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Study and Development of RGO and RGO- MoS_2 QD Composite as Materials for Super Capacitors

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Abstract: In this work the synthesis was done for RGO and RGO- MoS_2 QD Composite by hydrothermal method. The incorporation of MoS_2 QD into the RGO layers enhances the capacitance by increasing the surface area. We got a maximum capacitance value of 290 F/g at 1 mV/s scan rate for RGO- MoS_2 QD Composite. We got a maximum capacitance value of 233 F/g at 1mV/s scan rate for RGO. The Composite gives lesser charge transfer resistance as inferred from EIS compared to RGO. This shows that the Composite is a better conductor compared to RGO and is thus a better material for making a super capacitor.

Keywords: Carbon nano fibres, Carbon nano tubes, Electrical double layer capacitors, Polyaniline.

I. INTRODUCTION

A. *Need for Supercapacitors*

Natural resources for generating energy like coal, petroleum and natural gas are depleting very fast due to growth of economies, human population and industries. These non-renewable sources of energy are not likely to sustain for long. Hence, it is important for scientists of the 21st century to work on methods that can help people to harness energy from the natural renewable sources of energy. Emphasis has to be laid on the fact that the materials or devices we develop should not pollute the environment. Besides making them efficient is a commercial compulsion. One major area of research for clean and green energy has been energy storage.

The devices we conventionally use to store energy are batteries and capacitors. However, in the recent years, a lot of work has been carried out on super capacitors because super capacitors have some advantages over batteries. Batteries have high energy density but low power density whereas supercapacitors have a relatively lower energy density and a relatively higher power density. Besides, to fulfil our needs based on energy and power requirements in some specific areas we can also make batteries and supercapacitors to work in conjunction.

B. *Classification of Super Capacitors*

Supercapacitors are basically of two types. They are Electrical Double Layer Capacitors (EDLC) and pseudo capacitors. In EDLCs energy is stored by absorption of ions where as in pseudo capacitors energy is stored due to the fast redox reactions that occur on the surface. EDLCs are also called as non-faradaic supercapacitors and pseudocapacitors are also called as faradaic supercapacitors based on whether or not these super capacitors obey Faraday's laws of electricity. Carbon based materials are more suitable for EDLCs while polymers and certain transition metal oxides are more suitable for pseudo capacitors. The differences in properties of pseudocapacitors and EDLCs are mainly due to the difference in mechanism of action. In EDLCs an agglomeration of charges occurs. EDLCs have high energy density, good cycling stability but low power density [1]. However, in pseudocapacitors an actual chemical reaction takes place. Ions or particles tend to accumulate on the surfaces of electrodes and this makes the cycling stability less [2]. Hence, it is important on our part that we make supercapacitors that can combine the best properties of EDLCs and pseudocapacitors without compromising on the negative characteristics of both such types of super capacitors. Such super capacitors are hence called hybrid super capacitors.

C. *Faradaic and Non Faradaic Processes*

Faradaic super capacitors or pseudo capacitors operate by the mechanism of an actual redox reaction that occurs at the electrode surface unlike the non-faradaic super capacitors (EDLCs) which simply store charge because of accumulation of opposite charges that attract each other. Mainly, the transition metal oxides like RuO_2, Co_3O_4, and MnO_2 when used with conducting polymers undergo redox reactions and are considered ideal materials for the purpose of making a faradaic super capacitor. What we mean from a faradaic process is that charge actually penetrates the electrical double layer and passes on during the processes of charging and discharging on the application of a potential. There are a few types of faradaic processes. Some of them include reversible adsorption, redox reactions of transition metal oxides as mentioned above and reversible electrochemical doping in conductive polymer based electrodes. An example of the first kind would be adsorption of hydrogen on the surfaces of silver, platinum or gold. In case of these faradaic processes the electrochemical activity occurs both on the surface and bulk. But in an EDLC, the electrochemical activity occurs only at the surface. This is why the capacity of non faradaic super capacitors is less than that of faradaic supercapacitors. But since faradaic processes are slow to occur, the power output of faradaic supercapacitors are less than that of non faradaic super capacitors.

D. Materials Used for Supercapacitors

Till now many materials have been developed so that they could be used in a supercapacitor. Generally carbon based materials like Carbon Nano Tubes (CNT), Carbon Nano Fibres (CNF), porous carbon nanomaterial, graphene behave as perfect materials for EDLCs. It has been observed that among these materials graphene is the best.

Graphene is one among the hardest materials on Earth. Hence, it has a high degree of mechanical strength. It is very sensitive owing to its very high ratio of surface area to volume. Multilayered materials and single layered materials show different conductivities. It is isolable into a single layer [3], thus generating many more favourable unique properties from the point of view of electronics. The single layer of graphene exists because of aromaticity. Because of large surface area, it can be used to hold more charge and thus the device can have more capacitance. Besides it is eco-friendly. Recently research has focused on devising flexible materials.

Some transition metal oxides like RuO_2, Co_3O_4, and MnO_2 are used as pseudocapacitive electrode materials for super capacitors. Transition metal sulphides and hydroxides also show similar properties. Conducting materials like Polyaniline (PANI), Polypyrrole and PEDOT-PSS have been developed for use in pseudo capacitors. Recent research on this area has focused on transition metal dichalcogenides like MoS_2, VS_2, WS_2, NbS_2 etc. These conducting materials are graphene like layered materials having high surface area. Transition metals are characterised by variable oxidation states. Presence of variable oxidation states enables them to undergo a large variety of redox reactions.

In this work we have synthesised Graphene Oxide (GO) from graphite by modified Hummer's method [4]. The synthesised GO was subjected to reduction by acid to yield Reduced Graphene Oxide (RGO). Simultaneously we treated the developed GO with MoS_2 Quantum Dots (QD) and then reduced it with acid to make RGO- MoS_2 QD Composite. As the RGO sheets are stacked by Vander Waal's forces, to get exfoliated RGO sheets we developed RGO- MoS_2 QD Composite. Quantum dots are very small semiconductor particles only several nanometres in size. Their optical and electronic properties differ from that of large particles. Quantum dots exhibit properties that are intermediate to bulk semiconductors and discrete molecules. Another interesting property is size dependent fluorescence. In recent past a lot of work has been carried out to use quantum dots in enhancing the performance of super capacitors. Quantum dots [5] are used as a spacing agent between the successive layers of the graphene allowing for more surface area to be exposed for retaining charge. Conventionally carbon quantum dots which show EDLC like behaviour were used for the purpose. But in our quest to devise hybrid super capacitors we have used Molybdenum sulphide (MoS_2) quantum dots. MoS_2 quantum dots show both EDLC and pseudo capacitive behaviour. The electrochemical performance of the synthesised Composite material was studied. We use Cyclic Voltammetry to evaluate capacitance and here is an example of a plot.

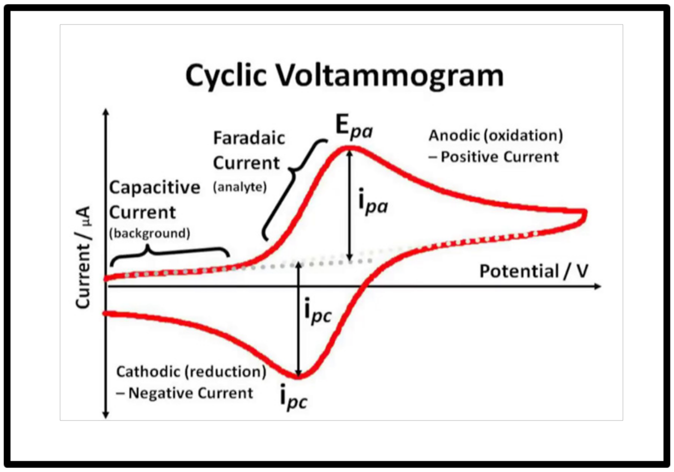

Fig. 1: A General Cyclic Voltammetry Curve

II. EXPERIMENTS

A. Synthesis of GO

The synthesis of Graphene Oxide (GO) was carried out by modified Hummer's method. 25 ml of concentrated H_2SO_4 was taken in a 250 ml conical flask and 1 g of graphite powder was added to it. The mixture is shaken well whilst being stirred in an ice bath. 7 g of $KMnO_4$ crystal was added to it. The mixture was cooled in an ice bath after stirring in room temperature for 2 hours. 100 ml of distilled water was added to it. 30% H_2O_2 was added until evolution of gas was seen. The mixture was then filtered and washed in dilute HCl followed by water. After washing the precipitate was dried and kept for future use. Graphene Oxide flakes were obtained.

B. Synthesis of RGO

First 1 mg/ml of GO was taken in 40ml of distilled water. Then it was sonicated properly for 45 minutes to ensure proper dispersion. To this solution 1ml of 55% (w/v) HI was added and it was followed by sonication for an additional 15 minutes. The mixture was taken into a quartz autoclave and heated at 100 degrees Celsius for 12 hours. After reduction the precipitate was washed properly with distilled water followed by methanol. After proper washing it was dried in vacuum oven in 80 degrees

Celsius. The Reduced Graphene Oxide (RGO) was procured and kept for future use.

C. Synthesis of MoS_2 QD

15 mg of Ammonium-Tetrathiomolybdate $(NH_4)_2MoS_4$ was taken in 60 ml of distilled water and sonicated for several minutes for proper dispersion. 1.5 ml of Hydrazine-hydrate was added to it and it was hence as a reducing agent. The mixture was sonicated for another 30 minutes after Hydrazine-hydrate was added. After the completion of ultrasonication, the mixture was transferred to a stainless steel autoclave of volume 100 ml. Then it was hydrothermally treated at 200 degrees Celsius for 24 hours. The Molybdenum disulphide Quantum Dot (QD) solution was stored for prior use.

$$(NH_4)_2MoS_4 + N_2H_4 \rightarrow MoS_2 + (NH_4)_2S + N_2 + 2H_2S$$

D. Synthesis of RGO- MoS_2 QD Composite

For the preparation of RGO- MoS_2 QD Composite, 40 mg of GO was taken in 40 ml of MoS_2 quantum dot solution. It was then sonicated for 45 minutes. The solution was continuously stirred for 12 hours. After that 1 ml of 55% (w/v) HI was added to the above solution and it was taken in 50 ml of quartz autoclave and heated at 100 degree Celsius for 12 hours. After reduction, the precipitate was washed properly with distilled water repeatedly followed by methanol. Then it was dried at 80 degree Celsius and the RGO- MoS_2 QD Composite was procured for future use.

E. Fabrication of Device

For the electrochemical performance testing, a symmetric two electrode setup has been designed by using two stainless steel electrode and a separator. For the electrode material preparation the equivalent quantities of materials were taken in two vials and the slurry was prepared in 100 µl of ethanol and then it was dispersed properly. Then the material was drop casted on the corresponding stainless steel electrodes and was left till it dried up. A fresh solution of 1 M Na_2SO_4 was prepared. Then a separator was dipped in the freshly prepared 1 M Na_2SO_4. Then separator was sandwiched in between the two electrodes and put into the 'SWAGELOK' system.

III. RESULT ANALYSIS AND OBSERVATIONS

A. UV Absorbance Spectroscopy

UV spectroscopy [6] refers to the absorption spectroscopy or the reflectance spectroscopy in the Ultra Violet region. From the UV absorbance spectroscopy we got the following results. We took the UV Absorbance spectroscopy of GO and RGO.

UV Visible spectra of GO and RGO are shown in Fig. 2 (A) and (B). In case of GO two kinds of characteristic peaks were observed in these spectra to identify GO. The peak at 303 nm is due to n → π* transition of (C=O) double bond. The other peak appeared at 243 nm due to π→π* transition (C=C) double bond.

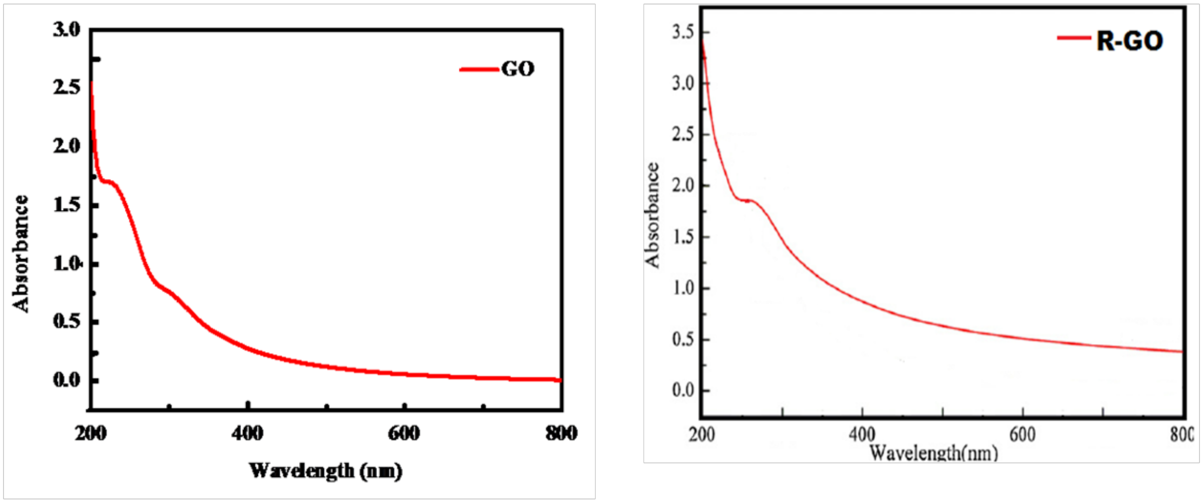

Fig. 2: UV Absorbance Spectroscopy Results of (A) GO and (B) RGO

B. IR Spectroscopy

Infra Red Spectroscopy [7] is the study of interaction of Infra Red radiation with matter. It covers a range of techniques mostly based on absorption spectroscopy. IR spectroscopy is based on the fact that molecules absorb frequencies that are characteristic of their structure. These absorptions occur when the frequency of the absorbed radiation matches the vibrational frequency. Such frequencies are called resonant frequencies. In our experiment we have confined our measurements in the middle energy region i.e. the region where the range of wavelengths is in between 4000 cm^{-1} and 400 cm^{-1}. We had taken the IR spectroscopic data for GO, RGO and RGO- MoS_2 QD Composite. For the case of GO, a broad peak was observed at wave numbers in the range 3000-3600 cm^{-1}. This suggests the presence of OH groups which might be present as the alcoholic functional group (C-OH), carboxyl group (COOH) or water. A sharp peak was observed at 1648 cm^{-1} which indicates the presence of C=C double bonds as in an alkene. A minor peak continues the peak at 1648 cm^{-1} to stretch to around 1750 cm^{-1} suggesting the presence of (C=O) double bond. A sharp peak was observed at 1425 cm^{-1} which implies the stretching of aromatic (C=C) double bonds. Another broad peak was observed at 1156 cm^{-1} and this might be due to the presence of (=CH-H) group. No such peaks were observed in RGO or the Composite as all the oxygen containing organic groups got reduced by the acid.

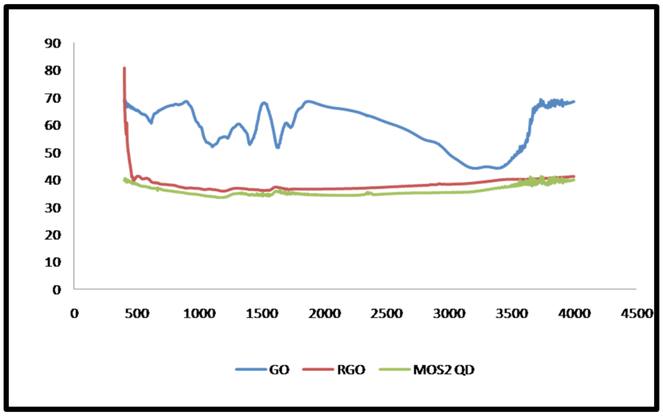

Fig. 3: FTIR Spectra of GO, RGO and RGO- MoS_2 QD Composite

C. *Cyclic Voltammetry Results*

From the data obtained in the cyclic voltammetry experiment capacitance ‘C’ can be obtained as the ratio between area of the curve ‘A’ upon the Potential window taken ‘V’ times the scan rate ‘S’. Further specific capacitance ‘C_S’ can be calculated as capacitance obtained ‘C’ upon the mass of the sample ‘M’. To study the electrochemical performance of as synthesised electrode materials, the Cyclic Voltammetry (CV) technique was executed in symmetric two electrode system. The CV performance of RGO and RGO- MoS_2 QD composite is shown in Fig. 4 (A) and (B). From the cyclic voltammetry data, RGO gives specific capacitance value of 233, 201, 162, 120, 107, 74, 50, 33, 29 and 17 F/g for scan rates of 1, 2, 4, 8, 10, 20, 40, 80, 100 and 200 mV/s respectively. Further the CV results of RGO- MoS_2 QD Composite was carried out under similar conditions. The specific capacitance values are 290, 263, 226, 176, 162, 125, 93, 63, 56 and 37 F/g for scan rates of 1, 2, 4, 8, 10, 20, 40, 80, 100 and 200 mV/s respectively. The overlapped CV curve at RGO- MoS_2 QD Composite and RGO electrode at 20 mV/s scan rate is shown in Fig. 5 (A) and (B). From the CV curve, it was observed that the area under the RGO- MoS_2 QD Composite is more than the bare RGO electrode. Hence, the Composite electrode more specific capacitance value than RGO. It is because the Quantum Dots in the Composite are sandwiched in between the layers of RGO. This exposes more surface area and the capacitance value gets enhanced. The Overlapped CD curve of RGO and RGO- MoS_2 QD composite is shown in Fig. 5 (B). From the CD data, we get specific capacitance of RGO 100F/g and RGO- MoS_2 QD composite gives 166F/g. The Fig. 6 gives information regarding the specific capacitance versus scan rate. For a sample of fixed mass it has been observed that the value of capacitance goes on decreasing as the scan rate increases. This is because of insufficient ion diffusion within a small time interval. Because of the fact that the number of ions that diffused are insufficient, opposite charges do not agglomerate easily and hence capacitance decreases. It is to observed that even though at high scan rates the area under the I ~ V curve decreases, the magnitude of the scan rate is sufficiently high so that the net result is seen as a decrease in capacitance.

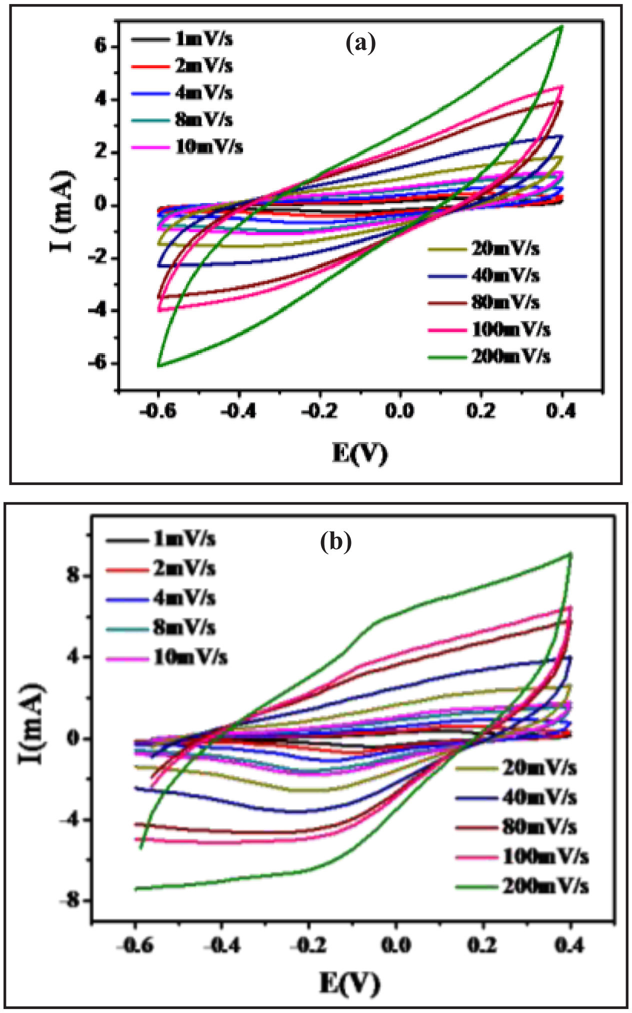

Fig. 4: CV Curve of (A) RGO & (B) RGO- MoS_2 QD Electrode in 1M Na_2SO_4 at 1V Potential Window

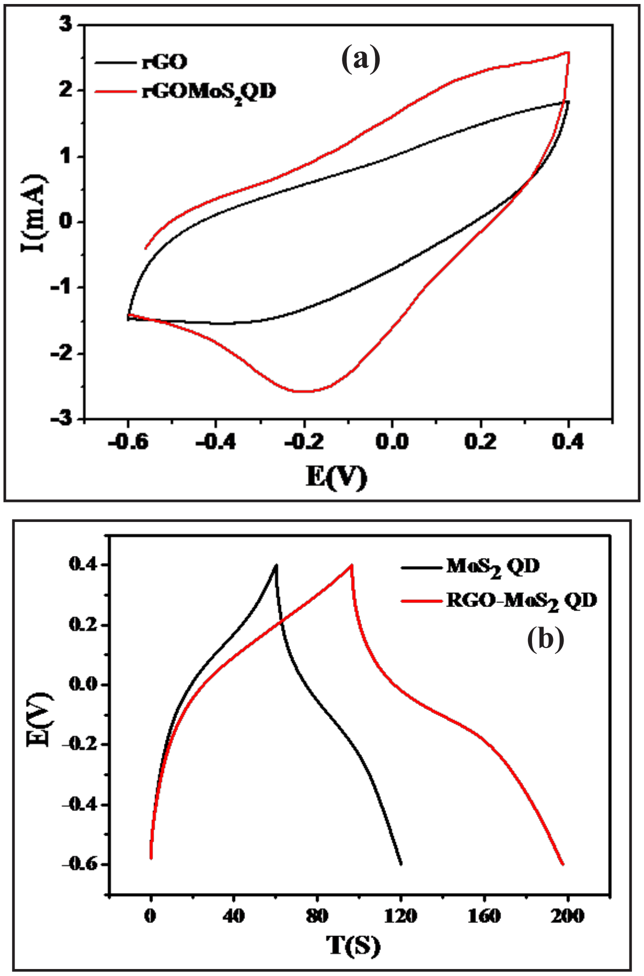

Fig. 5: (A) Overlapped CV Curve at 20 mV/s Scan Rate and (B) Overlapped Charging Time Discharging Time Curve of RGO & RGO- MoS_2 QD at 1A/g Current Density

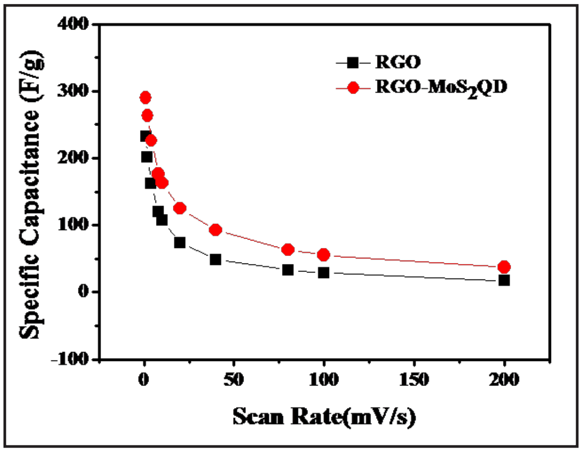

Fig. 6: Plot of Specific Capacitance Versus Scan Rate

D. *Impedance Spectroscopy Results*

Impedance spectroscopy [8] is a method used to evaluate the specific capacitance of the material. We used the Nyquist plot to represent the data. We have plotted the imaginary component of impedance against the real component of impedance under the variation of a parameter of angular frequency ‘ω’. The physical understanding of the above circuit diagram is that the capacitor of capacitance ‘C’ is connected to an AC source of peak voltage of E_0 with an internal charge transfer resistance in parallel and a solution resistance R_s in series. Charge transfer resistance ‘R’ is thought to be in series with the capacitance as the both the phenomenon occur in the double layer and the voltage is common. The solution resistance R_s is thought to be in series with these components as the current is common. The capacitive reactance of the capacitor is X_C.

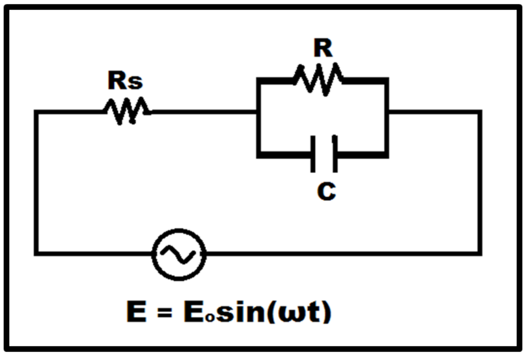

Fig. 7: A Circuit Diagram Giving a Representation of the Physical Case

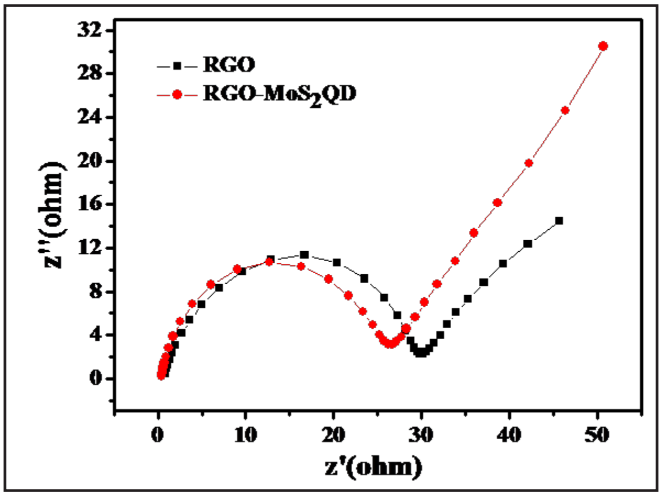

Fig. 8: Nyquist Plot for Impedance Spectroscopy ($y = z''$, $x = z'$)

In order to understand the electrical conductivity and ion transfer resistance of the supercapacitor test cell, the electrochemical impedance spectra was carried out at 0.1-100 Hz frequency range with an AC perturbation of 5 mV which is shown in Fig. 8. The curve fit of the plot between the imaginary part and real part of the Nyquist plot was found by extrapolating the circular portion of the plot.

The charge transfer resistance value of RGO was found to be 27.34 Ω whereas RGO- MoS_2 QD Composite has a charge transfer resistance of 24.00 Ω. The resistance of the solution was found to be 0.88 Ω for RGO and 0.41 Ω for RGO- MoS_2 Composite. Thus the solution resistance is observed to very less compared to the charge transfer resistance in both the cases.

IV. CONCLUSION

We have successfully synthesised RGO and RGO- MoS_2 QD Composite by hydrothermal method. The incorporation of MoS_2 QD into the RGO layers enhances the capacitance by increasing the surface area. We got a maximum capacitance value of 290 F/g at 1 mV/s scan rate for RGO- MoS_2 QD Composite. We got a maximum capacitance value of 233 F/g at 1mV/s scan rate for RGO. The Composite gives lesser charge transfer resistance as inferred from EIS compared to RGO. This shows that the Composite is a better conductor compared to RGO and is thus a better material for making a super capacitor.

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