SYNTHESIS AND CHARACTERIZATION OF MnO_2/rGO NANOCOMPOSITE FOR SUPERCAPACITORS

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Abstract – *In this paper we present a general approach for the preparation of rGO/MnO_2 nanocomposite. The Graphene oxide is produced by Modified Hummer's method and it gets reduced to get rGO. The MnO_2 nanoparticles were prepared by drop-feeding method and these MnO_2 is mixed with rGO in order to form nanocomposite. Then the samples are characterized by UV, FTIR, XRD, SEM and Cyclic Voltammetry. XRD peaks reveal the particle size of the MnO_2 nanoparticles and rGO/MnO_2. U-V Spectroscopy spectrum shows the absorbance for MnO_2 nanoparticles. FTIR confirms the presence of respective functional groups. Then SEM images indicate structure for the prepared samples. From the CV curve specific capacitance is calculated & high capacitance value found to be 678 F/g value at san rate 5 mVs^{-1}.*

Key Words: **rGO, Modified Hummer's Method, Drop Feeding Method, Cyclic Voltammetry, Specific Capacitance…**

1.INTRODUCTION

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. There has been great interest in developing and refining more efficient energy storage devices. Supercapacitors have attracted growing interest, due to their high power density, long cycle life, and fast charging rate, which is playing an important role in complimenting or even replacing batteries in many applications [1]. Supercapacitors also known as electrochemical capacitors have been a subject to many applications, research and development due to its high power density, environmental friendliness, long shelf life, long life cycle [2,3,4] and it bridges the energy gap between capacitors (high power output) and fuel cells/batteries (high energy storage) [5,6].

The carbon materials (activated carbon, carbon nanotubes, (CNT) and reduced graphene oxide (rGO)), transition metal oxides (ruthenium dioxide (RuO_2), manganese dioxide (MnO_2), nickel oxide (NiO), cobalt oxide (Co_3O_4) have been recognized as the most promising materials for supercapacitors. Among the transition metal oxides,

MnO_2 has attracted more attention as a pseudocapacitor electrode material and has been widely studied due to its high theoretical capacitance (1370 Fg^{-1}), natural abundance, environmental compatibility and low cost. In order to improve the electrical conductivity of MnO_2 electrodes, the incorporation of highly conductive secondary materials to form hybrid compounds is being investigated. The principal use for MnO_2 is for dry-cell batteries, such as the alkaline battery and the zinc-carbon batteryMnO_2 is also used as a pigment and as a precursor to other manganese compounds, such as $KMnO_4$ and in Supercapacitors. Composite electrodes integrate carbon-based materials with either conducting polymer or metal oxide materials and incorporate both physical and chemical charge storage mechanisms together in a single electrode. Graphene oxide holds great potential to be coupled with $MnO_{2,}$ because it has high conductivity, good chemical stability, and a large surface area. MnO_2/rGO composite electrode material is prepared by using appropriate methods on the purpose of using it in supercapacitor applications for energy storage.

2. EXPERIMENTAL PROCEDURE

Materials used

Graphite powder, Sodium Nitrate ($NaNo_3$), Sulphuric acid (H_2SO_4), Hydrochloric acid (Hcl), Sodium Borohydride ($NaBH_4$), Manganese Acetate, Ethanol, Ethylene Glycol, $KMnO_4$ etc.,.

Experimental steps were done in four parts, which are the preparation of the graphene Oxide by Modified Hummer's Method, reduction of graphene Oxide by chemical method, preparation of MnO_2 nanoparticles by drop-feeding method and the preparation of MnO_2/rGO nanocomposite.

2.1 PREPARATION OF rGO

All the reagents used were of analytical grade and no further purification was done before use. Graphene Oxide is prepared by modified Hummer's method by using the materials given above [7]. Graphene is reduced using chemical reagent reduction method by using the strong reducing agent which is Sodium Borohydride. 0.5g of GO is added to DI water and ultrasonicated for 2 hours [8]. Yellowish brown color is obtained. Then the solution is kept in oil bath and heated upto 80^0 C after these 3 grams of Sodium Borohydride ($NaBH_4$) is added [9]. After vigorous stirring for 2 hours, the mixture is washed with DI water and ethanol. Finally it is dried in an oven at 60^0 C for 12 hours.

2.2 PREPARATION OF MnO_2 NANOPARTICLES

Manganese Oxide is prepared by using Drop-Feeding Method [10]. $KMnO_4$ (0.25 M) is added to 50 ml DI water and Manganese Acetate ($Mn(CH_3CO_2)_2$) (0.375 M) is also added to 50 ml of DI water both the solutions are stirred separately for 30 minutes. 10 ml of ethanol is added to $Mn(CH_3CO_2)_2$ solution [4]. To this $KMnO_4$ is added dropwise until the precipitate turns to black color. Then it is finally filtered and washed with ethanol and dried in oven at 110^0 C [11].

2.3 FORMATION OF MnO_2/rGO NANOCOMPOSITE

The MnO_2/rGO nanocomposite is formed by using the polymer ethylene glycol. 100 mg of MnO_2 is added to 20 ml of ethylene glycol and it ultrasonicated for 1 hour, a brownish black color is obtained. To this colloidal solution add 100 mg of rGO. Then the colloidal mixture is allowed to stir for 30 minutes and dried in oven at 60^0 C for 24 hours [12].

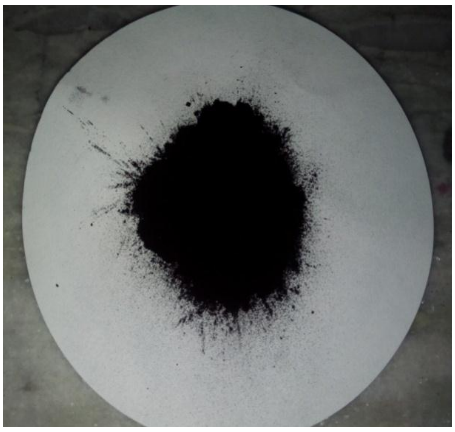


Fig-1: Prepared rGO/MnO_2 Composite

3. RESULTS & DISCUSSION

3.1 UV-VISIBLE SPECTRUM FOR MNO_2

The Fig 2 shows the optical absorption spectrum of bare MnO_2 nanoparticles prepared by drop feeding method. The spectrum shows a sharp peak at 335 nm [13]. The absorbance value is found to be 9 for the corresponding peak. By using this peak value band gap is calculated. The calculated band gap value for Manganese Oxide nanoparticles is 3.70 eV.

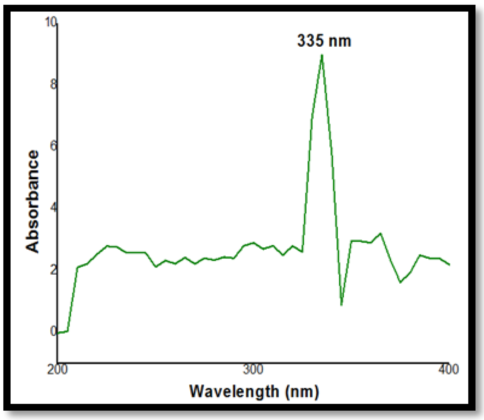
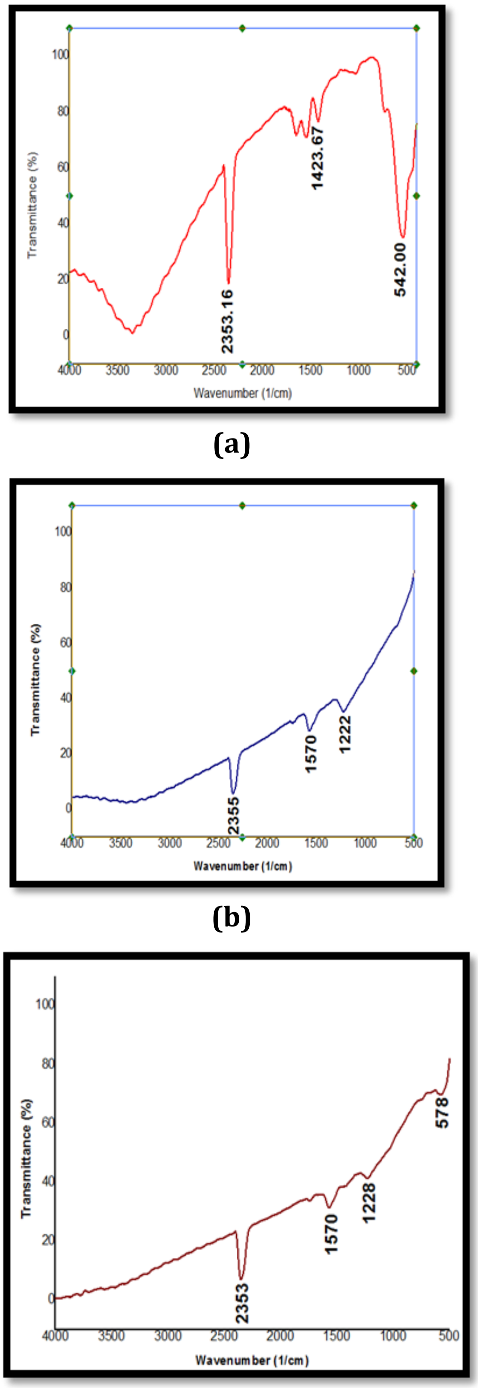


Fig-2: UV Spectrum for bare MnO_2 Nanoparticles

3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The FTIR spectrums for the as prepared samples are shown in Fig. 3(a),3(b),3(c), an absorption band is observed at 543 cm^{-1}[14] and it corresponds to the characteristic stretching collision of O–Mn–O, which demonstrated the presence of the MnO_2 in the sample. The band observed at 1423.67 cm^{-1} symbolizes the bending collision of adsorbed water molecule [17]. The typical broad absorption in the wavelength ranges between 3000 cm^{-1} and 2500 cm^{-1} are allocated for carboxylic O-H stretch. The next figure Shows the spectrum for rGO which indicates three wavenumbers 1222 cm^{-1}, 1570 cm^{-1}, 2355 cm^{-1}confirms the presence of many oxygen containing groups C-OH, C=O and O=C=O respectively [15,16].

The FTIR spectrum for rGO/MnO_2 nanocomposite is depicted in the last figure which denotes the peaks corresponding to the wavenumbers 2323cm^{-1}, 1570cm^{-1}, 1228cm^{-1}, 578cm^{-1} denoting the presence of functional groups such as O=C=O, C=O,C-OH, O-Mn-O respectively. These functional groups indicate the presence of both MnO_2 and rGO.



(a)

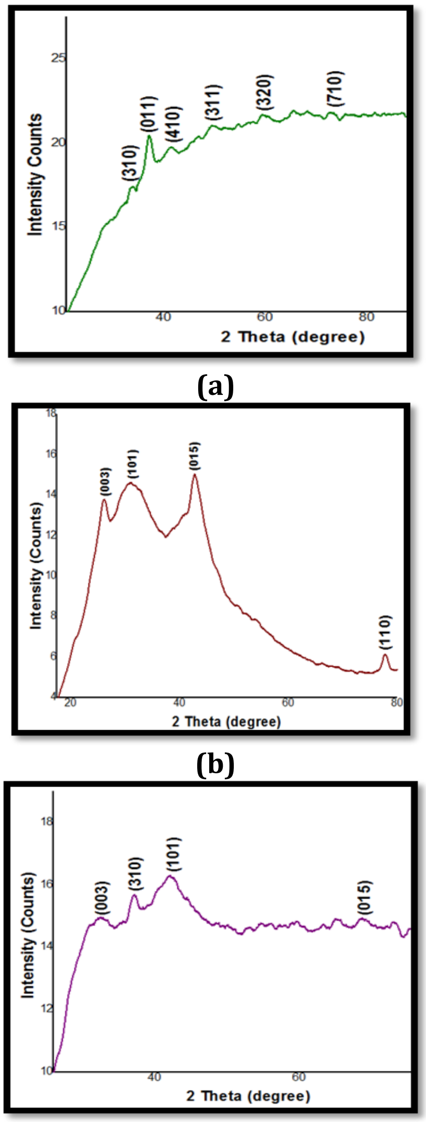
(b)

(C)

Fig -3: (a) FTIR spectra for MnO_2 (b) FTIR spectra for rGO (c) FTIR spectra for MnO_2/rGO Nanocomposite

3.3 X-RAY DIFFRACTION

The crystal Structures of MnO_2 and rGO are characterized by XRD. As can be seen in fig 4 all the diffraction peaks of the bare MnO_2 nanoparticles indicates the orthorhombic structure (JCPDS NO: 82.2169) with cell parameter a = 9.32, b = 4.45, c = 2.84. The good crystallization is proved by its reflection peak. The XRD pattern for rGO is depicted in the next figure four diffraction peaks at (003), (101), (015). (110) Corresponding to 2θ values 26.4^0,33.49^0, 42^0, 72.3^0 [7], the peak (003) confirms the successive reduction of graphene (rGO) from graphene oxide. The diffraction pattern depicted in the third figure exhibits no structural change and contains the combination of above two peaks at (310) and (003) confirmed the formation of MnO_2/rGO nanocomposite.



(a)

(b)

(c)

The particle size of MnO_2, rGO and MnO_2/rGO are calculated by using given XRD Data and the results of grain size are calculated using Debye scherrer's formula.

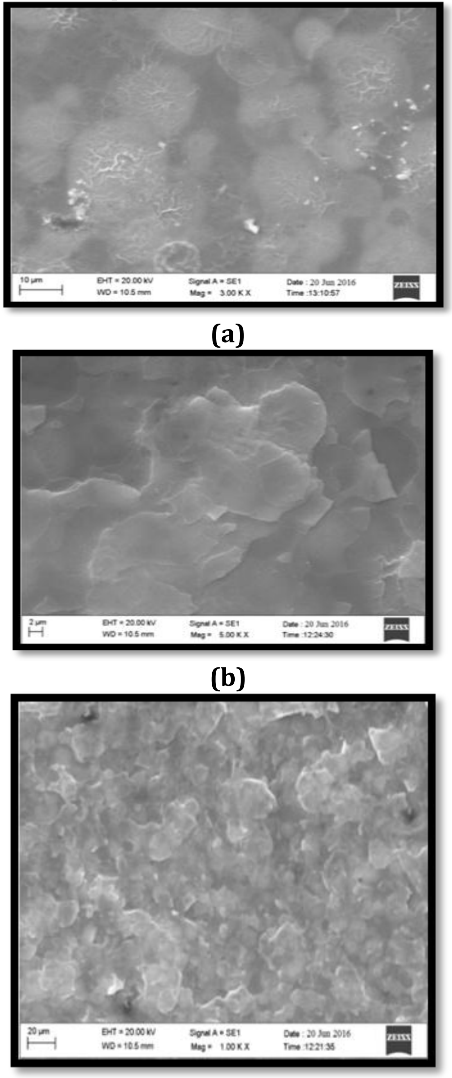
It is evident that the particle size is decreased from MnO_2 to rGO and it is further decreased for the prepared nanocomposite MnO_2/rGO.

Table -1: Particle Size for materials

Compound	Particle Size (nm)
MnO_2	9.32
rGO	7.20
MnO_2/rGO	3.12

3.4 MORPHOLOGICAL ANALYSIS (SEM)

The surface Morphological analysis for the prepared MnO_2, rGO and MnO_2/rGO nanocomposite was studied by using Scanning Electron Microscope. Fig 5(a) depicts the nanoparticles belong to the bare MnO_2 particles prepared by Drop-Feeding method is Spherical in shape. The next fig 5(b) shows the formation of flakes for reduced Graphene Oxide (rGO).fig 5(c) shows the combination of flakes (sheet like structure) and spheres indicating the collaboration of rGO and MnO_2nanocomposite.



(a)

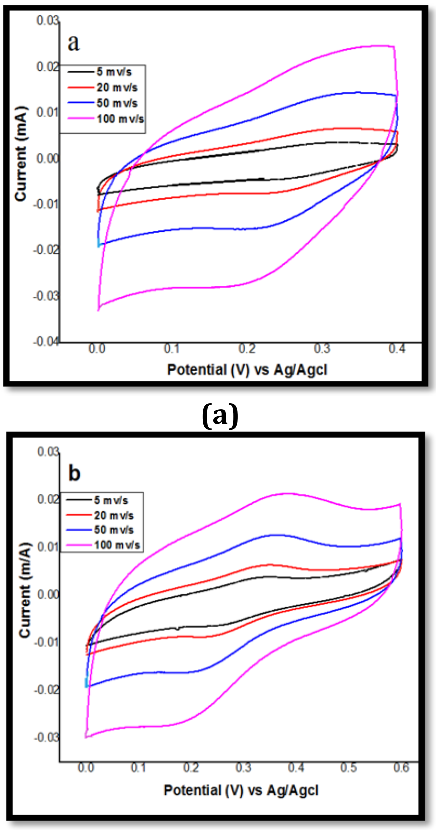
(b)

(C)

Fig-5: (a) SEM image for bare MnO_2, (b) SEM image for rGO, (c) SEM image forMnO_2/rGO

3.5 CYCLIC VOLTAMMETRY

The Cyclic Voltammetry characteristics curve for as prepared Manganese oxide (MnO_2) and reduced graphene-Manganese Oxide composite are shown in fig 6 (a) and 6 (b). It is evident from many reports that the electrochemical performances are increased by adding rGO to the pure MnO_2 nanoparticles (Any metal oxide). In this case 0.3 M of Sodium Sulphate (Na_2SO_4) is used as electrolyte at potential intervals from 5 mV to 100 mV. The setup consists of three electrodes Ag/Agcl as reference electrode, Platinum wire as counter electrode and Glassy Carbon electrode is used as working electrode. To this 0.1g of the respected sample that is our active material is immersed in the water to disperse it and in the working electrode a drop of the dispersed sample is coated and dried then the cyclic voltammetry for different scan rates are taken. The figures shows the CV curves over a voltage ranging from 0.0 to 0.4V vs. Ag/Agcl for MnO_2at a scan rate of 5 to 100 mV/s, and observed as the potential scan rate is increased, the CV for MnO_2shows quasi-rectangular shape indicating the good (ideal) capacitive behavior of the supercapacitor electrodes for MnO_2.The MnO_2/rGO nanocomposite shows a rectangular shape indicating the capacitance behavior after the addition of rGO to MnO_2.



(a)

(b)

Fig -6: (a) Cyclic Voltammetry Curve for Pure MnO_2, (b) Cyclic Voltammetry curve for MnO_2/rGO

3.6 SPECIFIC CAPACITANCE

Fig 7 provides graph for the calculated Specific capacitance against scan rate for MnO_2 and MnO_2/rGO composite electrodes. It can be seen that the specific capacitance decreasing with increasing scan rate from 5 to 100 mV/s. This may be due to the dependence of electrochemical performance on diffusion of electrolyte ions [18]. When the scan rate is high, the diffusion of electrolyte ions will be confined on the surface of the electrode. At low scan rate, the electrolyte ions are able to diffuse into deeper surface of the electrode and hence the Specific Capacitance values of MnO_2/rGO composite electrode are higher than the bare MnO_2 nanoparticles for all the scan rates and it is verified.

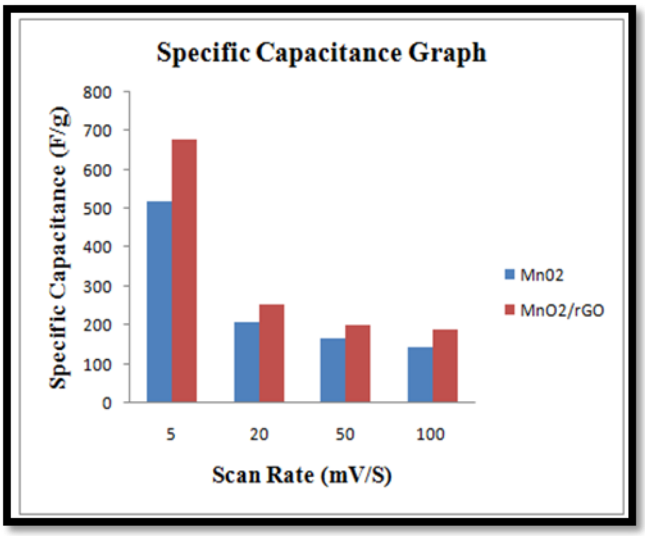


Fig- 7: Specific capacitance vs different scan rate of MnO_2 and MnO_2/rGO electrode materials.

The specific capacitance is calculated from the CV curve using the following formula [19]

$$C = \frac{\int ivdv}{2\mu m \Delta V}$$

Where C - Specific Capacitance, i and v are the current and potential that is area in the CV curve, μ is the scan rate (V/s), m is the mass of active materials (g), ΔV is the potential window of discharge (0.5V).

Table -2: Specific Capacitance Values for MnO_2 and MnO_2/rGO

S.no	Scan Rate (mV/S)	Specific capacitance (F/g)	
		MnO_2	**MnO_2/rGO**
1.	5	519	678
2.	20	209	255
3.	50	167	202
4.	100	144	188

The values are tabulated above and it is found that the highest capacitance value is found to be 678 (F/g) at a scan rate of 5 (mV/S)

4. CONCLUSIONS

The rGO/MnO_2 nanocomposite is formed by preparing MnO_2 and rGO separately and the result from all characterization revealed that this composite is well suitable for supercapacitor applications and especially Cyclic Voltammetry studies are taken to find the Specific capacitance value for the prepared samples it is found that an excellent capacitance is achieved by the MnO_2/rGO composite electrode material leads to a high capacitance value found to be 678 F/g value at san rate 5 mVs^{-1}Finally the composite prepared using this method is having high Capacitance. This material exhibits the promising potential candidate electrode material for future supercapacitor practical applications.

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