Preparation and characterization studies of Mn_3O_4 Nanoparticles/ Graphene sheet composites

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Abstract

Mn_3O_4 Nanoparticles/ Graphenesheet (GS) composites were synthesized by one of the low cost solvothermal process in ethanol solution. X-ray diffraction was chosen to measure the crystal structure of the Graphenesheet (GS) composites Nano particles. Fourier transform infrared (FTIR) spectrum analyzer was used to confirm the presence of oxygenated functional groups. The morphology and the structure were identified by the Scanning Electron Microscope (SEM).

Key words; *Graphene oxide(GO), Graphene Sheet(GS), XRD, FTIR, SEM, Raman spectroscopy,*

I. Introduction

Graphene based nanostructured materials are one of the great popular topics in the field of nanomaterial's and nanotechnology. Graphene, a dimensional layer of carbon atoms is understood to be the constructing block for all kinds of graphitic substances inclusive of carbon nanotubes (CNT), fullerenes, Graphite. These materials have become serious, utilization of renewable energy resources represented by the solar and wind energy which has been increasingly critical [1, 2]. They are taken into consideration as one of the maximum promising electrochemical strength garage materials. The batteries for wearable and transportable electric powered electric and hybrid vehicles. Super capacitors are of the most popular electrochemical systems [3, 5].They have received tremendous performance because of their high power density and excellent cycling life. MnO_2, NiO, Co_3O_4 are a group of very promising super capacitor electrodes materials to replace presence and toxic RuO_2[4].Super capacitor (Scs) also called electrochemical capacitors are emerging as to most promising

energy storage devices for the future due to their specific advantages of fast power release and long term stability over other storage devices[6]. Super capacitor or Ultra-capacitor have attracted enormous current attention's because of their excessive electricity density excessive charge/discharge fees and lengthy existence cycle performance. [7] The graphene metallic oxide hybrid composite is broadly utilized in superior electrochemical homes withinside the time period of electrode substances for super capacitor.[8] Super capacitor as are of the most popular electrochemical[9]. Systems have significant advantages in terms of high power density long cycle life and higher reliability [10]. Graphene oxide (GO) obtained by Hummers oxidation route always consists of various oxygenic functional group [11]. Graphane is often suggested as a replacement for activated carbon in super capacitors in part due to its high relative surface area [12,]. The surface area is one of the limitations of capacitance and higher surface area means a better electrostatic charge storage in addition graphene based super capacitors will utilize to its light weight nature [13,14]. Elastic properties and mechanical strength a graphane super capacitors is said to store almost as much energy as lithium – ion batteries charge and discharge in seconds and maintain this over terms of themselves change cycle[15-16]. Super capacitors also called electro chemical capacitors are emerging as the most promising energy store device for the function due to their specific advantage of fast power release and long term stability over after storage device [17].

2. Material and Methods:

Graphite Flake powder (FG), Sulfuric acid (H_2So_4), Potassium Permanganate ($KMnO_4$), Sodium Nitrate ($NaNo_3$), Hydrogen Peroxide (H_2O_2), Hydrochloric acid (HCL), Ethanol, Magnaesaccitate ($Mn(CH_3COO)_2.4H_2O$)

2.1 Synthesis of graphene Oxide (GO)

Graphite oxide (GO) was prepared by a modified Hummers methods and the preparation is described in a typical process. Concentrated H_2So_4 (70ml) was added in the mixture of Graphite Flak powder (FG) (1.5g), sodium nitrate (3.0g) $NaNO_3$ in the flask and then cooled on an ice bath and stirred for 45mintues $KMno_4$ (9.0g) of potassium permanganate was added very slowly and temperature was controlled under 293k. After stirring for 2 h. in the ice bath. The mixture was transferred into the water bath and kept at 308k for 1h. The water (140ml) was followed to add into the mixture and caused its temperature slowly up to 371k maintain at the temperature for 1h. The reaction temperature was found to increases rapidly to 100°c

with effervescence and the color changed to brown. Then the mixture 30ml of H_2O_2 was added to the above solution and the color changed to yellow. Finally the solid mixture was separated by the filtration and high speed centrifugation (6000rpms) washed with HCL solution and water respectively and dried in vacuum at 323k for 96h to get GO.

GO(50mg) became dispersed in ethanol (65ml) with the aid of using sonication for 3h after which the $Mn(CH_3COO)_{2.4}H_2O$ powder became delivered into the answer in step with Mn+2/Go mass percentage 50:50 ratio respectively and endured to ultrasonic dispersal for 1h. the received suspension became sealed in to a Teflon-covered autoclave(100ml) and heated at 473k for 12h. the closing merchandise have been filtered washed with ethanol and dried in vacuum at 323k for 24h. For contrast natural Mn_3O_4 and graphene sheets (GS) have been produced with the aid of using the above method.

3. Results and Discussion

3.1 XRD

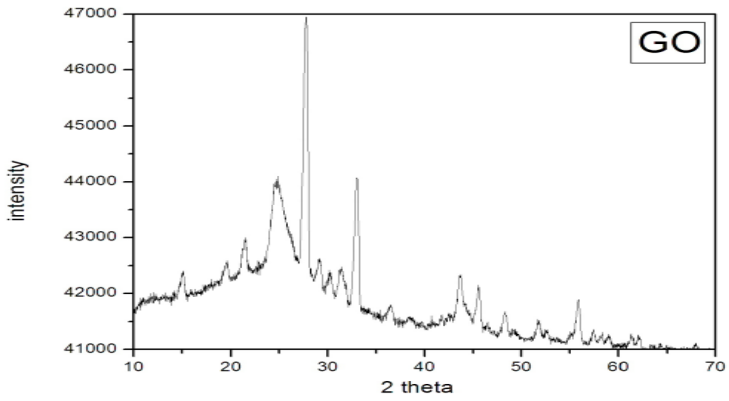
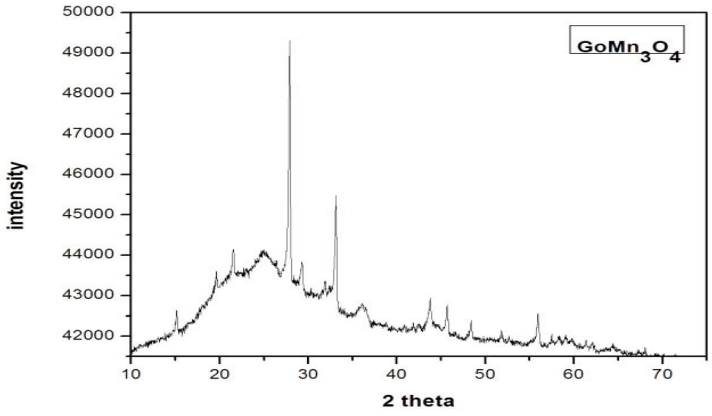


Figure 3.1 XRD pattern of Nano Graphene Oxide

X-ray powder diffraction is to most common analysis for the generalized characterization of crystalline and nano material which range of atom and also to verify the oxidation of single crystal or nano crystal. X-ray diffraction analaysis of nano Graphene Oxide sample. is shown in the Figure 3.1. The average crystalline size 'D' of the as obtained Graphene oxide nanoparticles were estimated by Debye-Scherrer equation

$$D=0.89\ \lambda/\beta \cos \theta$$

Where λ is the wavelength of the incident beam (λ =1.5406Å) and β is the full width at half maximum and θ is the Braggs diffraction angle. The average particle size was found to be 21nm. The peaks of the diffraction patterns can be compared with standard available data for the confirmation of the structure,15.74^{o},21.07^{o},25..06^{o},28.42^{o},33.07^{o},44.08^{o},45.02^{o}, 49.09^{o} 56.08^{o}, In the XRD pattern we can see a promint peak at 15.74º corresponding Prominent Plane. And also there is a clear shift in 2 θ value and full width maxima for a Prominent Plane this can be observed as we go from peak 21.07º, and also sharp peak at intense peak at 25.06º, the all this peak which confirms the good space structure the interlayer facing of nano grapheite oxide. According to the peak at 2 θ =70◦ this value is higher the interlayer facing of graphite powder this is due to the presence of oxygenated futional group and interrelated water molecules from the spectrum and also there is diffraction 2 θ = 15.74º which is mainly due to oxinated graphite. The diffraction peak of nano graphene oxide is found to around 28.42º around which crospands to the highly organized structure with on interlayer structure. The disappearance peak at 56.08º appearance of peak at 33.07º shows that product is computes oxidation ofter the chemical oxidation and exfoliation indicating the presence of de spacing of nano graphene oxide crystalline lattice. The XRD patterns agree well with the tetragonal hausmannite of the Graphene Oxide and it is confirmed that Graphene Oxide nanoparticles are of tetragonal hausmannite crystalline structure.



The XRD pattern of Mn_3O_4 nanoparticles is shown in Figure. 3.1b

The XRD patterns of GM composite prepared with Mn^{2+}/GO mass percent 50:50 ratio is shown in Figure1. The average crystalline size 'D' of the as obtained Mn_3O_4nanoparticles were estimated by Debye-Scherrer equation

$$D=0.89\ \lambda/\beta \cos\theta$$

Where λ is the wavelength of the incident beam (λ =1.5406Å) and β is the full width at half maximum and θ is the Braggs diffraction angle. The average particle size was found to be

19.1nm. The peaks of the diffraction patterns can be compared with standard available data for the confirmation of the structure,18.74º,28.07º,31..06º,32.42º,36.07º,44.08º,45.02º, 49.09º 56.08º, with the use of **JCPDS Card no; 24 0734**. The XRD patterns agree well with the tetragonal hausmannite of the Mn_3O_4 and it is confirmed that both pure Mn_3O_4 nanoparticles are of tetragonal hausmannite crystalline structure.

3.2 FTIR:

In order to analyze the presence of functional groups qualitatively in the GM composite materials, the FTIR spectrum was recorded between 400cm^{-1} and 4000cm^{-1} using brukker model IFS 66V FTIR spectrometer by KBr pellet technique and the resultant spectrum is shown in Fig. 2. The spectrum of GO, the absorption band 3403.65cm^{-1} is attributed to the C=O of carbonyl and carboxyl groups. While the absorption band 2923.06cm^{-1} is assigned to the vibration of the aromatic C=C, the C-O stretching band at 2852.68cm^{-1} can also be observed, to the GO the typical C=O absorption bands at 3403.66cm^{-1} of Mn_3O_4/GO almost disappear, in addition two new peaks located 620.86cm^{-1} and 641.87cm^{-1} occurred in the spectra of Mn_3O_4/GO can be associated with the coupling modes between the Mn-O stretching modes of tetrahedral and octahedral sites. The absorption peak at 641.87cm^{-1} is attributed to the band stretching modes of the octahedral sites, and displacement of the Mn^{2+} ions in the tetrahedral sites is negligible.

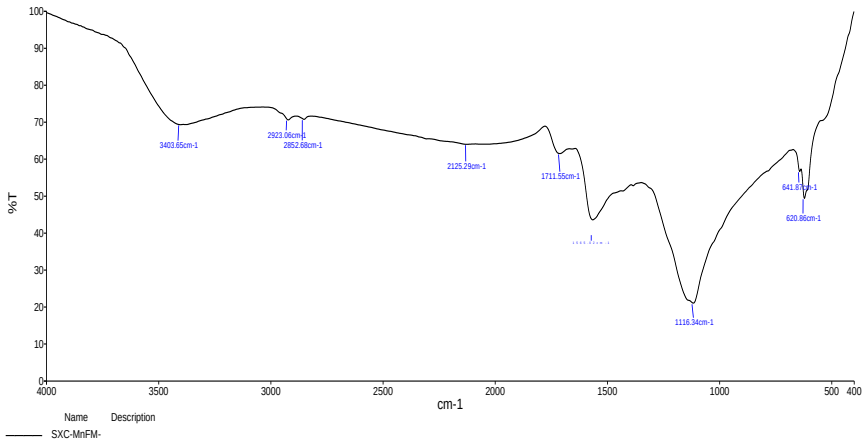


Figure3.2: FTIR analysis Graphene and Mn_3O_4 composites

Table 32. Frequency assignments for as prepared $Mn^{2+/}$GM nanoparticles

WAVE NUMBER (cm^{-1})	ASSIGNMENT
3403.66	OH broader band group
2923.06	C-H stretch at sharp band
2852.68	C ≡ C
2125.29	C=C stretch bond
1711.55	Mn-O-c groups
1116.34	C = H group

3.3 Raman Spectral Studies

The Raman spectrum is extensively used to represent the Nano substances consisting of graphene oxide (GO). As proven in Fig. 3.3 a. six distinguished peaks at 489 cm^{-1}, six hundred cm^{-1}, 994 cm^{-1}, 1300 cm^{-1},1650 cm^{-1},2700 $cm^{-1,}$ can arise for Go and Mn_3O_4 similar to D and G bands, respectively. It is widely recognized that the D band is ascribed to structural defects and disordered of Sp^3 carbon and G band to in aircraft vibration of ordered Sp^2 carbon bands. The Raman depth ratio of ID/IG may be used to symbolize the diploma of crystallization or defects and the decrease ratio stands for large crystallite length of the substances. The Raman spectral effects of 658 cm^{-1},1400 cm^{-1},1700 cm^{-1},2200 $cm^{-1,}$2850 $cm^{-1.}$ GO/Mn_3O_4 composite effects are proven in Fig. 4b the effects are implying that the expanded the D, G peaks upon the electrochemical discount of GO/Mn_3O_4 in addition to a shift of the D and G height position. Although a distinguished D,G height is usually a demonstration of ailment with inside the Raman spectrum of carbon substances and there are a few reviews at the lower of I(D)/I(G) ratio and in comparison to our hybrid composite.

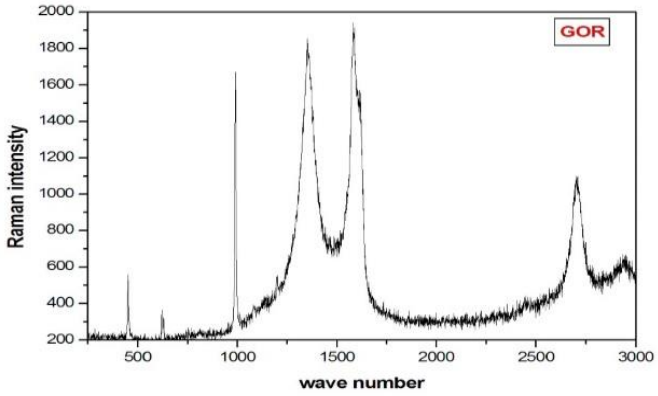


Fig.3.3 Raman spectra Nano Graphene Oxide

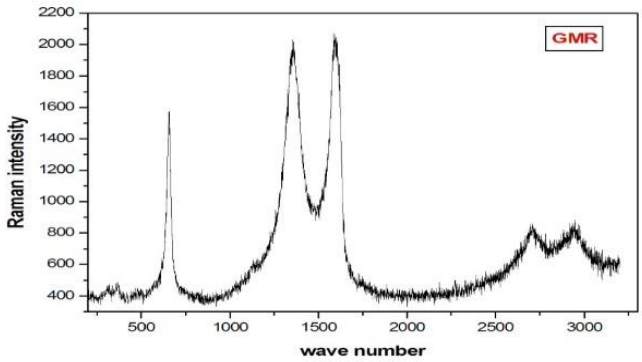


Fig 3.3 b GO/Mn_3O_4 composite Raman spectra of 50:50 ratio.

3.4 SEM studies:

The scanning electron microscopy (SEM) measurement was carried out using JSM840-A SEM instrument in order to analyze the structure and morphology of synthesized samples, the instrument was accelerated with 20kv and the sample were scanned at a working distance of 15mm, the sample were dispersed in isopropyl alcohol and scanned with a magnification of 10,000x, the SEM images $Mn^{2+/}$GO sample shown in Figure 3.4 respectively. The SEM images the particle size of the pure $Mn^{2+/}$GO spherical shape and circular shape, agglomerated shape were found to be the range 20-50nm.

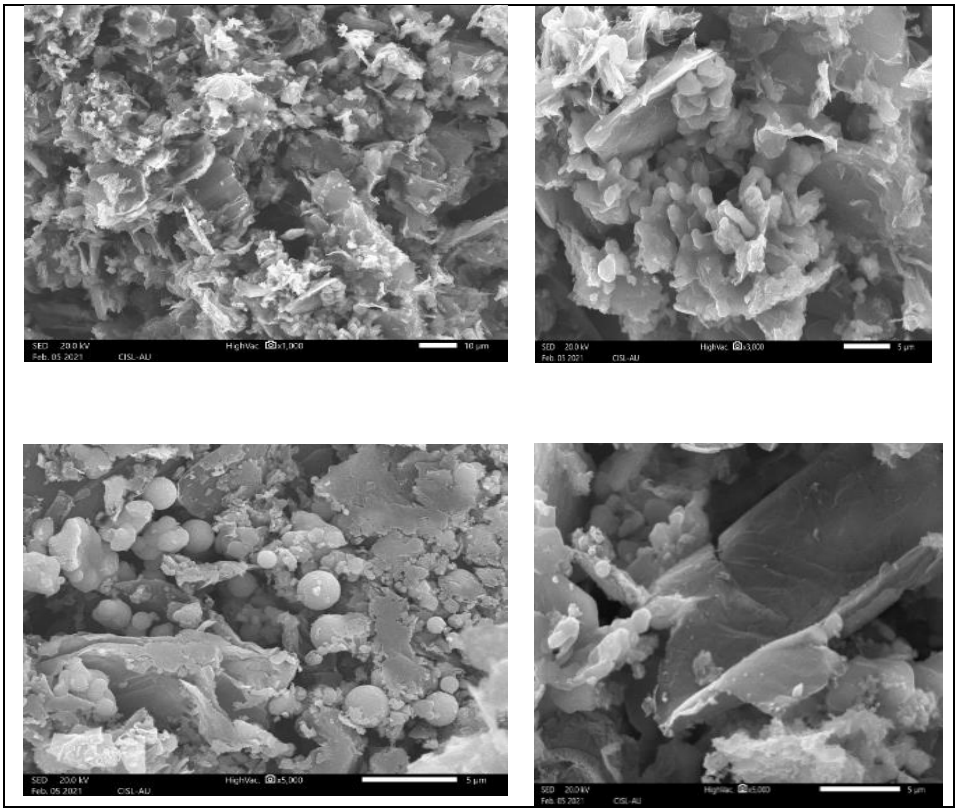


Figure 3.4: SEM analysis of GO and GO Composites Mn_3o_4 with a mass percent of 50:50

4. Conclusion

We have introduced a simple preparation and characterization studies of Mn_3O_4 nanoparticles graphene sheets composites in an efficient way. This work confirms the existence of functional oxygen groups it is confirmed that Mn_3O_4 nanoparticles are of tetragonal hausmannite crystalline structure by XRD patterens and the functinal groups were presenteded in the prepared sample were identified using FTIR analysis which range of 400-4000cm^{-1} the bond between 1711-2125cm^{-1}. SEM images show the surface morphology of prepared nanoparticle in the magnification of different micro meter SEM images are spherical shape and circular shape, agglomerated shape were found to be the range 20-50nm. The Raman spectrum is often used to characterize D, G peaks increase after the electrochemical reduction of GO, as well as a change in the position of the D and G peaks, therefore, the synthesized Mn_3O_4 nanoparticles graphene sheets composites exhibits many interesting and unique properties that can used in variety of application. Its futures application of supercapsitor battery studies the sample.

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