A STUDY ON ELECTROCHEMICAL PROPERTIES OF REDUCED GRAPHENE OXIDE-COPPER OXIDE NANOCOMPOSITES UNDER FACILE CHEMICAL TREATMENT

S.Yuvashree^a, S.Sharvasri^b, J.Balavijayalakshmi^{c*}

^aPhD Scholar, Department of Physics, PSGR Krishnammal College for Women, Coimbatore, Tamilnadu, INDIA. ^bM.sc student Department of Physics, PSGR Krishnammal College for Women, Coimbatore, Tamilnadu, INDIA. ^cAssistant Professor, Department of Physics, PSGR Krishnammal College for Women, Coimbatore, Tamilnadu, INDIA.

ABSTRACT

Graphene, a monolayer of carbon atoms packed into a dense honeycomb crystal structure has attracted considerable attention and numerous investigations because of its unique nanostructure and its extraordinary properties. Graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), are ideal platforms for constructing graphene-based nanostructures for various applications. In this present work, metal nanoparticles are decorated onto the graphene surface which helps to increase the conductivity of nanocomposites and enhances the properties of the material. Thus graphene based metal nanocomposites are prepared by chemical reduction method. The structural and morphological properties of the prepared nanocomposites are investigated by X-Ray diffraction analysis and Field emission scanning electron microscopy (FE-SEM). The presence of functional groups in the synthesized nanocomposites is studied by Fourier transform infrared spectroscopy (FT-IR). XRD reveals that the product is well crystallized. Thus the prepared nanocomposites can be tested for sensing applications.

Key words - Graphene oxide, Copper oxide, XRD, Electrochemical behaviour.

INTRODUCTION

Graphene, a 2D sp² carbon networking material with a single-atom thickness, has attracted intensive interest because of its significant mechanical, electrical and thermal properties [1]. The unique properties of graphene include fast electron transportation, high thermal conductivity, excellent mechanical stiffness and good biocompatibility, which results in promising applications in field-effect transistors, electromechanical resonators, solar cells and electrochemical sensors. It has been observed that graphene oxide (GO), especially reduced graphene oxide (RGO) has functional groups such as carboxyl (-COOH) and hydroxyl (-OH) groups giving rise to the better conductivity, which are promising in the applications of cellular imaging, biosensor fabrication and drug delivery [2]. Recently, it has been reported that electrodes modified with RGO in the presence of interfering agents exhibit a remarkable electrochemical biosensing capacity in detecting electro active biomolecules comparing to bare electrodes and carbon nanotube-based electrodes. Graphene and its nanocomposites have been widely exploited in biomedicine for drug/gene delivery, cancer therapy, tissue engineering and biosensing [3]. In recent years, noble metal nanoparticles have been used widely due to their interesting electronic, optical, mechanical, magnetic and chemical properties, which differ greatly from those of bulk substances. Among various metal nanoparticles, copper nanoparticles (Cu NPs) have been widely used in many fields due to their excellent physical and chemical properties, easy preparation and the low synthetic cost. Surface modification of RGO by the coating of copper oxide has gained much interest because of their better tunability of particle size, shape and high specific surface area [4].

2. EXPERIMENTAL

2.1 Reagents

Graphite powder, Conc.Sulphuric acid (98% H_2SO_4), potassium permanganate (KMnO₄), hydrogen peroxide solution (30% H_2O_2), sodium nitrate (NaNO₃), sodium hydroxide (NaOH) and cupric chloride , sodium borohydride (NaBH₄) are purchased from sigma Aldrich and are used as recessived without further purification.

2.2 Preparation of reduced graphene oxide/ Copperoxide nanocomposites

The rGO/ Copper oxide nanocomposite are synthesized by dispersing 50 mg of GO in 25ml of distilled water by ultrasonication for 1hour to form the GO solution and various concentrations of cupric chloride solution (0.002M, 0.004M and 0.006M) is then added into the above solution and stirred for 1hour at room temperature. Then NaBH₄ solution (25mg) is added and stirred for 4hrs at 60°C. Thus the formed solution is left undisturbed for overnight and dried at 60°C for 12 hours.

3. RESULTS AND DISCUSSION

3.1 FT-IR Spectral analysis



Figure 3.1 (a-c) FT-IR spectra for rGO-CuO nanocomposites (a) 0.002M (b) 0.004M (c) 0.006M of various concentrations of copper oxide nanoparticles

The FT-IR spectra of rGO-CuO nanocomposites with various concentrations of copper oxides are shown in the Figure 3.1(a-c). The band obtained around 1205 cm⁻¹ is attributed to the C–O stretching vibrations of epoxy and alkoxy groups. The aromatic C=C stretching vibrations are observed around 1681 cm⁻¹. The bands around 3709 cm⁻¹ and 2389 cm⁻¹ corresponds to O-H and C-H stretching vibrations respectively [5]. The band observed around 1536cm⁻¹ corresponds to C=O carbonyl stretching vibrations of reduced graphene oxide. It is further observed that by increasing the concentration of copper oxide nanoparticles onto the rGO surface, the intensity of the band decreases. The bands appeared at 576 cm⁻¹ and 505 cm⁻¹ corresponds to the Cu–O stretching vibrations [6].

3.2 XRD Analysis



Figure 3.2 (a-c) XRD pattern for rGO-CuO nanocomposites (a) 0.002M (b) 0.004M (c) 0.006M of various concentrations of copper oxide nanoparticles

The XRD pattern for rGO-CuO nanocomposites with various concentrations of copper.oxide nanoparticles are shown in the Figure 3.2(a-c). The diffraction peaks exhibited at 2 θ values of 32.5°, 35.7°, 50.25°, 53.8°, 58.5° corresponds to (110),(111),(112),(020), (202) planes, confirms the formation of CuO monoclinic phase which is well matched with the JCPDS Card no. 41-0254 [7,8]. Small additional peaks at 26.1° and 42.9° correspond to (002) and (100) planes may be attributed to the

reduced graphene oxide. The crystallite size of rGO-CuO nanocomposites for various concentration of copper oxide nanoparticles (0.002M, 0.004M, 0.006M) is found to be 19.28 nm, 20.91 nm and 30.18 nm respectively. It is found that on increasing the concentration of copper oxide nanoparticles, the intensity of the diffraction peaks increases. It is observed that the crystallite size increases because of the incorporation of copper oxide nanoparticles onto the surface of reduced graphene oxide sheets which could also be evidenced from SEM analysis. The sharpness of the peaks suggests that the samples are well crystallized.

3.3 SEM analysis



Figure 3.3 SEM analysis for 0.006M of rGO-CuO nanocomposites

The Surface Morphology of rGO-CuO nanocomposites are investigated using Scanning Electron Microscope. Figure 3.3 shows the SEM analysis for 0.006M of rGO-CuO nanocomposites with different magnifications. It is evident from SEM images that the CuO nanoparticles are homogeneously distributed over paper-like surface of rGO, thereby conforming the incorporation of CuO nanoparticles into the rGO [9].

3.4 EDAX Analysis



Figure 3.4 EDAX Analysis for 0.006M of rGO-CuO Nanocomposities

An EDAX spectrum shows the presence of elements in the synthesized rGO-CuO nanocomposites. Figure 5.4 shows the EDAX Analysis for 0.006M of rGO-CuO nanocomposities. The presence of carbon, oxygen and copper elements without any impurities confirms the formation rGO-CuO nanocomposites in the prepared sample [8, 10].

4. ANALYTICAL PERFORMANCE



Figure 4 (a &b) Cyclic Voltagramm curve for (a) bare GO (b)RGO/CuO nanocomposites modified GCE

Electrochemical measurements are carried out using electro chemical workstation. A three-electrode configuration is employed, consisting of a modified glassy carbon electrode (3mm in diameter) serving as the working electrode and Ag/AgCl (3M KCl) and platinum wire serving as the reference and counter electrodes respectively. The electrochemical measurements are carried out in the electrolyte solution of 0.1M phosphate buffer solution (PBS). To measure the electro-chemical behaviour for prepared GO and RGO/CuO nanocomposites cyclic voltammetry (CV) is employed. CV are carried out in PBS from -1 to 1 V with a 20 mV/s scanning rate. No redox peak is observed for bare GO electrode. In contrast a pair of strong redox peaks is observed at 0.1V and -0.3V for RGO/CuO modified electrode [9, 11]. The strong peak suggests the removal of a significant amount of functional groups which shows high conductivity for RGO/CuO nanocomposites compared to pure GO.

5. CONCLUSION

The study outlines the successful preparation of the RGO/CuO nanocomposites by chemical precipitation method. FT-IR indicates the interactions between the functional groups present in the prepared nanocomposites. All diffraction peaks in the 20 range corresponds to the monoclinic structure of CuO nanoparticles and the crystallite size increases as the concentration of copper increases. The formation of nanocomposites is also confirmed by surface morphology. EDAX analysis confirms the presence of elements in the prepared nanocomposites. Cyclic voltammetry shows that the prepared RGO/CuO nanocomposites provide high current response compared to GO. Thus the fabricated biosensor can be applied in biosensing applications.

6. ACKNOWLEDGEMENT

We acknowledge Tamilnadu State Council for Science and Technology for their financial assistance.

REFERENCES

[1] Abdullahi Mohamed Farah, Force Tefo Thema and Ezekiel Dixon Dikio, Int. J. Electrochem. Sci., 7 (2012) 5069 – 5083.

[2] Sijie Wan, Feiyu Xu, Lei Jiang, and Qunfeng Cheng, Adv. Funct. Mater. (2017), 1605636.

[3] Fatemeh Emadi, AbbasAmini, AhmadGholami & YounesGhasemi, Scientific Reports | 7:42258.

[4] Jonghoon Choi, Hana Oh, Sang-Wook Han, Seokhoon Ahn, Jaegeun Noh, Joon B Park, Current Applied Physics, S1567-1739(16)30335-2

[5] Chandrama Sarkar and Swapan K. Dolui, RSC Adv., (2015), 5, 60763.

[6] S.R. Kiran Kumar, G.P. Mamatha, H.B. Muralidhara, M.S. Anantha, S. Yallappa, B.S.Hungund and K.Yogesh Kumar, Journal of Science: Advanced Materials and Devices, S2468-2179(17)30051-5.

[7] Xiaolin Wang, Enli Liu, Xiaoli Zhang, Electrochimica Acta, 130 (2014) 253–260.

[8] Harish Kumar and Manisha, Asian.j.chem., (2018), vol 30, no 1, 59-62.

[9] Youcheng Zhao, Xinyu Song, Qisheng Song and Zhilei Yin, CrystEngComm, (2012), 14, 6710–6719.

[10] Minmin Liu, RuLiu, WeiChen, Biosensors and Bioelectronics 45 (2013) 206–212.

[11] Jian Song, Lin Xu, Chunyang Zhou, Ruiqing Xing, Qilin Dai, Dali Liu and Hongwei Song, ACS Appl. Mater. Interfaces, (2013), 5,12928–12934.

