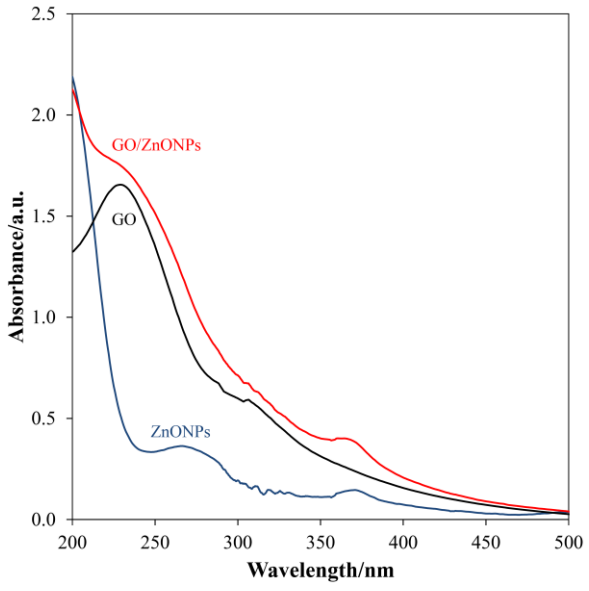

Figure 2 UV-Vis. absorption data of various aqueous dispersions

It is clear from Fig. 3 that the RZOP paper has a stable and flexible view, eventually, it can be a good nominee as a flexible working electrode in many electrochemical applications. SEM, Raman, and XRD techniques were performed to explain morphological, structural, and crystallographic, properties of the produced FPEMs.

Figure 3 Digital photographs of RZOP

Fig. 4.a presents SEM image of RGP and this figure indicates that rGO sheets show a wrinkled surface orientation in the paper-like material. ZnONPs demonstrate hexagonal shapes with a mean particle size of 150 nm in Fig. 4.b. Surface structure of RZOP shows that rGO layers are doped with ZnONPs as large as a few μm, in which surface scene of RZOP totally changes when compared to that of RGP. These large crystals in the RZOP structure can be attributed to aggregation of ZnONPs during the high flux vacuum-filtration process.

Raman spectrum of RGP reflects D and G bands at 1355 and 1602 cm^{-1} for defects and in-plane vibration of sp^2 carbon atoms as usual for carbon nanomaterials, respectively [17,18] (Fig. 5). These bands shift to lower energy regions, and are observed at 1313 and 1554 cm^{-1} for RZOP, indicating insertion of ZnONPs between the layers of rGO in the paper-like material. Obviously, it can be claimed from Fig. 5 that the intensity of D band diminishes when compared to the intensity of G band after doping RGP with ZnONPs, which is associated with the reduction

of defect density by patching disorders of rGO layers with ZnONPs [14].

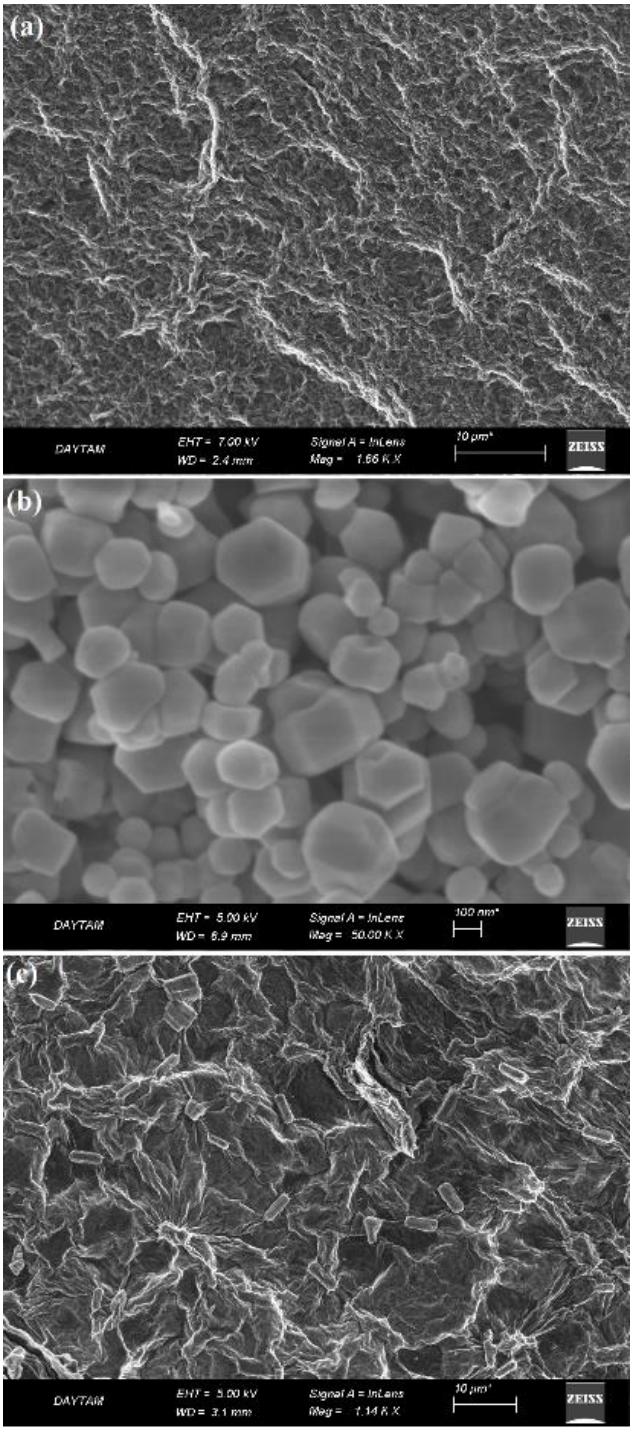

Figure 4 SEM images of RGP (a), ZnONPs (b), and RZOP (c)

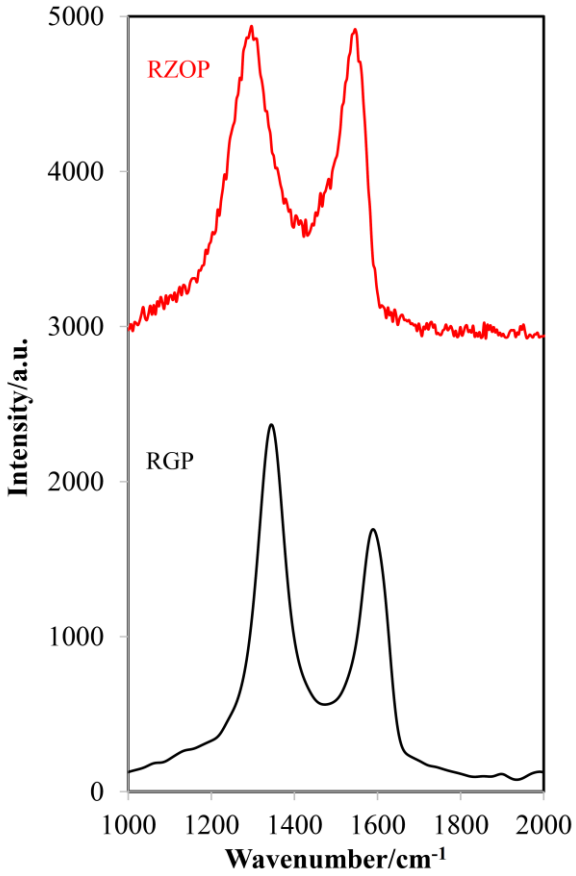

Figure 5 Raman spectra of RGP and RZOP

In Fig. 6, XRD data of ZnONPs includes the defined peaks at 31.8°, 34.5°, 36.3°, 47.5°, and 56.6° for the orientations of 100, 002, 101, 102, 110 depending on the joint committee on powder diffraction standards (JCPDS) with card number of 36-1451 [19]. RGP contains a single peak at $2\theta=24.4°$ corresponding to 002 of rGO flakes [2,7]. It is essential to mention that RZOP illustrates XRD character of both rGO and ZnONPs, affirming the success of composite formation by proposed method for FPEM.

Electrochemical performance of the prepared FPEMs can be assessed using CV experiments. CVs of both RGP and RZOP in 0.1 M KNO_3 solution containing 10 mM $K_3Fe(CN)_6$ were represented in Fig. 7. In this figure, a reversible peak pair of redox of $Fe(CN)_6^{-3/-4}$ is observed [14] for both paper-like materials as expected, which means that these materials may be performed as working electrode for many electrochemical applications. Electrochemical performance of

these electrodes can be compared by calculating the potential difference between cathodic and anodic peaks (ΔEp), in which lower ΔEp value stands for a better electrochemical activity. ΔEp values for RGP and RZOP were measured as 430 mV and 340 mV. This case exhibits the contribution of ZnONPs to the electrochemical activity in the FPEM structure.

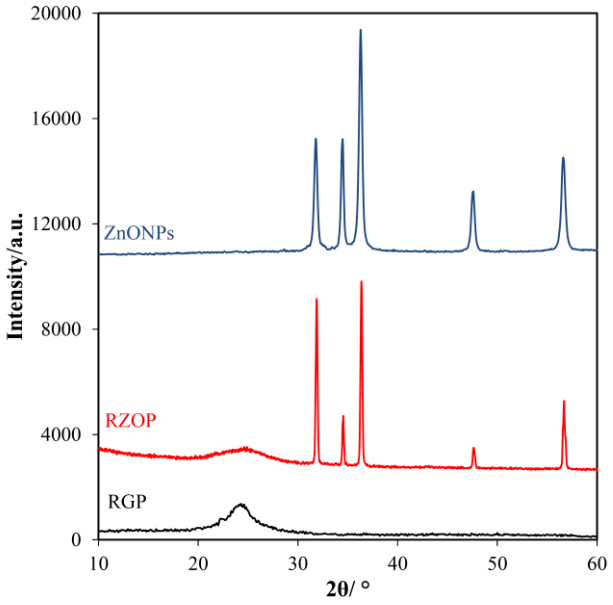

Figure 6 Powder XRD patterns of different samples

To show the available potential region of the FPEMs, CV experiment was designed in the potential range of +0.9 V and -0.9 V as shown in Fig. 8. We have employed both RGP and RZOP as working electrodes in acidic, basic and neutral phosphate buffer solutions (PBSs) and we have not observed redox peaks in neither of the working electrodes. This situation implies that RZOP can be proposed as working electrode in a large potential region for aqueous solutions at different pHs. Moreover, capacitive current of RZOP is higher than that of RGP. So, RZOP can be proposed as working electrode for flexible supercapacitor studies.

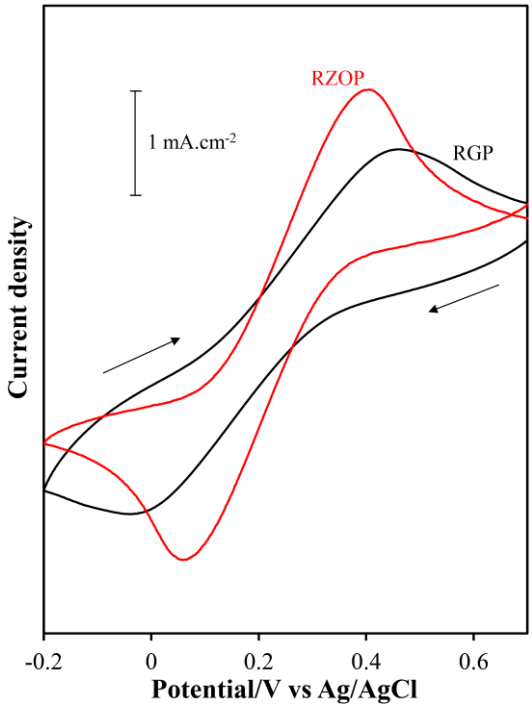

Figure 7 CVs of RGP and RZOP in 0.1 M KNO_3 solution containing 1.0 mM $K_3Fe(CN)_6$. Scan rate: 50 $mV.s^{-1}$

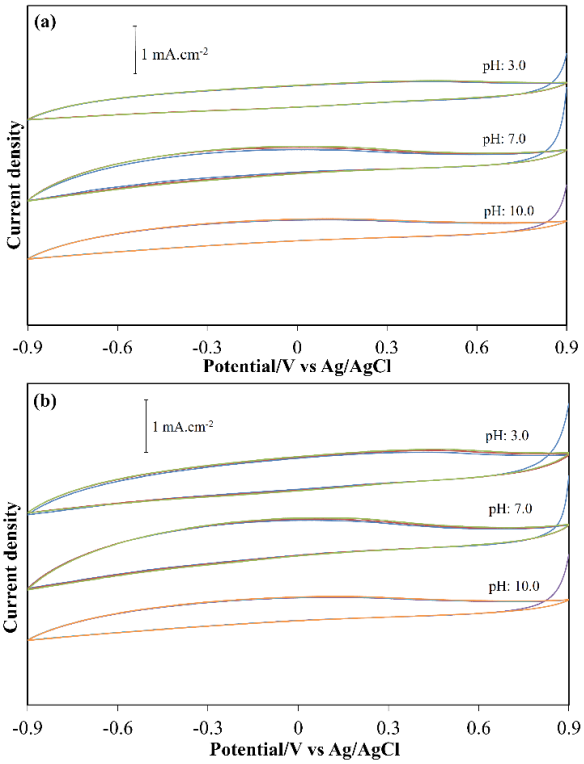

Figure 8 Successive three CV scans of RGP (a) and RZOP (b) in 0.1 M PBS at different pHs. Scan rate: 50 $mV.s^{-1}$

4. CONCLUSIONS

Graphene-based FPEM including ZnONPs were fabricated by using a basic and affordable approach. SEM and XRD analysis results expressed the insertion of ZnONPs between rGO flakes during paper-like material formation with vacuum-filtration process. Raman spectroscopy ratified the adsorption of ZnONPs to defected places of rGO layers. Electrochemical performance of RZOP was better than that of RGP and both FPEMs exhibited utilization as working electrodes in a large potential window for acidic, basic, and neutral aqueous solutions.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors

Authors' Contribution

The authors contributed equally to the study

The Declaration of Ethics Committee Approval

The author declares that this document does not require an ethics committee approval or any special permission

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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