Importance of Graphene Composites in Enhancing the Conductivity of Transition Metal Oxide

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Abstract:

In this study, graphene oxide (GO)- Mn_2O_3 composites with varying weight ratio GM1 (GO: Mn_2O_3; 1:1), GM2 (GO: Mn_2O_3; 1:2), GM3 (GO: Mn_2O_3; 2:1) have been synthesized by one step solvothermal rout. The characterization of the samples was done using XRD and FESEM. Further, the impedance of these samples was studied as a function of temperature at 5 kHz frequency using LCR meter. The impedance was found to be decreased on increasing temperature and graphene content in the composites which confirm the importance of conducting material in transition metal composites.

1. Introduction:

Now a day, nanotechnology and science lead to the creation of innovative nanostructured materials and devices that directly impact our lives [1]. The most beautiful aspect of nanotechnology is an interdisciplinary field that brings physicists, chemists, biologists, and techno enthusiasts together [1-4]. The significance of nanotechnology will further increase in the future as miniaturization becomes more vital in areas such as computing, sensors, biomedical, and many other applications [2]. Currently, material scientists are working on materials with better properties that give more satisfactory results in nanoscience and technology. In this respect, the discovery of graphene, graphene-based transition metal oxide composites, and graphene-based polymer nanocomposites is significant and will play an essential role in our lives soon [5].

Graphene, one of the allotropes of carbon, is a planar arrangement of carbon atoms into a two-dimensional (2D) honeycomb hexagonal lattice with a carbon-carbon bond length of 0.142nm. The carbon atoms have sp^2 hybridization in this structure. Each carbon atom forms four bonds. One σ bond with its three neighbors and one Π bond oriented out of the plane [5, 6]. However, manganese is a transition metal and is found to have many oxidation states, namely, +2, +3, +4 so that it has many oxides like MnO, MnO_2, Mn_2O_3, Mn_3O_4, and Mn_5O_8 [712]. Due to this, manganese has attracted many researchers all over the world. Manganese oxides are cheap, non-toxic, plentiful, and have a wide range of optical, electrochemical, magnetic, and catalytic applications [7-12]. In particular, Mn_2O_3 is of great interest to the scientific community because of its low cost, high theoretical specific capacity, natural abundance of Mn on earth, and eco-friendly nature. [7-10] However, the use of Mn_2O_3 is significantly limited due to its poor electrical conductivity. As mentioned above, graphene has very high electrical conductivity, high mechanical strength, large surface area, and chemical stability [6]. Thus, composites of graphene- Mn_2O_3 is a suitable way to overcome the low conductivity problem of Mn_2O_3.

Hence, in this work, graphene oxide composites with Mn_2O_3 with a varying weight ratio have been synthesized using the solvothermal method. Moreover, a detailed dielectric study has been done to understand the impact of graphene oxide in Mn_2O_3.

Key words: Composites, Conductivity, Graphene

2. Experimental Procedures

2.1 Materials Used:

Graphite powder (SDFCL, India), sulphuric acid (H_2SO_4, 98%, SRL, India), hydrogen peroxide (H_2O_2,30%, Rankem, India), potassium permanganate ($KMnO_4$, SRL, India,), sodium nitrate ($NaNO_3$, Rankem, India), manganese chloride ($MnCl_2$, SRL, India), sodium hydroxide (NaOH, Qualigens, India), polyvinylidene fluoride (PVDF, Alfa Aesar, India) were used as received without further purification.

2.2 Preparation of Graphene oxide

In this work, Graphene oxide (GO) and Mn_2O_3 were prepared using modified Hummer's Method, and co-precipitation method **[6**, **9].** In this work, GO-Mn_2O_3 nanocomposites (GMs) in three different ratios were prepared using a simple solvothermal process. For GM1 (GO: Mn_2O_3; 1:1), 150 mg of as-prepared GO was added to 10 ml of DI water and sonicated for 30 min to form a homogeneous suspension. Further, 150 mg of as-prepared Mn_2O_3 was added to 10 ml of DI water and sonicated for 30 min. The above two suspensions were mixed and further stirred for 30 min. Then, the resulting mixture was transferred to a Teflon-lined stainless steel autoclave and was heated at 200^oC for 6 h in a hot air oven. This was then allowed to cool naturally to room temperature. Finally, the resultant nanocomposite was ground to form fine powder. For GM2 and GM3, exactly same procedure was followed with just one difference. For GM2 (2:1), 300 mg of GO and 150 mg of Mn_2O_3 was taken and for GM3 (1:2), 150 mg of GO and 300 mg of Mn_2O_3 was taken.

3. Results and Discussion

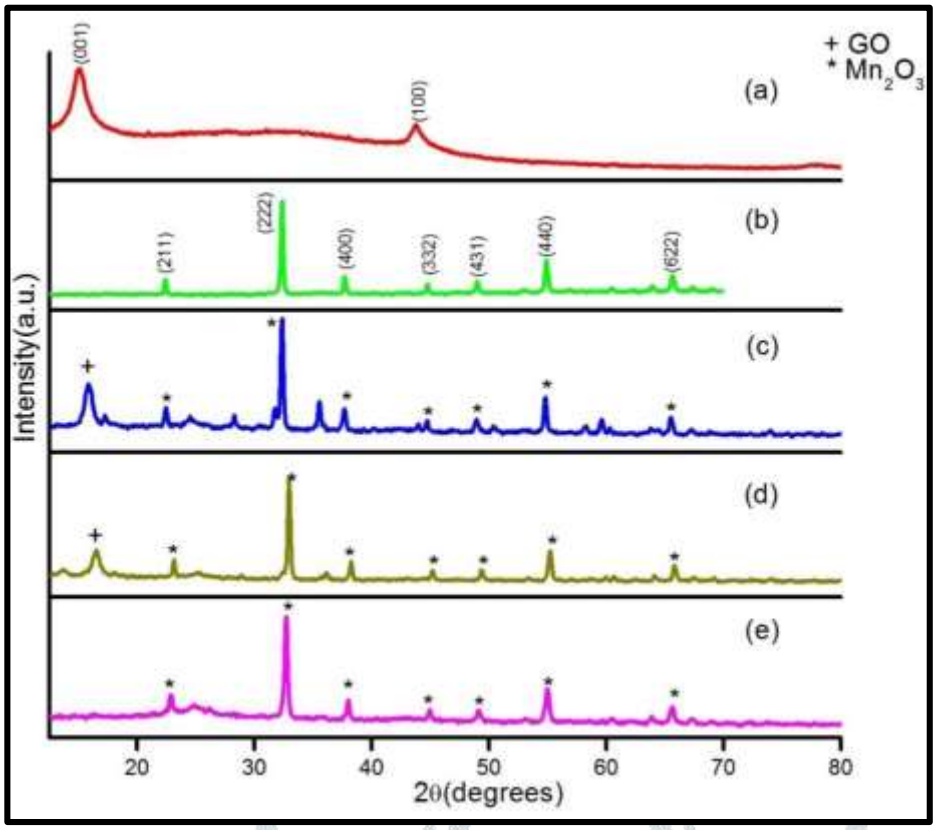

Fig. 1. XRD spectrum of (a) graphene oxide, (b) Mn_2O_3, (c) GM1, (d) GM2, (e) GM3

To study the structural analysis of as synthesized powder samples of graphene oxide, Mn_2O_3, and graphene-Mn_2O_3 composites, X-Ray diffractometer (XRD) measurements were performed in the range of 10□ to 80□ at room temperature. The XRD pattern of GO was found to exhibit an intense peak at $2\theta=12.66^o$ which corresponds to interlayer spacing of around 0.73 nm. and planes (001) and (100) [6]. This indicates that separation between the layers has increased on oxidation of graphite powder to graphene oxide which is shown in Fig. 1. The XRD spectrum of Mn_2O_3 is reported in Fig. 6. The peaks were observed at $2\theta= 23.15^o$, 32.96^o, 38.29^o, 45.13^o, 49.37^o, 55.09^o and 65.84^o corresponding to (211), (222), (400), (332), (431), (440) and (622) planes of cubic phase of Mn_2O_3 respectively. These peaks were found to be matching well with the literature [9, 10]. Fig. 1 also shows the XRD spectrum of the composites of graphene oxide and Mn_2O_3. For GM1, the peaks at $2\theta= 12.54^o$ corresponds to graphene oxide and at 23.15^o, 32.96^o, 38.29^o, 45.13^o, 49.37^o, 55.09^o and 65.84^o correspond to Mn_2O_3. For GM2, a peak at 12.54^o corresponds to graphene oxide while sharp peaks at 23.15^o, 32.96^o, 38.29^o, 45.13^o, 49.37^o, 55.09^o and 65.84^o correspond to Mn_2O_3. In GM3, the peak corresponding to graphene oxide is not obtained because of less content of graphene oxide in comparison to Mn_2O_3. But, peaks at 23.15^o, 32.96^o, 38.29^o, 45.13^o, 49.37^o, 55.09^o and 65.84^o indicate the presence of Mn_2O_3.

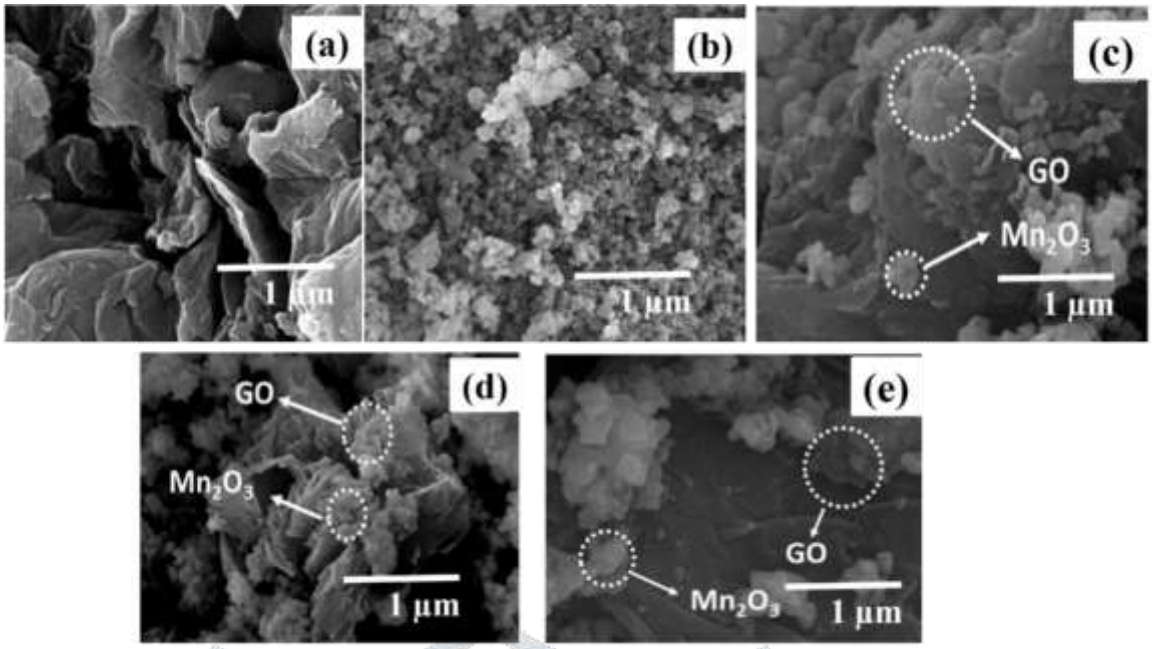

Fig. 2. FESEM image of (a) GO, (b) Mn_2O_3, (c) GM1 (d) GM2 (e) GM3.

Further, to study the morphology of all the samples, Field emission scanning electron microscopy (FESEM) analysis was performed which is displayed in Fig. 2. The FESEM image of GO shows sponge like structure of GO which shows the presence of porous, and interlinked sheets of graphene while Mn_2O_3. exhibits spherical shaped particles with porous morphology [9, 13]. Furthermore, FESEM images of the three composites i.e. GM1, GM2 and GM3 are also shown in Fig.2 (c-e). The morphology of composites shows the presence of both layer- like structure and spherical particles (as is indicated by the dotted circles). This is attributed to the presence of graphene oxide and Mn_2O_3 in these composites.

To study the impedance of all three samples, powder sample is convert into solid pallet form. For this power sample is mixed with binder (PVDF). This resultant mixture was grinded till the powder appeared fine. Further, the resultant mixture is used to formed pallet using Hydraulic press and then sintered at 200□C for 2 hr. and impedance analysis has been performed in a temperature range of 10□C to 100□C. In Fig. 3, a comparison study of composites with PVDF has been studied and the obtained results show that PVDF shows high resistance in comparison of composites. Fig.3 shows that the impedance of the films decreases as the temperature increases. This is mainly occurred due to the conduction increases on increasing the temperature and hence impedance decreases [14, 15]. As is clear from the Fig.4 that maximum impedance corresponds to PVDF film having no graphene content, followed by GM3 (33.33% graphene content), GM1 (50% graphene content) and GM2 (66.67% graphene content). Thus, as the graphene content increases, the conduction increases due to high electrical conductivity of graphene and hence impedance decreases.

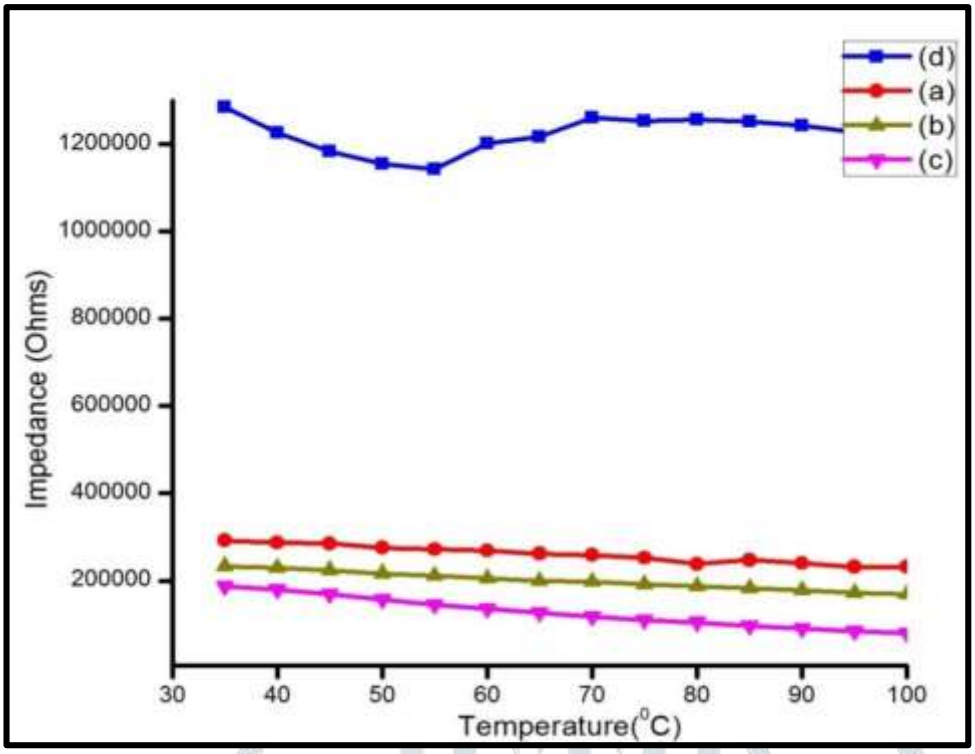

Fig. 3. Variation of impedance of (a) GM3, (b) GM1, (c) GM2 films with temperature.

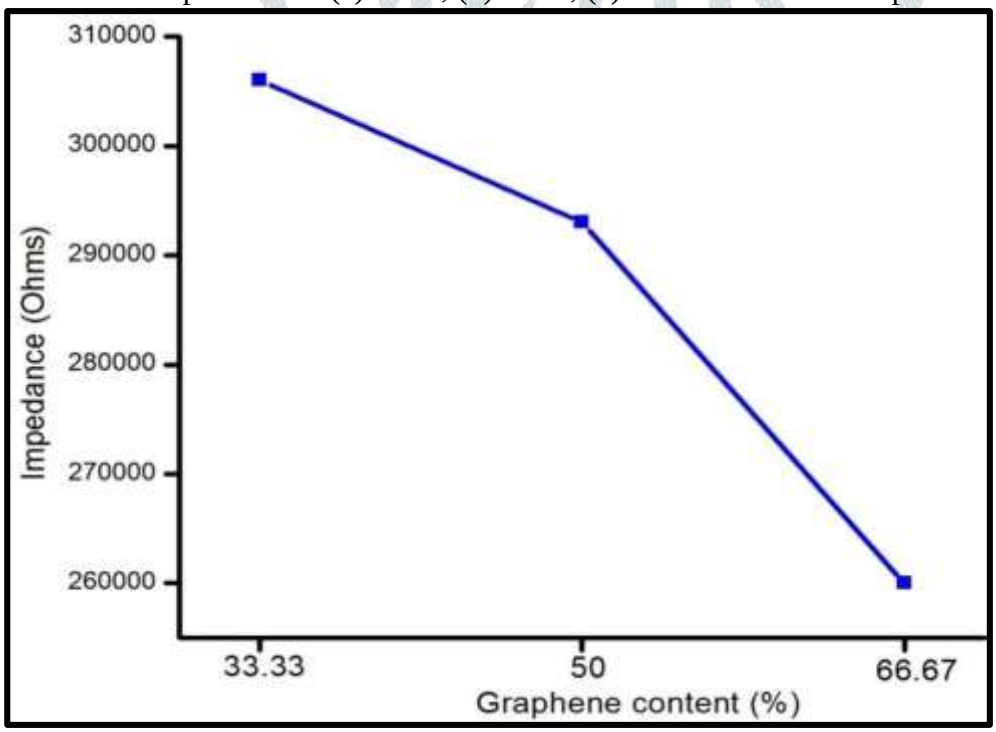

Fig. 4. Variation of impedance with graphene content at room temperature. Here, X-axis shows 33.33, 50, and 66.67% graphene content corresponding to GM3, GM1, and GM2 respectively.

4. Conclusion

In this work, the composites of GO-Mn_2O_3 in ratios 1:1, 2:1 and 1:2 were prepared successfully using solvothermal method. XRD and FESEM analysis confirm the pure phase synthesis and morphology of these composites. Further, the impedance study of all three composites show that the impedance of all the samples decreased with the temperature increase. Also, the effect of graphene's conductivity on the composite was seen. As the graphene content in the composites increased, the impedance was found to decrease.

5. References

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