Metal oxide Graphene Composites as advanced Energy Storage and Conversion Materials.

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DEPARTMENT OF PHYSICS

FACULTY OF BASIC AND APPLIED SCIENCES

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Final Approval

It is certified that the work presented in the thesis entitled **"Metal oxide Graphene Composites as advanced Energy Storage and Conversion Materials** "by Tariq Nawaz bearing **Registration No. 125-FBAS/MSPHY/F12** is of sufficient standard in scope and quality for award of degree of MS Physics from International Islamic University, Islamabad.

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As a partial fulfillment for the award of the degree of

MS Physics

Declaration

It is certified that work contained in this thesis titled "Metal oxide graphene composites as advance energy storage and conversion materials" is carried out by Tariq Nawaz Reg# 125 FBAS/MSPHY/F12 under my supervision at the Department of Physics, International Islamic University, and Islamabad, Pakistan.

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To

AMMA-G-GULL

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BABA-G-GULL

Acknowledgements

Survival of the fittest , interdependence of the economies , development of the countries ,needs of the world and many other slogans and parameters have taken the quantum leap during the last 2 decayed or so. The futuristic initiatives and approaches of the development keep.oneself to be in an active mode all the time. The case leads us to some job oriented and task oriented goals in our life. Every human being is a horrible story in itself. Some people are deceived by the circumstances; some meet the total loss while some retrieve its dwindling power, scattered ideas in the reutilization by facing all sort of the music. The last case may be taken as mine. My dwindling power to fight against all the bitter realities were innovated once gain by the ALMIGHTY ALLAH and made be able to carry on this contribution for my personality and intellectual development. I have no suitable words to thank THE ALMIGHTY ALLAH for the blessings.

Though my great father **Mohammad Nawaz** paid the debt of nature in 2007 but in real sense he was the main pillar and source of motivation. I am speechless while thanking him .May he be in peace. My mother **Pirzadi Safi un Nisa** and my brothers **PSP Zahid Nawaz Marwat** ,**Tahir Nawaz Marwat** and my sister **Advocate (HC) Mussarat** were the key players for motivating me for the futuristic goal which I achieved in shape of the this report. Regards and thanks to all of them.

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Tariq Nawaz Marwat

Table of Contents

Abstract

The present scenario for the production of the energy resources especially new energy materials have been the priority of the researchers. Metal oxide especially with the zero band energy materials i.e. graphene were synthesized hydrothermally and solovthermaly in controlled conditions. MoO3 nanoparticles along with GO were prepared. The composites were deposited over ITO to fabricated electrodes for Photo electro chemical cell, Li ion batteries and Super capacitors. XRD , UV,DRS,SEM ,EDX results showed promising results that lead us to get the linear sweep Voltametry and cyclic Voltametry to check CURRENT –BIAS response and charge transportation potentials of the prepared electrodes. It was observed that in the absence of light source, current in µA was noticed. While in the presence of light source the current in m.A was observed. Compared to around 300 micro ampere currents, the composite photo anodes registered photocurrents up to 1.9mA. The photo current responses showed the well fabrication of the electrodes to be used for energy storage and conversion materials.

Chapter One Introduction

The tale of two centuries reminds us the journey of the research and development in the globe. It was the 20th century that faced the horrible devastation of science in the form of world wars and nuclear arms race. Now it is the 21st century that has been reshaped by the science and research towards the new visions and innovations for the benefit of the mankind. More energy is the cry of the day and a new world order. The economies of the world have become dependent upon the energy resources. United Nations through its millennium development goals urges the nations to produce clean truly renewable and cheap energy resources. These must be in accordance with the need of environment as well. In this back drop the R&D throughout the world is now been focused on new materials for the production of soft energy like hydrogen as future fuel. This development leads us to the concept of energy storage and conversion materials that may be helpful to utilize the natural resource of energy like SUN.

1.1 Energy storage and conversion materials.

The recent developments in the field of research and development has made the energy storage and conversion devices and material as the main focus of concern. It includes the Li ion batteries, super capacitors and Photo electrodes etc.

1.2.1 Li ion Batteries

With the increasing global demand for energy technology, Li ion batteries are one of the most promising candidates in the list of energy storage devices. Since 2010 the demand for Li ion batteries has tremendously been increased. The Li metal and intercalation positive electrodes like TiS2 developed the Li ion batteries. The primary parts that a Li ion batteries have positive electrodes, the negative electrodes and the third is the electrolyte used in the proper construction of Li ion batteries[1]. The efficiency of Li ion batteries is dependent upon the cathode materials. For a perfect battery, the cathode efficiency must be upgraded[2].Materials like Lithium, nickel oxide, cobalt oxide and titanium sulphide have been used in the manufacturing of Li ion batteries with commendable efficiencies[2]. Li ion batteries have many uses multidimensional especially in business and energy sectors. A serious concern about the safety of the Li ion batteries is due to its flammable liquids electrolytes. This factor effect the durability and reliability of the Li ion batteries[3]. Figure 1.1 shows s a typical Li ion battery.

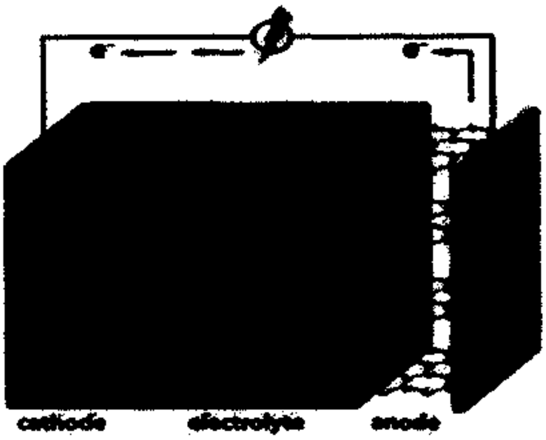

Figure 1.1 Li ion batteries diagram.

Electrons are produced with the migration of Li ion from anode materials to cathode[4]. Due to the high energy density and its light weight have made the Li ion batteries an eye opener for the future research in the field of materials sciences[5] .

1.2.2. Super Capacitors.

Along with the use of Li ion batteries the super capacitors are also the promising candidate for the purpose of energy storage and conversion. Super capacitors or electro thermal capacitors are the major source for their application in the electronic devices and grids[6]. These super capacitors have gained a considerable attention of the researchers and technologists in comparison to Li ion batteries due to its prominent features of power density ,long life span and charging capacity[7]. The storage principal of the super capacitors is dependent upon double layer effect. Electrochemical capacitor comprises two electrodes connected by electrolyte which may be the mixture of ions (positive &negative) in a solvent. These capacitors are designed inform of metal foils coated with activated carbon. The most important feature of the super capacitors is its use in the hybrid vehicles and devices for the storage of energy with a considerable efficiency.

Figure 1.2 shows the schematic process in a super capacitor.

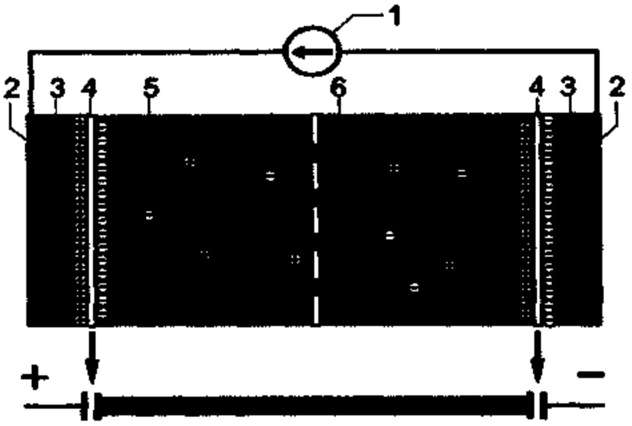

Figure 1.2 super capacitors

1.Powersource 2.collector 3.electrodes 4.doublelayers 5.electrolyte 6.separator[8]. Nowadays super capacitors are fabricated by using Graphene nanoparticles to enhance their efficiency. It improve the surface area and charge transportation[9].

1.2.3 Photo electrodes.

Photo electrodes are used in PEC/ PV cells for the conversion of energy. These electrodes are made up of semiconductors in a specific combination. Like in PEC cells photo anodes and photo cathodes (n-type-type combinations) are used for photo catalytic /photo electrochemical activities These PEC cells are the solar cells used as energy conversion devices/material. These cells do electrolysis of water to produce hydrogen and oxygen. It has been termed as an artificial photosynthesis[10] and has been referred as a way to store solar energy in hydrogen as a future fuel. This PEC cell has been suggested the promising candidate for the production of truly renewable energy. In fact the main role in the assembly of PEC cell is played by the semiconductor material that converts photons into electrons hole pairs.

1.3 Photo Electro Chemical Cell.

In Photo voltaic i.e. (conversion of sun light to electrical energy) the solid state devices were thoroughly used. These devices were usually made up of silicon. Due to the advent of modern new generation PV cells based on Nano sized materials gave new ideas and innovation to the PEC cells. It has become an alternate materials for the already used solid state devices[11].

A general kind of a photo cells device is based upon the semiconductor materials. It will be in contact to an electrolyte .This assembly is termed as Photo electro chemical cell[12]. A PEC cell is comprised of semiconductor working electrodes that may be n-type or p-type. Counter electrodes is also made up of metal or semiconductor. The electrodes are in contact due to an electrolyte between them. The electric field present in the semiconductor tries to separate electron and holes[13]. A photo electro chemical cell can produce not only electrical energy but also it can give electro chemical energy as well. This also provides a platform for the system of energy storage components[14]

1.3.1 Principal of PEC cell.

The operational principal of PEC cell is based on n-type semiconductors and regenerative cell to produce electric current from the sun light [11]. While having a general principled view of a PEC cell the combination for the electrodes may be followed as,

- Photo anode –n-type semiconductor ,cathode –metallic
- .photo anode n-type semiconductor. Cathode-p-type SC
- Photo anode –metallic, cathode-p-type semiconductor.

Figure 1.3 is the illustration of PEC cell along with energy diagram.

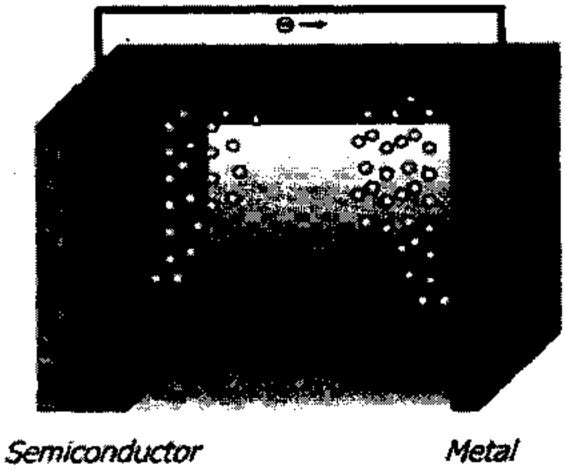

Fig1.3 PEC cell.

1.3.2 Application of PEC cells

I. **Photo catalysis.** To accelerate a photoreaction is termed as photo catalysis. Photo catalysis involves the light absorption on the substrate. The activity of photo catalysis is dependent upon the quality of catalyst to lead the production of electron hole pair. The advent of water electrolysis by titanium oxide made the practical application of photolysis possible. The result is homogeneous and heterogeneous photo catalysis.

II. **Water Splitting.**

PEC is used to produce hydrogen gas as a fuel. It utilizes light energy i.e. photons to perform reaction. In the result of water splitting H_2 and O_2 are evolved

It was in 1972 when the TiO_2 electrodes based water splitting activity was performed. It was the start of a new chapter in photo catalysis and a working application of PEC cell[15]. The details are given in under the next heading.

1.4 Photo Electro Chemical Water Splitting.

The use of a proper catalyst and sun light leads us to the production of hydrogen gas. In other words water splits in to H_2 &O_2. The obtained hydrogen gas from the reaction is termed as a future fuel that may be reliable, sustainable, durable and eco-friendly as well. In this regard the photo catalytic water splitting has gained a considerable attention for the production of future energy[16]. The intense need for the technology of water splitting is to find out a semiconductor exactly suitable and needed for the process of water splitting. The well known Fujushima and Honda at the primary stages used TiO_2 as semiconductor for the production of hydrogen through water splitting[17]. The analytical approach of the process of water splitting gives the idea of natural photo synthesis in plants. But in the technology of water splitting, the semiconductor materials and its crystallinity and the size of particle matters a lot[18]. To achieve high efficiency water splitting, lot of semiconductor materials have been studied and explored.

1.4.1 Principal of water splitting.

Photo catalytic water splitting for the production of H_2O_2 is based on the particles of semiconductor that has three step principal to carry on the

I. Absorption of photon –the photon energy should exceed the band energy of the semiconductor. It will proceed with the generation of electron holes pairs.

II. Separation of charges and transfer of carrier particles.

III. Chemical reaction on the surface (carriers and compounds likes H_2O).

Another possibility is that the electron and holes can recombine without chemical reaction[19]. Figure 1.4 shows the photo catalytic water splitting for the production of H_2 and O_2.

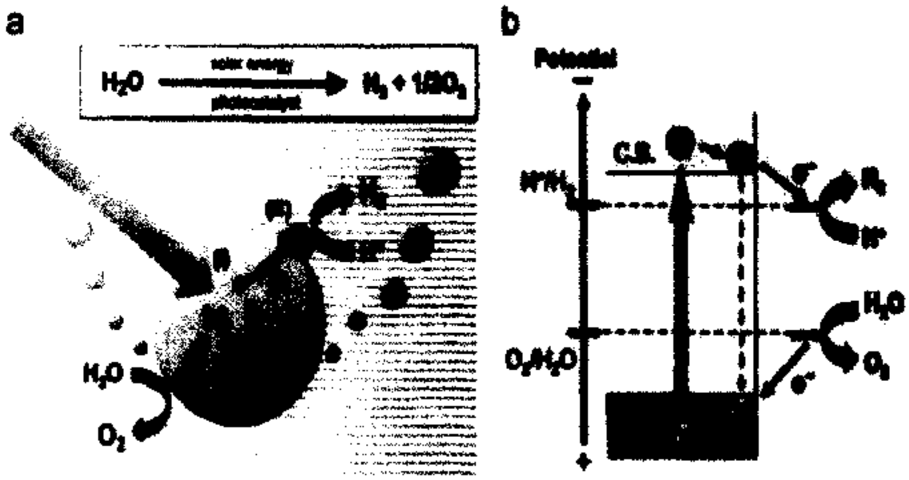

Fig 1.4 schematic presentation of water splitting.

It has been observed that solar water splitting depends upon the band width of the semiconductors. For the ideal water splitting the minimum required band gap energy must be 1.23 eV. But in practice photon should have more energy than the prescribed theoretical limits. The reason is the loss of energy during the reaction of water splitting. The energy losses may be due to the recombination of charge carriers. Loss of voltage and loss of potential due to the resistance of electrodes[20]. For the process of water splitting the efficiency matters a lot. So far the benchmarking efficiency has been reported up to 10%. This efficiency is required for the commercialization of the technology. The literature reveals that mostly the efficiency values have been calculated under the operation of artificial sun light. By using UV source 4% of photo conversion efficiency was measured for TiO_2 electrodes. Another experiment shows that under the mercury light and TiO_2 dopes with Pt an efficiency of 2.7% was obtained[21]. Another efficiency of 1.9% was achieved by Radecka by using xenon lamp. Mishra used mercury-xenon lamp and got 3% for the TiO2 electrodes. It showed that artificial sources have been used for the water splitting in most cases. It has been considered convenient to use artificial source for different reasons. Artificial sources are stable and stationary with constant intensity with respect to time.

1.4.2 Basis for Photo Electro Chemical Water Splitting.

As has been described earlier that water splitting is compared to the artificial photosynthesis, Gibbs free energy is involved here. It converts photon into the chemical energy that leads the process of water splitting[22]

$$H_2O \longrightarrow \tfrac{1}{2} O_2 + H_2 \quad \text{..............................(1.1)}$$

1.5 Hydrogen -----------A Soft Future Fuel

Hydrogen is not known as a primary source of energy like coal, gas and oil. It is considered as an energy carrier. A really versatile fuel that is predicted to be a truly renewable source of energy to cope up with our needs of the energy. To convert the hydrogen in to other sources, fuel cell are designed. But the most important feature of hydrogen is that it doesn't remains in free state naturally[23]. The hydrogen gas is synthesized by the photolysis. Cracking of methane and hydrocarbon etc. It has been explored that hydrogen has comparatively low heating values than methane, gasoline etc[24]. Viewing from different angles, it can be find that hydrogen can be used as fuel in vehicles and automobiles in future[25]. Another advantage of using hydrogen is that the vehicles will exhaust zero carbon emission of gases. The commercialization of the technology to produce hydrogen will lead the globe towards the green economy.

One of the most important features of hydrogen is that it differs from many other material and gases as well.

Hydrogen is comparatively safe and non poisonous. Due to low solubility in water it has low hazardous effects on the ground water[26]. Due to its non pollutant nature it has no role in water pollution[27]. In spite of having a lot of benefits of hydrogen there is still a challenge regarding its cost effectiveness.

1.6 Nano Materials for PEC cells

The advent of Nano technology in the running century has made a classic route towards the wonderful materials i.e. the Nano materials. The development of these nanostructures/ Nano materials leads the research and technology towards the refined ideas of the conversion of energy and the proper utilization of truly renewable energy sources[28]. Since the reported activity of Honda and Fujishima many Nano sized materials have been tested as Nano materials for PEC. The successful activity of the solar based water splitting of the Fujishima used TiO_2 anode and cathode was of the Pt for the efficient production of oxygen and hydrogen.TiO_2 has been considered the suitable material for PEC water splitting [29][30]. TiO_2 has the band energy of 3.2 eV so that it can't absorb the V/IR lights necessary for the process of water splitting. To overcome the difficulty some sort of doping is performed to make the band gap narrow. This sensitizes the TiO_2 for the absorption of required frequency of light working in PEC[31]. One of the best example is C- doped TiO_2 (nano films) that showed 11% efficiency of conversion. In this case 8.35% was the maximum photo conversion efficiency[32].

In the study of nano materials for PEC, ZnO_2 the semiconductor materials are also used ion PEC for the process of water splitting. It is reported as a wide band semiconductor material. This materials has been checked as a photo anode in PEC[33].

Hematite (Fe2O3) is another material successfully been used in as PEC nano material for the solar water splitting. The reason for its use is its narrow band gap of 2.1 eV. But the low charge transport quality is a serious hurdle in hematite while using in PEC cells. This factor affects the overall efficiency of the PEC cells. To tackle with this limit, different types of doping techniques are performed for increasing the electrical conductivity of hematite[34]. WO_3 is another material used as anode in PEC cell[35]. Research studies have focused on the nanostructure designs for the efficiency of PEC based on WO3 materials.

Other materials like CuO and MoO_3 have also been used and tried to be explored foe PEC cell activities.

So far many developments have been reported for the manufacturing of Nano materials for PEC solar water splitting. The materials and examples discussed earlier in the paragraph shows the concepts for the design of Nano materials for an efficient PEC performance for the water splitting.

To enhance the properties of semiconductors, composite materials are used extensively. One of the most important material to which the nano particles are added is a wonder materials ---Graphene.

1.7 Graphene--- A New Material.

Generally graphene is termed as pure carbon sheet that is very thin and transparent as well. Its weight is very low as compared to other materials like steel but also many times stronger than the still too. It has a permissible efficiency for conduction. It is known as graphite single atomic layer. Before 2004 it was believed that the thermal stability matters a lot for the existence of 2-D compounds at their separation.

In the series of properties of graphene first come its electronic properties.

The graphene most interesting feature is that it has a nearly zero band gap in sheets form which enables the charge carries i.e. electron and hole to move uninterruptedly.

In the form forms of nano ribbons it has the band gap of 3.8ev[36]. Its electronic mobility has been reported as 2000,000cm^2/v/s[37]. While it's light absorption for white light is 2.3%[38]. The chemical properties of graphene includes the burn temperature i.e. 350Ċ and specifics surface area is 1168m^2/g[39]. Its mechanical properties show that graphene tensile strength is 130Gpa along with thermal conductivity of 2-4Kw/m/K for the suspended (freely) Graphene[40].Figure shows the honey comb lattice of graphene sheet.

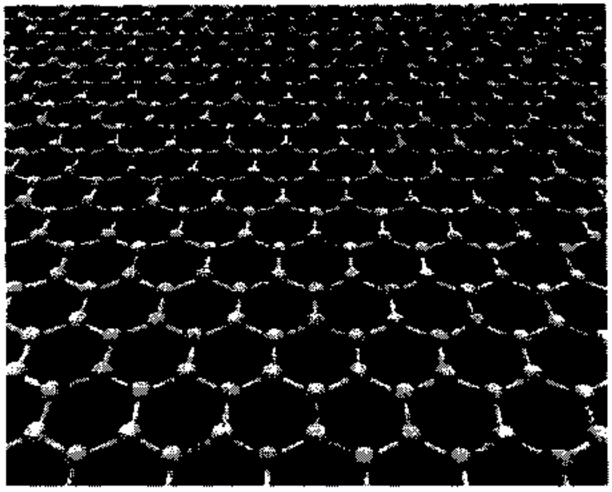

Fig1.5Honey comb graphene.

Its highly packed structure, periodic array of carbon shows its stability.

Application of graphene is also studies in different aspects. The main examples of the use of graphene are in energy storage and conversion materials like PEC electrodes and Li ion batteries as well.

1.8 Nanocomposits.

Nano composites are described as multi-phase materials along with 1-2-3 dimensions but less than 100nm[41]. Porous media, colloids, gels and polymers can be summed up in the defining features of Nanocomposits. Basically Nanocomposits are made for the purpose of enhancing the optical, electrical and mechanical properties of any semiconductors.

1.8.1 Metal Oxides Nanocomposits.

As earlier discussed that Nanocomposits are multiphase 3-D materials. One of the main types of the nanocomposite is metal oxides semiconductor Nanocomposits. So far TiO_2, WO_3, ZnO_2, and iron oxides have been used as metal oxides semiconductors for different application. Most commonly in photo electrochemical water splitting, for the manufacturing of electrodes for PEC cells and Li ion batteries which are used as energy storage and conversion material. In other words these metal oxides nanocomposite are the composite materials for energy storage and conversion devices.

Most importantly while making Nano composite graphene nanostructures are used for the enhancement of metal oxide semiconductors. A progress has been reported for Graphene /metal oxide nanocomposite as electrodes materials for Li ion batteries and super capacitors[42]. While discussing graphene metal oxide composite for energy conversion materials ,graphen has taken quantum leap in its popularity and usage in composites form. In nanocomposite form graphene has very promising properties of the charge carriers and production of electron hole pair[43].Similarly iron oxide graphene composites[44]were fabricated successfully for the PEC water splitting.

1.9 MoO_3 Nanoparticles.

Nano material have been used for different application in physics ,bio medicine ,energy application and in polymers science etc. The block D element i.e. molybdenum can't be found in free state, rather it is found in combined state with oxygen. Its chemical composition shows 66% molybdenum and 33% oxygen.

The physical properties of MoO_3 are its density (4.70g/cm^3),and molar mass (143.94g/mol).while its thermal properties i.e. melting point is 795Ċ and boiling point is 1155Ċ. Generally these are manufactured through wet chemical purification and roasting methods.

The application of molybdenum oxide can be studied in electrochemical capacitors, in nanowires, coating, catalytic application, hydrogenation catalysts and pigments etc.[45].

1.10 MoO_3/GO Nanocomposites.

In the ongoing studies we have the discussion about the metal oxides and graphene nanocoposite via different channels and dimensions. The basic reason for the composites formation is a targeted and desirable flow of charges, and efficient conduction by narrowing the bandwidth of the semiconductors. In fact the composite materials allow the smooth transfers of electron hole pair through the conduction band. Following the same concepts and ideals for an efficient charge transform, MoO_3

has been utilized to synthesis the nano composites with the well-known graphene oxide. Due to its considerable band energy, Mo can been taken as well qualified metal in its oxides state for the conduction of charges.

1.10.1 Methods for synthesis of GO/MoO_3 Nano composites.

For the synthesis of MoO_3/Go nanocomposite at the first stage graphene was synthesized by using modified hummers' method. For the synthesis of composites solvothermal method was used in the presence of HNO_3, and graphene oxide waters in various ratios. The composites were synthesized in autoclave at a temperature of 160Ċ[46]

1.10.2 Application of MoO3/Go nanocomposites.

The main applications of the MoO3/Go nano composite are for the fabrication of electrodes for efficient Li ion batteries. These composites can be used for the production of electrodes and its materials for high density super capacitor and thermal capacitors as well. Another application of this synthesized nanocomposite is its utilization for electrodes for photo electro chemical cell used for the sun light driven water splitting. Not only these but many other dimensions are available which can be driven by the use of MoO_3/Go nanocomposiote. These may include nano sensors and bio medical application etc.

1.11 Objective of the present work.

So far the nanocomposites of the MoO_3/GO have been used for the efficiency building of Li ion batteries and electrode fabrication for the super capacitors. Also it has shown promising results in enhancing the density and capacitance of the electrode materials. But the brief study shows that it has not been reported for the fabrication of electrodes for PEC cell used for hydrothermal solar water splitting. Our objective of the work is to explore the properties of MoO_3/Go nano composites for the effective water splitting to produce hydrogen as a future fuel. We will employ different characterization techniques for the morphological studies of the synthesized materials and samples. Huge attention has been focused upon the synthesis of such composites material that may be helpful in producing the cheep sources of energy. Theoretically our work will leads to a compatible paten, publications and well qualified report writing in future. Also the work will be hallmark for many other application like solid state engineering device fabrication, sensor studies and bio medical devices as well.

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Chapter 2 Literature review

Since long there has been a quest for more energy, science and technology and research and development has improved through various research activities. So far a considerable development has been reported about energy storage and conversion materials. These materials have been utilized for the manufacturing of Li ion batteries, super capacitors, and photo electro chemical cells for the conversion of solar energy into electrical or electrochemical energy and for the production of hydrogen as a future fuel.

In April 1998 OcsarKhasleve and john a turner reported direct water electrolysis and it was achieved with the help of novel and integrated monolithic PEC-PV design. Upon illumination this photo electro chemical cell made the water split directly. Light was the only input in the system. Based on the short circuit and low heating value for hydrogen, the efficiency of 12.4%was recorded[47]

In June 2007 Gerhard Peharz, Frank Demorth, Ursula Wittstadt worked on integrated system combined efficient solar cell in optical concentrator with an electrolyte membrane. Hydrogen and oxygen were produced by the activity of solar splitting. The solar to hydrogen efficiency (thermo natural) for the prototype system was measured to be 18% with an area of 96cm^2. The report was published by ELSEVIER [48]

Steven Y Reece, Jonathon A Hamel, Kimberly sung, Thomas D jarvi studied the worked on the development solar water splitting. The earth abundant materials were used in these cells at almost neutral conditions. The experiment was performed with and without the connection wires. Triple junction was the main feature of these cells for the production of hydrogen and oxygen as well. The efficiency for this device along with the wires was recorded 4.7% and than 2.7% for the wireless configuration. The sun illumination was about 100 mw/cm^2.[49]

In 2002 Shah U.M Khan and William B.inglerjr used TiO_2 as a very promising catalyst for water splitting.TiO_2 was synthesized through chemical modification and combustion with gas flame (natural). This modified TiO_2 showed phenomenal water splitting with the 11% of conversion efficiency. The upper limit of the photo conversion efficiency was reported 8.35% through the illumination of 40mw/cm^2[32]

Zhigangzou, Jinhua Ye, KazuheruSayama worked considerably to develop catalyst using less energetic and more abundant light. It was shown permissibly that indium tantalum (oxide) through doping of Nickel yielded photo catalyst in series that also included direct water splitting with .66% quantum yield. They concluded that the solar as a light source can be efficiently utilized for the production of water splitting.[50]

Xia0-Yen Zhang .Hao-Ping Li, Xiao LI-Cui synthesized TiO/ Graphene sheets composites through sol-gel method. Graphene oxide was used as primary material. The prepared sample was evaluated for the production of hydrogen under visible light. The effects of these nano sheets and calcinated[51]atmosphere was tested and investigated for the photo catalyst.

Te-Fu-Yeh ,JaroslaveCihral ,Chih Yung Chang, studied electronic properties of graphene that were high tunable due to their specified and unique structure. Go was studied as a considerable material that mediate the photo generation of charges for the decomposition of water. They introduced different strategies for the tuning of electronic structure of Go with different materials specially as a mediator in water splitting.[52]

In 2011 Weiwei Zhou, Jixin Zhu ,Chuanwei Cheng, Jingping Liu, HaunpingYang,Chunxio Cong worked upon the new way on the assembly of graphene with other metal oxides that included nanowires and particles as well. It was considered the very first report and work in which the metal oxides and nano wires that were supported by substrates were totally coated with graphene shells. The properties of these materials were integrated for energy storage materials like Li ion batteries. It was presumed that the super effectiveness of these electrodes were due to the graphen.[53]

In 2006 A.B Murphy P.R.F Burnes,L.KRandiniya , I.C Plumb, I.E Gray,M.D Horn, J.A Glasscock studies and examined the influences of light sources and its choice for the photon conversion on the semiconductor electrodes . The conversion efficiency for the xenon lamp was compare to the efficiencies calculated from the incident photon conversion. For xenon lamp the large bang gap energy semiconductor like TiO_2. The efficiencies were calculated while taking into consideration the losses based on imperfect absorption. Reflection and the recombination of the charge carrier. The reliable efficiencies were calculated by measuring the incident photon conversion efficiency. It was integrated on AM1.5 on the spectrum.[21]

Abiye Kebede Agegenehu, Chun-jurn Pan, Johns Rick, Wei-Niensu, Bing Joe Hwang in the Nano chemistry laboratory Taiwan demonstrated the loading on Ni &NiO nanostructures uniformly on the graphene sheets. The activity of water splitting from the solution of methanol was carried on fourfold for the NiO/GO and 7-fold for the Ni/Go under visible illumination. The effective and highest activity was considered to be based on lowest charge recombination. On the basis of the above work a method for the evolution of high density hydrogen gas was proposed. The under discussion research work showed that the catalyst that was loaded on Graphene sheets of large area considerably increased the rate of evolution of hydrogen gas via direct activity of water splitting. The above worke gave a solid idea about the use of graphene and was concluded that graphene and its nanostructures can be utilized in cells, batteries and super capacitors as well.[54]

G Parasad and O N Serivastava worked on the high efficient PEC cell i.e. 17.1 %(WSe_2). The electrodes of WSe_2 were fabricated through vapor transport technique and employed $SeCl_4$ as carrier. The photo electro chemical cell was than fabricated. The WSe_2 crystals were etched in aqua regia for enhancing the efficiency of the cell and electrode materials. The efficiency of 17.1% was reported .this was a very good correspondence towards an efficient solar cell. The high efficiency was marked due the materials (SeCl4 as carrier) improved quality[55].

In 2005 Nelson Kelley, Thomas L. Gibson design and characterized the photo electrochemical device for the generation of hydrogen gas by using the technique of solar water splitting. The research group worked to get the optimal results for the designing the double silicon based electrodes, material. The triple function Si cells that were coated with ITO. It was arranged so that the outer layer of the semiconductor was p –layer. Such cells operation was recorded for about short time or fewer hours along with the STH efficiency of 3%. To enhance the efficiency and increase the life of the cell the different types of methods were devised I.e. to make ITO coating extra durable , protection of ITO with fluorinated SnO2:F, protection of ITO with glass as well. But in the 2nd method the STH efficiency was up to (5-6)%. The life time was for about 31 days. This way of production of hydrogen was considered a major improvement[56].

Yang Hou ,FanZou, Alex Dagg, and PingyngFeng in the department of chemistry university of California designed , synthesized and characterized a new hetrojunction of Fe_2O_3/graphene core shells nanorods for the PEC water splitting. The process was carried on hydrothermally through the deposition of Fe_2O_3 on ITO substrates along with graphene inter coating by PC reduction and spin coating. This designed hetro junction yielded the photo current density of 1.97MA/cm^2 at 1volt along with the efficiency of 0.53% of photo conversion under the radiation of Xenon lamp. The overall results concluded that it demonstrated the advantages of graphene mediated core/shells hetro junction and provided priming vision and insight for the future research and development[57].

Stephanie L .Candelaria, Yuyan Shao, Wei Zhou , Xiolin Li, Jie Xiao, Ji- Guang Zhang in the department of Material science and Engineering ,University of Washington worked upon the carbon nanostructures for energy storage and conversion materials. The group studied the synthesis and application of nano carbon electrodes for the devices like Li ion batteries, and super capacitors as well. It was also studied for the development of materials foe the storage of methane gas as well[1].

R S Mane, B R Sankapale, CD Lokande, studied on the PEC cells based on chemical deposition of nano crystal Bi2S3 thin films in 1999. Bismuth sulphide nanostructure thin films were prepared and deposited having various thicknesses with a grain size of 7 to 34 nm. Chemical bat deposition method was applied on Florin doped tin oxide glass substrates. At the temperature 6C, the films were prepared. The particle size and the thickness of theBi_2S_3 were reported to cause main and significant changes in the performance of PEC cells.[58]

T Bak, J. Nowotny, M.Rekas, C. C Sorell in a review article discussed PEC H_2 generation through solar water splitting. The work was focused on the issues related to materials for the development of PEC cells of higher efficiencies. Different fabricated PEC cells were studied and overviewed. Also it structure and impact of material selection on the STH conversion were studied. A very important issue in the whole work was the bulk vs. interface properties at solid-solid interfaces, liquid –solid interfaces[20].

Alberto Adan-Mas and Die Wie 2013 Department of Metallurgy university of Cambridge studied PEC properties of novel material graphene and its derivatives multidimensional. The aim of the review was to see and analyze the PEC properties of graphene (pristine), graphene oxide and reduced graphene oxides as well. Its impact was also studied on the semiconductor catalysts. The group worked to improve the materials performance and its functioning in PV cells and photo catalysts for anti pollution reagents.[59]

Yueliu, Wei Wang, Line Gu, Yewu Wang, Yulong Ying, Yiyn Mao, Luwei Sun in their work, fabricated the flexible CuONanosheets and reduced Graphene oxide nano composites for Anode materials for highly efficient Li ion batteries. A nano porous network (unique three dimensional) was developed with CuONanosheetsthat were embedded within the graphene layers. These hybrid composites were studied as binder free anodes for Li ion batteries. An efficient and high capacitance cycling performance was developed from nanoporous sheets/composites of nanostructures that offered the electrical conducting channels that favored electrical penetration of electrolyte. These electrolytic capabilities of CuO/Graphene nano composites have promising results for Li ion batteries[60].

In 2011 Arghya Narayan Banerjee focused on the designing, fabrication, and photo catalytic activity of nano structured semiconductor materials with special focus on TiO_2 based structures. The main focus was on the deposition techniques through different channels to fabricate nonmaterial that included TiO_2/organic-inorganic composites materials. In technical terms TiO_2 showed promising reactivity under the UV light. Its energy was recorded to exceed the band energy of TiO_2. The basic working principal of TiO_2 photo activities were considered with the band structures and modification of surface in nonmaterial (TiO_2) in the doping context. The optical and electronic properties were explored with the detailed fabrication of 0-1-quasi-2 dimensional TiO_2[61].

Hailiang Wang, Yongye Liang, TissaphernMirfakhri, Zhuo Chen, Hernan Sanchez studied on the advanced super capacitors based on graphene materials. Generally the super capacitors hat operated in aqueous solution were of low cost energy storage devices but the main flaw that was noted was its low energy density. $Ni(OH)_2$ nanoplates and the nanoparticles of RuO_2 were grown on the graphene Nanosheets to increase the capacitance of the materials. Ni $(OH)_2$ /graphene and RuO_2/graphene electrodes were made as pair for affording the high performance with high energy and power densities at 1.5V. High power density of 21kw/kg was achieved at the energy of 14wh/kg by using $Ni(OH)_2$/graphene and RuO_2/graphene made electrodes[62].

Jingdon Lin ,Peng Hue, Yan Zhang, MeitingFan,Ziming He along with their co-workers , in the solar Fuel lab school of chemical engineering Nanyang Technology Singapore focused on understanding the PEC properties of rgo $-WO_3$ photo anodes for effective solar (direct) water splitting. Natural graphite in its power form was taken along 37% HCL, 98% H_2SO_4 and 25% ammonia solution along with 20 % H_2O_2. Modified hummers method was followed to synthesis GO and r-GO. The composites of WO_3 and Graphene were prepared through thermal treatment. The electrodes were prepared through dip coating using the substrate of FTO[63].

G H Shih, C.G Allen, B.G Potter Jr in 2009, produced thin films that were based on RF sputtered Ge ITO nano composites for application in photovoltaic's. Its influence was studied on the resulted optical absorption and charge transport characteristics. In the modification of phase assembly, the deposition control and thermal annealing was recorded successful. This factor enabled to manipulate the volume fraction Ge, crystal size and its morphology and its distribution in ITO phase. These proceedings suggested for the formation of large band gap with low electron affinity between ITO & Ge [64].

In 2013 TengZahi, Fuxin Wang,Minghaoyu,ShileiXie, Chaolun Liang with their other co-workers worked on 3-D MnO_2/GO composites with high capacitance for high performance in super capacitors. Large area, mass loading strategy was reported for MnO_2-GO composites for the application of super capacitors. MnO_2/G/NF with the mass of MnO_2 13.6 mg/cm^2 produced promising areal capacitance for about 3.18F/cm^2. The electrochemical properties of MnO_2 attributed to increase conductivities, and ion accessible area in electrolyte. ASC based on MnO_2/g gel at positive and G gel/NF at negative electrodes were able to achieve promising energy density of 0.72mWh cm^3. These ASC also showed cyclic stability excellently[65].

In 2013 Yu Liu, You long Ying, Yiyn Mao, studied the Cu/r-go nano hybrid films with high capacitance. CuO NS and r-GO lamellar films were prepared through vacuum filtration and hydrothermal reduction respectively. The material were mixed electro staticaly in the combination of negatively charged GO with positive charged CuO. The well prepared lamellar films showed the capacitance for about 163.7F g which was comparatively higher than 69Fg for CuO NSs & 66Fg for r-GO. The mixed (sandwich) lamellar films surface provides a smooth path for the for ion –electrolyte access CuO NSs and also exposes the r-GO for the electrolyte as well. This research provided the way to make the composite electrodes materials for the efficient capacitors. [66]

In 2013 XiaomiaoFeng ,Zhenzhenyan, Ningna Chen Yu Zhang,Yanwen Ma synthesized the shape controlled Graphene/MnO_2 nano composites using hydrothermal method for the application of energy storage materials. The mechanism of different structures of the above composites was discussed. The MnO_2 nanopetals in composite form with graphene showed better experimental results of the capacitance of the capacitors. Its specific capacitance was recorded as higher as 516.8F/g at the scan rate of 1mv/s. this study provided the facile an in situ method for preparing the metal oxide graphene composites for energy storage.[67]

Yomnhmin He, Wanjun Chun, Xiaodong Li, Zhinxing Zhang, worked upon the 3-D Graphene/MnO_2 for ultra light super capacitors. Due to the intriguing properties, graphene has been one of the most important candidates for the electrode materials for the energy storage materials. The use of free standing and light weight 075g/cm^2 with ultra thinness of ≤200μm loaded on MnO2 @9.8mg/$cm^{2.}$ This lead o a high areal capacitance of 1.42F/cm^2 .on the basis of the graphene materials electrochemical performance of symmetrical capacitors[68].

In 2012, Junsheng Zhu, Dianlong Wang, Lin Wang, Wanlog You, Qiuming Wang in the school of chemistry Herbin Institute of Technology synthesized SnS/Graphene composites for the application of high storage capacity of Li ion Batteries. The composites ere synthesized through the method of homogeneous precipitation. The well prepared nano composites materials were employed the techniques of XRD, Raman spectroscopy along with TEM and its chemical analysis as well. The results showed that SnS had a promising dispersion over the grapheneNanosheets. The electrochemical performance was tested by galvanic static charging –discharging test. The composites' were able to retain the capacity of 679mAh/g after 30 cycles. The material reported to have high Li storage capacity. The results of the nanocompsiotes lead to synergic performance that uplifted the electro chemical behavior[69].

Xiaocehen Dang, Peng Wang, Wiengjing Fang worked on thin films on graphen in large size through liquid precursor based chemical vapor deposition. The group synthesized large sized thin films by chemical vapor deposition method under the atmospheric pressure on copper files. Ethanol or pentene were used as a precursor. The Raman spectroscopy technique, STM and TEM resulted that the prepared films showed hexagonal lattice. The continuity of these films was confirmed through the measurement of optical and electrical properties. The films with graphene in liquid precursor showed low defect density[70].

In 2013 M.Sookhakian, Y M Amin, S Bradaran, M T Tajabadi synthesized thin films of layer to layer graphene-zinc sulphide –ploypyrole through electrophoretic deposition for the designing of solar cell. A photovoltaic electrode that was organic-in organic was designed. These electrodes consisted of graphene sheets ZnS_2 nanostructures, and PPY nanotubes. These were fabricated On ITO glass substrates by layer to layer deposition. The structural morphology was studied with the help of XRD, TEM and energy dispersive x-ray analysis. The materials properties were applied for the solar cells. It was concluded the PPY was a best sensitizer and hole accepters as well. Based on the results, ZnS acted as connection media i.e. a bridge, and graphene sheets played the role of best conductive material, collector and transporter. The conclusive results was that these material can increase the PV efficiencies[71].

James G Radich .Paul J Mcginn, PrashantV.Kamat, in an article discussed briefly the properties of graphene and its application in compost form for electrochemical energy materials. Graphene based materials for the preparation of electrodes were the main focus of the article. Graphene were prepared by following the hammers method by using different oxidizing agents like $KMNO_4$, H_2SO_4, etc. the prepared graphene were reduced with the help of hydrazine. It was reported that mostly anode materials have been prepared from graphene instead of graphite. In general practices Co and Mn are used as cathode materials in Li ion batteries. In composites form the graphene based materials i.e. G-$LiFePO_4$ the capacity was recorded up to 160mAh/g compared t the pure $LiFePO_4$. The composite of graphene with SnO_2 hase been used for the anode preparation[72].

Zhaoaxia Song, Yujuan Zhang, Wei Liu, Song Zhang along with their coworkers synthesized graphene /Co3O4 hydrothermally and for the studying the application of nanocomposite material for super capacitors.XRD, SEM, STM were used to know the morphology of the composites materials. Very fine isolated homogeneously nano particles were assembled in a flower shape. The electrochemical behavior was studied through CV and galvanic static measurements. An improved capacity and performance i.e. redox performance was reported. This was due to the composite structures and its combined properties. Good cyclic performance and columbic efficiency with a specific capacity of 400F/g at current density 0.5 to 2A/g.[73]

In 2011 DongyingFu,Gaoyi Han, Yenzhen Chang and Jianhua Dong synthesized ZnO/G nanostructures (hybrid) for the photo degradation of pollutants in water. Go was dispersed in ethanol and GO-ZnO were prepared. ZnO-GO were thermally treated at different temperatures.XRD, SEM, STM,X-RAY photoelectron spectroscopy, Raman spectroscopy,photoluminance techniques were used for the study of prepared samples. Bothe sides of graphene sheets were coated with ZnO nanoparticles. Methylin blue was investigated for the photo degradation in the presence of these hybrid materials[74].

In 2010, Tuan Anh Pham, ByungChoon Choi, YeonTaenJeong prepared cadmium sulphide quantum dots over grapheneNanosheets and studied its facile immobilization and application i.e. for its optical properties. Through the facile approach for the first time graphene and inorganic semiconductors like CdS were used to prepare the novel hybrid material. With the help of modification in kinetic method, amino-functionalized CdS quantum dots were prepared. Natural graphite was exfoliated to obtain the graphene oxide Nanosheets. The immobilization of the quantum dots was performed through the amide action and reaction between the amino group and acyle chloride group attached to the grapheneNanosheets. NMR, xrd, xps, edx, SEM, tem were the techniques used for the characterization of the prepared samples. Photo luminance was measured to study the optical properties of CdSgraphene hybrid material and Cds quantum dots as well[75].

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Chapter 3

Experimental Methods and Materials

3.1 Materials &Reagents.

Commercial graphite, HCL, HF, Distilled water, Ethanol, Acetone, $KMNO_4$, H_2SO_4, and Ammonium Molybdate salts, HNO_3, ITO substrates.

3.2 Purification of commercial graphite.

To purify the commercial graphite and for the oxidation and reduction of graphite, modified Hummers method was followed[76]. 2g of commercial graphite was taken in 150 ml HCL or HF solution was kept on vigorous stirring for about 2 hours to disperse the graphite clearly. As the commercial graphite may have many impurities, the solution is allowed to settle down and then decanted carefully. To normalize the PH of the solution 150 ml distilled water was added to wash it through stirring for 10-15 minutes. This was repeated one more time. Finally Acetone or ethanol was added to set the PH of graphite solution. After having neutralized PH the solution was filtered and dried at 100Ċ for about 6 hours 1.75 g was the net output of graphite after purification. The pure graphite was weighted prepared to oxidize it in the next step.

3.3 Oxidation of Graphite to Graphene oxide.

$NaNo_3$ was added into pure graphite with the ratio of 1:2. 50 ml of H_2SO_4 was taken per gram of the mixture. An ice bath reaction set up was arranged to maintain the temperature at zero .in H_2SO_4 the mixture of graphite and $NaNO_3$ was mixed slowly and gradually. Some fumes were observed due to the heat up of acid, but the ice bath maintained the temperature at 0Ċ. During the vigorous stirring $KMNO_4$ was added in 5:2 gradually while maintaining the temperature with the range of 5-10Ċ. The stirring was carried out for 30 minutes or so. The ice bath was removed and the solution was kept at constant stirring for about 18 hours at 35-40 Ċ to disperse the layers of Graphene oxide. After stirring distilled water was poured in to normalize the PH. 6ml H_2O_2 was added during the stirring as well to neutralize the Graphene oxide solution. 200 ml of water was again used to wash it properly .30 ml HCL along with 50ml of distilled water was added and steeled down. In the last acetone or ethanol was added for 5-10 minutes stirring which resulted the neutralized PH of Graphene oxide solution. After filtration the **GO solution was kept in vacuum oven at 80Ċ to dry. The dried GO** sheets were obtained which were grinded to powder form. Fig 1 shows the Go sample solution.

Figure 3.0-1GO liquid sample.

3.4 Reduction of GO to r-GO.

Generally for the reduction of Graphene, hydrazine has been used extensively. Graphene oxides are then reduced with or without the reducing agents as well[77]. I proceeded without the reducing agent.

Before filtration of the primary GO solution we divided the 300 ml solution in to two beakers of 150 ml. For the reduction of GO, we transformed the 150 ml GO into Teflon lined autoclave and kept it at **200Ċ for 6 hours. The autoclave was cooled down at** room temperature and well prepared reduced Graphene was obtained dried and grinded to the powder form. Figure 02 Shows the reduce GO samples obtained hydrothermally.

Figure 3.2rGO Powder and liquid Samples.

3.5 Synthesis of MoO_3 Nanocomposites.

Solvothermal method at 160Ċ for 6 hours in 100 ml autoclave was followed. Solvent was ethanol or ethanol water mixture. GO was added to AMTH solution and reduced under hydrothermal conditions to r-GO.

In the back drop of synthesis technology for Nano composites, MoO_3/GO nanocomposite were synthesized solvothermally[46]. Ammonium heptamolybdate/Ammonium molybdate tetra hydrate (AMTH) in the quantity of 1 gram was dissolved in 50 ml ethanol. Next, 6 ml of HNO_3 was added into Graphene water of different volumes and ratios.

Several samples were prepared by the solvothermal method with different volumes of Go waters.

The detail description of the samples composition was as following.

Sample#2. 50mg GO+15 ml water at 10:3 +1 gm AMTH +6ml HNO_3.

Sample#3. 50mg GO +40 ml water at (10:5) +1gm AMTH + 6mlHNO_3.

Sample3A 50mg Go +40ml water same compositions as sample 3 at low temperature (140Ċ).

Sample#5. 50mg GO +35ml water +1gm AMTH and 6ml HNO_3.

Sample#5A (at low temperature).

Sample #6. 50mg GO +45ml water (10:9) +1gm AMTH+6ml HNO_3.

The Figure given below shows the pictorial presentation of the synthesis of MoO_3/GO nanocomposite.

Figure 3.3 syntheses of nano composites.

3.6 Thin Film Deposition and Use of ITO Substrates.

3.6.1 Substrate cleaning.

For the proper cleaning of the substrates, the ITO glass substrates were kept in ethanol and sonicated for about an hour. The well washed substrates were than dried at room temperature.

3.7 Materials/composites deposition.

3.7.1 Spray deposition.

For the thin film deposition, 50mg of MoO_3/Go composite material was ultra sonicated in ethanol. Argon gas was used as carrier of the aerosol in the spray gun. The vapors (nano composites) were deposited slowly and steadily on the film placed on a hotplate at 150Ċ. The films were than properly dried and collected safely. Contacts wires were attached to the deposited films with the help of silver paste and dried under the tungsten filament lamp. The deposition of the films through spray gun is shown in the following figure.

In fact the SEM has very much advantageous than OM due its large depth of field, higher magnification and resolution. I had my focus on the study of the surface and coarseness of Go and MoO_3/GO composites surfaces.

Fig shows the schematic diagram of SEM.

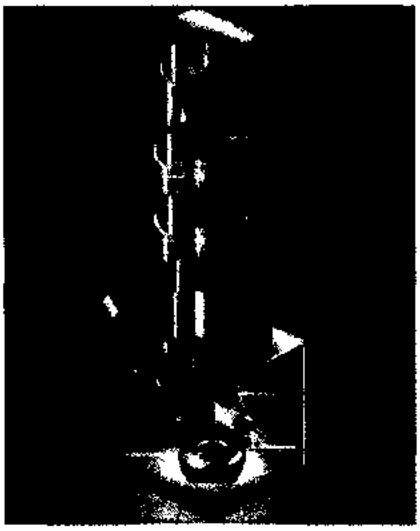

Figure 3.5 scanning electron microscope

3.8.2 X- Ray Diffraction.

X ray diffraction is considered a rapid technique (analytical) extensively used for the study of crystalline materials and also provide the unit cell structure of the materials. The three dimensional behavior of crystalline substance was studies and discovered by Lave in detail.[-portxray r---] The CRT produces these X rays and filters to monochromatic light.

We know that all the crystalline materials have their specific characteristics which can be studied through x- ray diffraction.generaly crystals are referred to be the regular arrays of atom and their planes are separated by the distance d. The beam of x-ray strikes the sample. The angle of incidence is θ.

Figure 3.4 spray deposition and electrodes with wire contacts.

3.8 Characterization Techniques.

To study the Nature nomenclature and morphology of the materials, there is an extensive use of characterization techniques.

For the structural study of graphene oxide, reduce graphene oxide, and MoO_3/Go composites we have used different techniques like SEM, XRD, UV, DRS, CV, and FTIR etc.

3.8.1 Scanning Electron Microscope (SEM)

Generally the SEM is used within the dimension of 10 nm for the differentiation of thin films.

Mainly the SEM consists of two main components i.e. electron console and electron column. In electronic console the control knob and all switches facilitate us to adjust and fabricate the SEM instrument.

It is comprised of the following parts.

Electron gun, condensed lenses, apertures, scanning system, specimen chamber and vacuum system as well. The well generated beam of electron is focused and specimen is scanned by EM deflection. Energetic signals are produced when the beam strikes the sample.

The scattered ray is than given by Brags Law

$$n = 2d\sin\Theta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

n is the integer ,d is spacing of diffraction planes and θ is the incident angle.

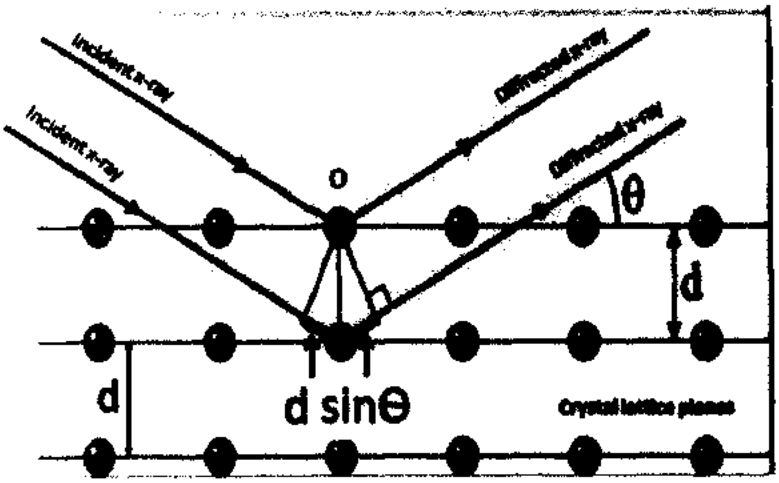

Figure 3.6 schematic representation of Brags law

3.8.3 Ultraviolet Visible Spectroscopy.

This is referred to be an absorption spectroscopy in general terms. The visible and near UV lights are used in UV spectroscopy. In the UV measurement the absorption of light gives the information of the transition of electron that take place in a material. The transmitted light is explained by the BEER-Lambert law. The law states that the light fraction which is measured after the interaction with sample depends on the path of light through the sample, cross-section of absorption σ for transition, and the population difference at initial state N1 and the last stat N2 of the first initial state E1 and final E2 energy levels

$$ {}^{I}/_{Io} = e - \sigma(N1 - N2)t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2)} $$

In simple word the Beer law says the concentrations and absorption are related in direct proportion for the molecules to be absorbed. The Lamberts says the radiation fraction absorbed is not dependent on the intensity of the radiation. So the Beer-Lamberts law can be expressed as

$$ \log 10\ Io = \frac{\varepsilon \iota c}{I} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.4)} $$

Io shows the intensity of incident radiation.

Io = incident radiation intensity

I = transmitted radiation intensity

ε = known as the molar absorption coefficient constant for each absorbing materials

ι = absorbing solution path length in cm

c = absorbing species concentration in mol dm^{-3}

3.8.4 Photo Electro Chemical Measurement.

To know the quality and performance of the fabricated nanostructures and composites materials, the current –voltage curve give the best deduced information of the whole engineering of the composites prepared in this work. PEC measurements were made in an open type three electrode cell using Na_2SO_4 as the electrolyte. Electrical contacts with the working electrodes fabricated from the different WO_3/graphene composites were made using a copper wire and silver conducting paint. A Pt wire was used as the counter and Ag/AgCl as reference electrode. Linear sweep voltammograms were recorded under a range of applied potentials. All photocurrent measurements were recorded under one sun illumination using an AM 1.5G xenon light source.

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Chapter 4 RESULT AND DISCUSION

X Ray Diffraction analysis.

4.1 X RD analysis of GO-rGO

Figure 4.1a shows the x-ray diffraction pattern of Graphene oxide (GO) andreduced graphene oxide (rGO) simultaneously. Graphene oxide has an intense diffraction peak at 10.80° degree with a d spacing of 8.17A°. The chemical oxidation disrupted the ordering of the layers in graphite and introduces the functional groups of oxygen on graphite. The inter layer space is being recorded up to .733 nm that falls greater than the well calculated .335nm for graphite.

Figure 4.1b shows the XRD pattern of reduced graphene oxide. The graphene oxide has been reduced chemically. Due to the chemical reduction the sharpness of the peaks normalizes and a low intensity peaks appears at 24.8°. This change in peaks formation is due the exfoliation of the layers of graphene oxide. The results show the graphene has been successfully oxidized and chemically reduced as well.

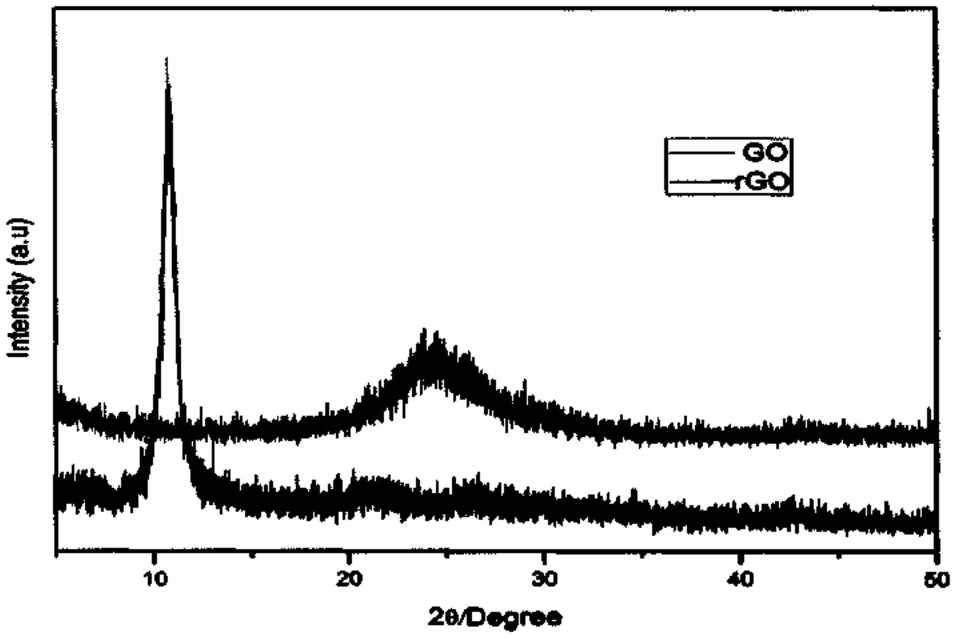


Fig 4.1 XRD pattern of GO and r GO

Figure 4.2 depicts the XRD pattern of MoO_3 prepared under hydrothermal conditions at a temperature of 160Ċ. The pattern was matched to the standered JCPDS card number 01-073-0039 of hexagonal MoO_3. The peaks are intense showing the very good crystalline nature of the prepared MoO_3 sample. No other peaks either from impurities or from the other phases of MoO_3 were observed showing that the procedure we adopted give phase pure MoO_3.

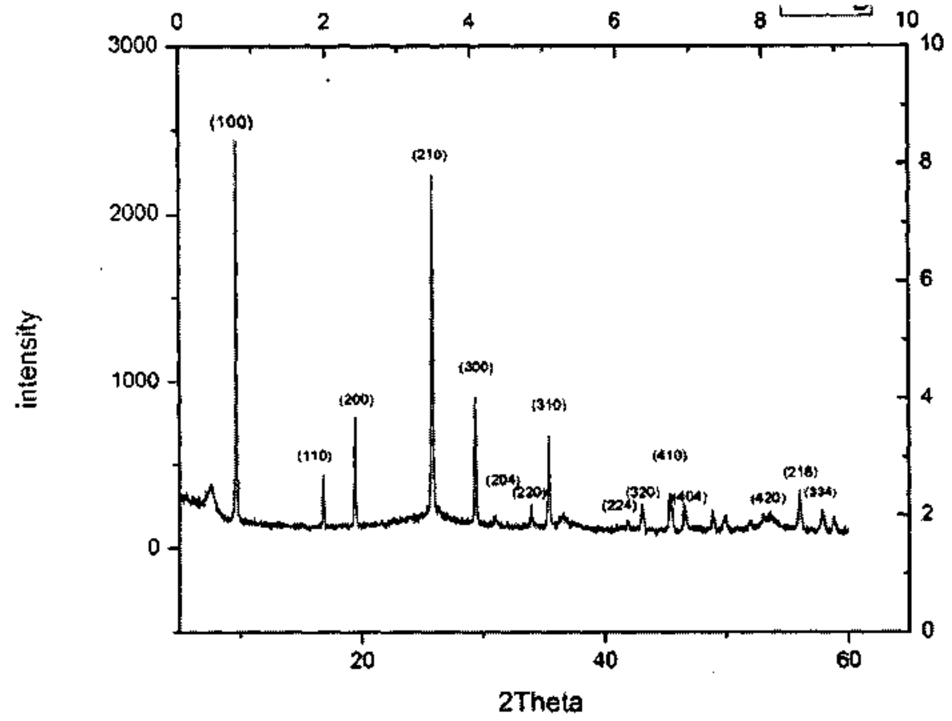


Fig 4.2 Pure MoO_3 X-RD pattern

4.2 Composites Sample 1 (MoO_3-GO)

Figure 4.3 describes the x-ray diffraction pattern for MoO_3-GO composites in powder form synthesized under the high temperature of 160 Ċ. The pattern shows the structural analysis if the sample. The reflection of the high intensity was observed at plane (010) comparatively for the oxidized hexagonal graphene at 10 °θ. The other peaks were indexed for hydrated hexagonal MoO_3 in the conformity with JCPD No.01-073-0039. No other specific peaks for impurities were observed that shows the quality of the nanostructures synthesized solvo thermally. For the high intensity peaks the FWHM are .0787,.0984,.1771, .1378 respectively. Based upon the Scherrer calculations, the average grain size was calculated to be 67 nm. It may be noted the reflections from the MoO_3 are of very high intensity that suppresses the diffraction counts coming from the GO and hence the peak from GO is not visible in the XRD pattern.

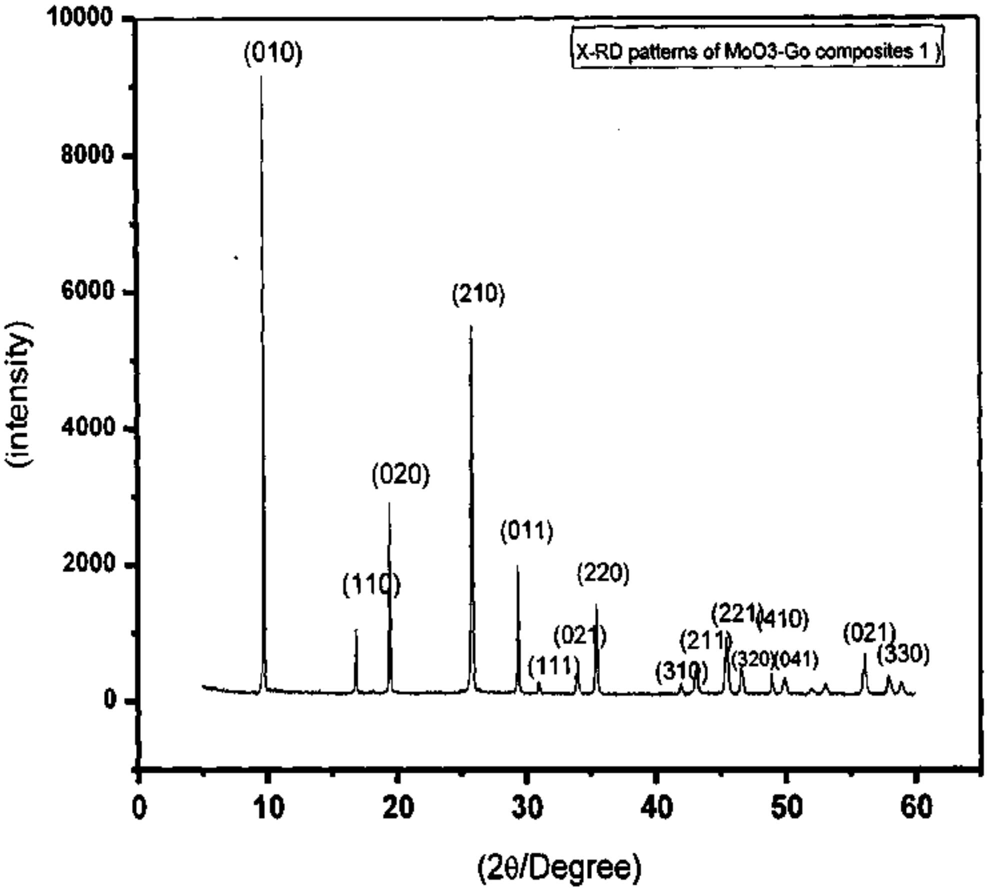


Fig 4.3 X-RD patterns of MoO_3-GO composites 1

Samples with different composition and temperatures were synthesized and studied with XRD as shown in Figure 4.4 onward. Differences in the samples were brought by varying the compositions of the starting materials during hydrothermal synthesis. All the recipes produce phase pure hexagonal MoO_3 with slight variations in particle size as calculated using Scherer equation ($D= 0.9\lambda/\beta Cos\theta$) with different crystal sizes of 75nm, 60nm.

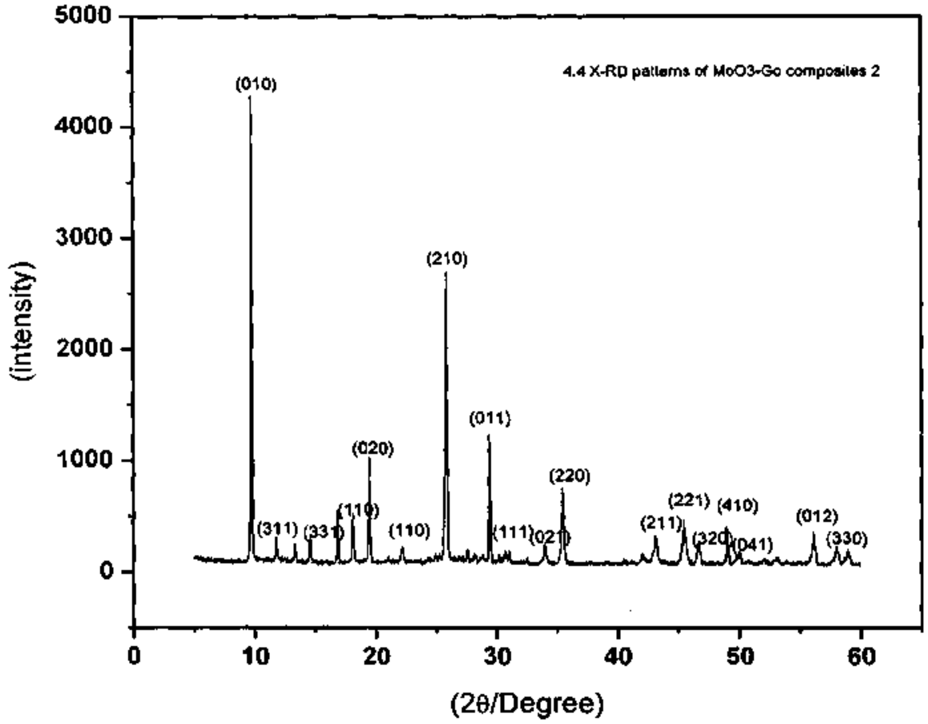


Figure 4.4 X-RD patterns of MoO_3-GO composites 2

This pattern describes the hexagonal structures of MoO_3 analyzed according to the JPCD No01-073-0039. The grain size for the composite was calculated 75 nm.

X-RD Pattern sample 5.

The figure below shows the patter for MoO_3-GO composites sample 5.The sample was synthesized with comparatively different ratio at 160 Ċ. The same characteristic peaks were observed with different hexagonal structural planes. The high intensity peaks were observe at 19.348°, 25.689°, 29.287, for MoO_3.The rest of the peaks were also analyzed for hydrated MoO_3 under JPCD No.029-1022.

In size for the above sample, calculated according to the sharer equation is 60nm.

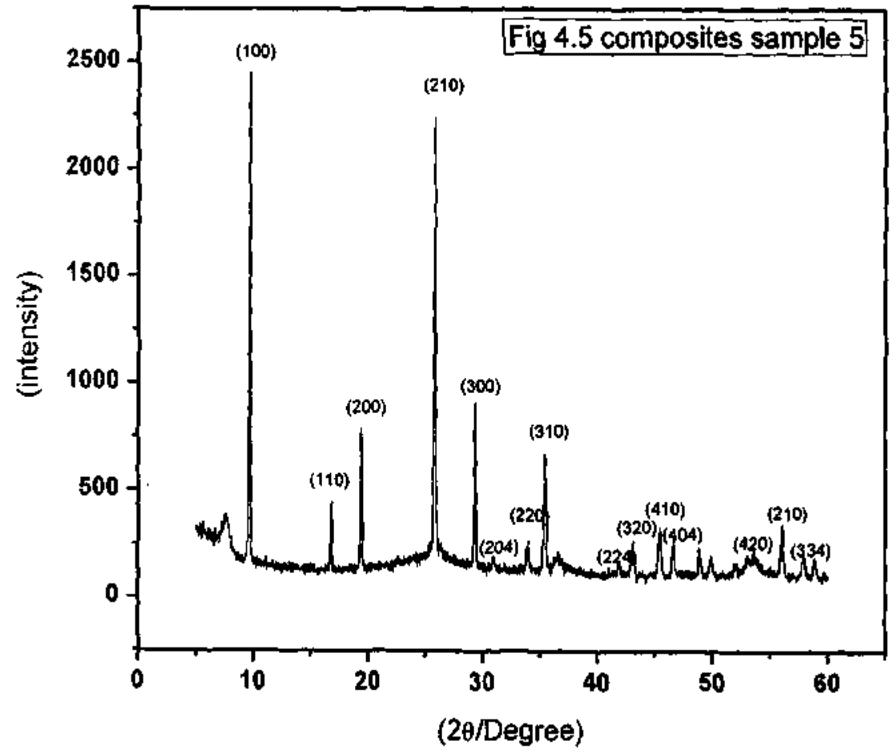


Fig 4.5 composites sample 5

Comparative low & High Temperatures Nanocomposites sample patterns.

The below figures shows the x rd patterns of the MoO_3-Go composites prepared at high and low temperature (135Ċ 180Ċ). The high intense peaks were observed at 9.170°, 19.365, 25.689 at the planes (020)(210).(011) respectively. The peaks were confirmed according to JPCD No.01-073-0039. The particle size was calculated as 80 nm.

In the second case of sample 6b, while at low temperature of 135Ċ the particle size is 66nm observed.

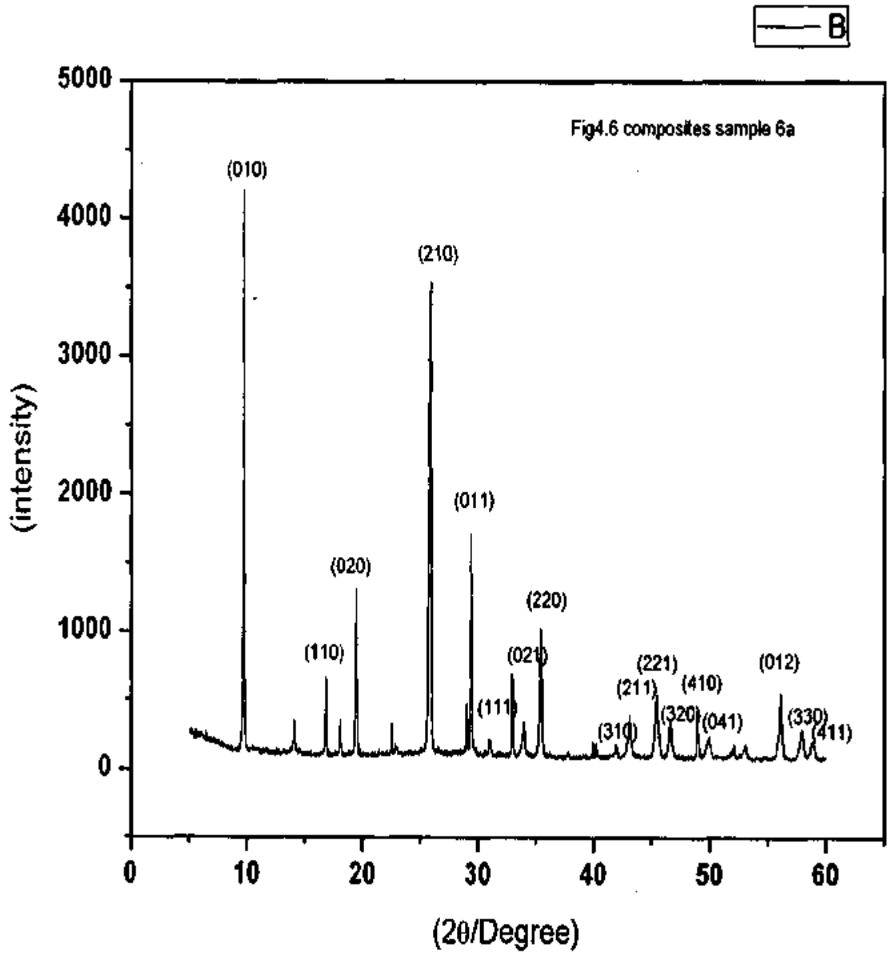


Fig4.6 composites sample 6a

The below x-rd pattern shows the synthesized MoO_3 at low temperature. The prepared sampled was crystallized in hexagonal phase of MoO_3. The peaks diffraction was indexed in confirmation of JPCDS; 21-0568, a .10.552A° and C = 14.888A°. As such no impurities peaks were observed in the pattern. Te particle size was for about 60 nm under the above study[78].

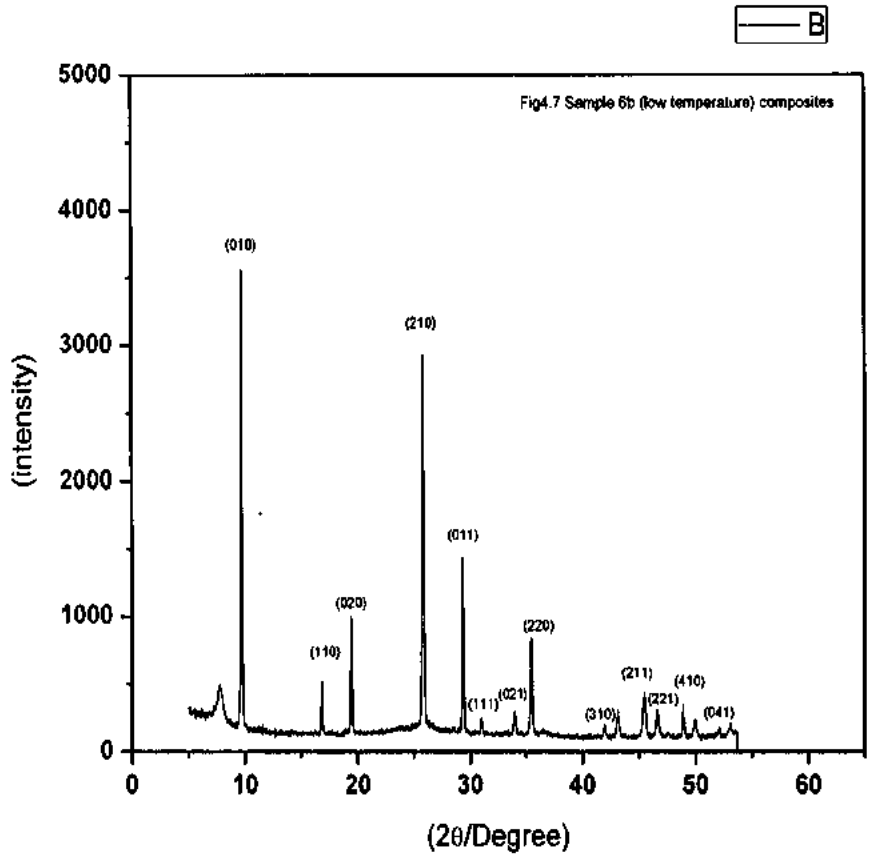


Fig4.7 Sample 6b (low temperature) composites.

4.2 *UV Visible Absorbance for GO*

The below figures shows the UV visible spectra by plotting between the absorption and wavelength for the Graphene nanoparticles. The spectra were collected by dispersing the graphene and its composites in isopropanol by ultrasonication. In the pattern shown in Fig 4.8, two different peaks types were observed. In the spectrum the first peak showed a sharp absorption for Graphene at 310nm corresponding to n-π* and another at 230 that corresponds to π-π* transition peaks. It has been shown the lower the dispersion of Go –the lower will be the absorption as well.

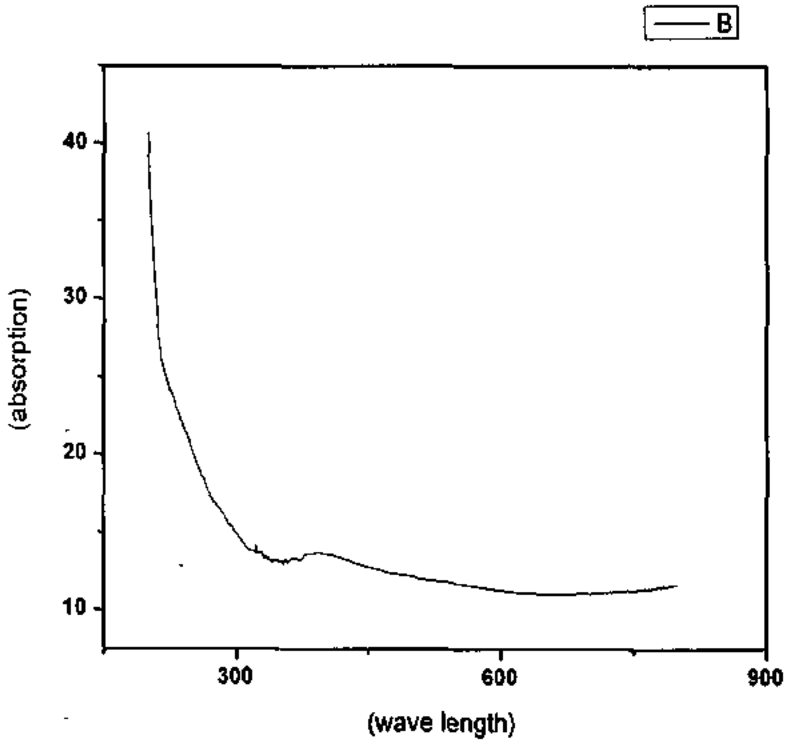
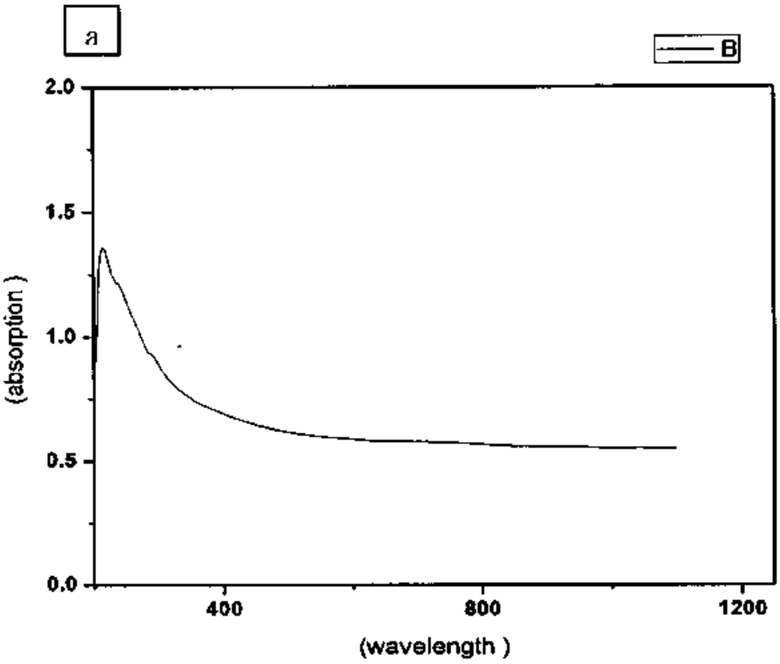


Fig 4.8 UV visible spectrum for Go 1

4.3.1 UV visible spectrum for MoO$_3$-Go composites

Figure 4.9 shows the absorption spectra for the composites of MoO$_3$-GO. Careful analysis shows that a sharp absorption band occur at around 380 nm.



4.8 b UV visible for MoO$_3$-GO

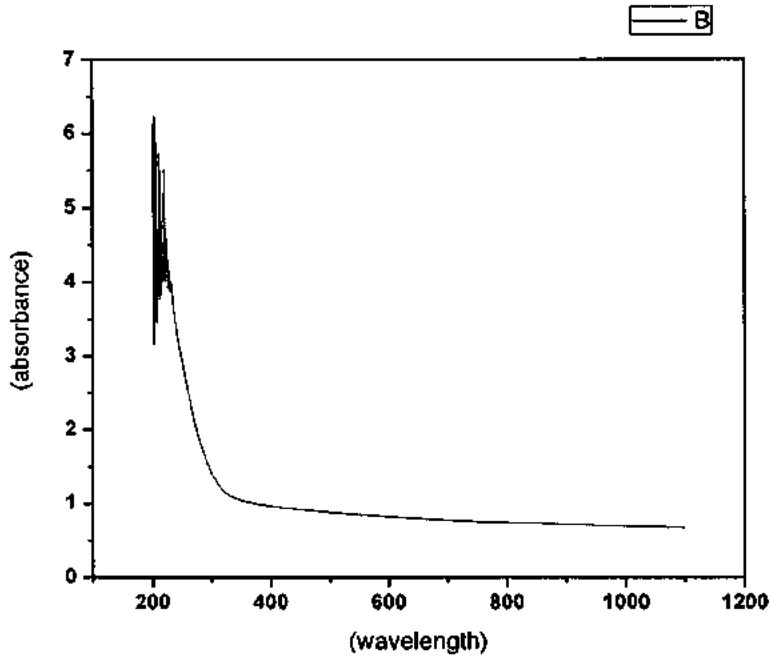
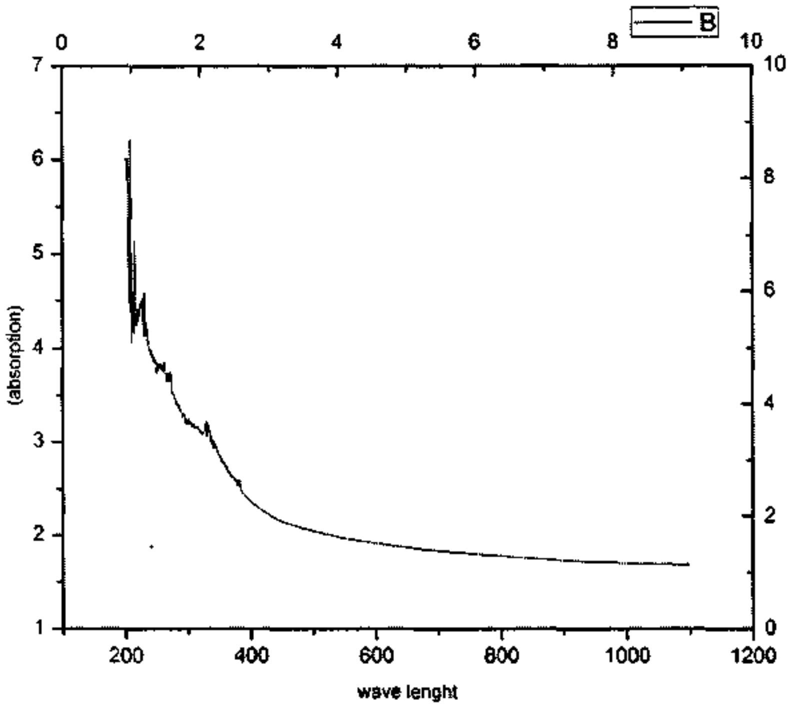


Fig 4.8c UV MoO$_3$-GO composites 1

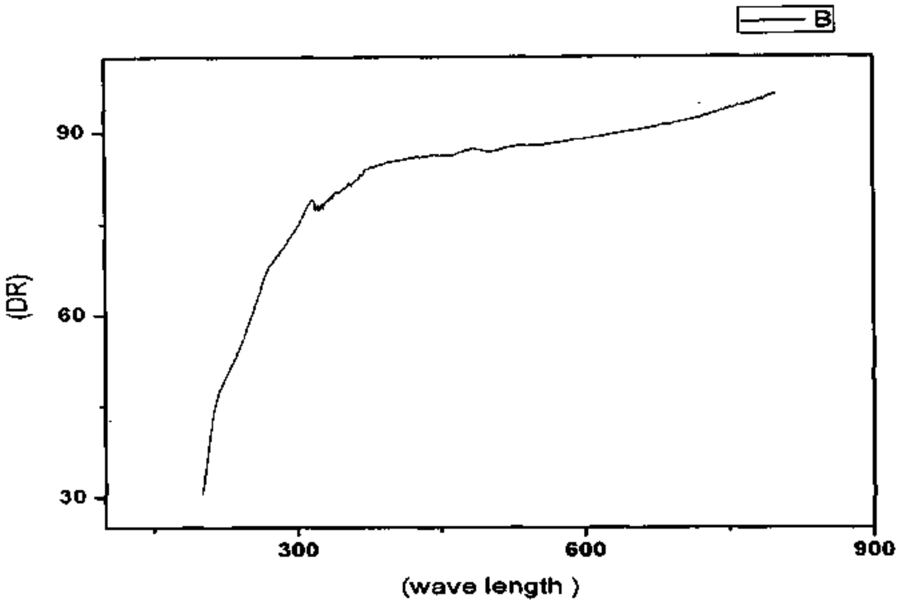


4.8 d Absorption curve for MoO$_3$-GO (low temperature)

4.4 Diffused Reflectance Spectrum for MoO$_3$-GO nanocomposites.

In below figure the case of diffused reflectance curve a sharp fall of the reflection can be seen at about 300 and 400 nm respectively for the composites of MoO$_3$ –GO. The optical absorption for MoO$_3$/GO is shown in the range of 400 to 800 nm.

The band gap for MoO$_3$ is calculated by using the KMF DRS sheet while plotting $(F(R_\infty)hv)^{1/2}$ VS h^{v}. The optical band gap for MoO$_3$ obtained from the pattern is 2.98ev. This amount is greater than the bulk i.e. 2.95ev. The reason is the reduction in the particle size. The below graphs shows the curves obtained for the samples synthesized at different temperatures[78].



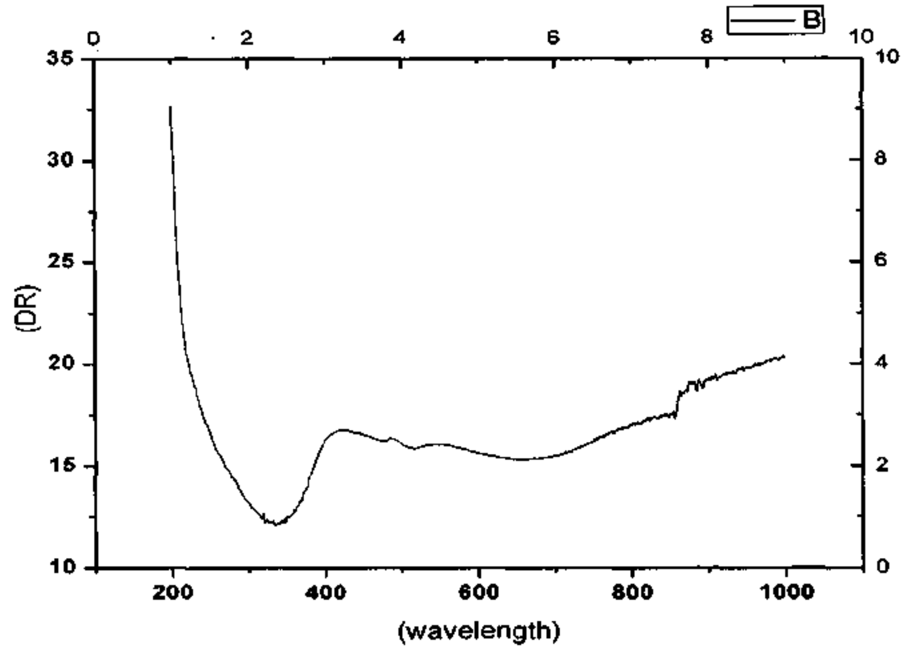


Fig 4.9abc Diffused reflection curve for MoO_3-GO.

The above figure shows the DRS cures for the MoO_3-GO nano composites prepared at comparatively different temperatures (140Ċ and 160Ċ) and different concentrations of GO i.e. 10mg/ml and MoO_3.

4.5 SCANNING ELECTRON MICRO SCOPY ANALYSIS (deposited on ITO) Sample 1.

The SEM images given below shows the morphology of the composites of MoO_3-Go obtained solve-thermally at 160Ċ and spray deposited over ITO at 150Ċ.For the pure MoO_3 sample, a very large number of hexagonal rods can be observed. The diameter of the rod varies from 300 to 400 nm respectively. A slight agglomeration can also be seen in the nano rods as well.

Figure 4.10 shows the SEM image of the MoO_3 sample prepared hydrothermally at 160Ċ and spray deposited over ITO substrates. A rod like morphology can be observed with diameters ranging from 150 to 250 nm and lengths between 30 to 50microns. In the high magnification SEM images, it was observed that the rods have hexagonal shapes. The SEM image in Figure 4.11 shows the morphology of the composites of MoO3-Go obtained solve-thermally at 160Ċ and spray deposited over ITO at 150Ċ. Compared to the Figure 4.10 shows the SEM image of the MoO3 sample prepared hydrothermally at 160Ċ and spray deposited over ITO substrates. A rod like morphology can be observed with diameters ranging from 150 to 250 nm and lengths between 30 to 50microns. In the high magnification SEM images, it was observed that the rods has hexagonal shapes. The SEM image in Figure 4.11 shows the morphology of the composites of MoO_3-Go obtained solve-thermally at 160Ċ and spray deposited over ITO at 150Ċ. Compared to the pure MoO_3 sample, the MoO_3 nanorods in the composite appear to be hollow representing nanotube like morphologies. It can also be seen in the image that graphene is evenly dispersed and wrapping the nanotubes at the outer sides representing the formation of a composite where the two phases are in intimate contact. The graphene appears transparent to the electron b eam during imaging showing the few layered nature of the graphene sheets. It must be noted that the starting materials were MoO_3 precursor salt and GO. The GO gets reduced hydrothermally under elevated pressure and temperature. During the conversion of GO to rGO, the formation mechanism of the MoO_3 nanorods also changes and it can be assumed that GO preferentially etch the hexagonal rods along the long axis rather than the lateral edges that leads to the formation of hollow tubular nanostructures. The exact mechanism behind the formation of MoO_3 nanotubes is however unknown and needs further experimental verification. The pure MoO_3

sample, the MoO_3 nanorods in the composite appear to be hollow representing nanotube like morphologies. It can also be seen in the image that graphene is evenly dispersed and wrapping the nanotubes at the outer sides representing the formation of a composite where the two phases are in intimate contact. The graphene appears transparent to the electron beam during imaging showing the few layered nature of the graphene sheets. It must be noted that the starting materials were MoO_3 precursor salt and GO. The GO gets reduced hydrothermally under elevated pressure and temperature. During the conversion of GO to rGO, the formation mechanism of the MoO_3 nanorods also changes and it can be assumed that GO preferentially etch the hexagonal rods along the long axis rather than the lateral edges that leads to the formation of hollow tubular nanostructures. The exact mechanism behind the formation of MoO_3 nanotubes is however unknown and needs further experimental verification.

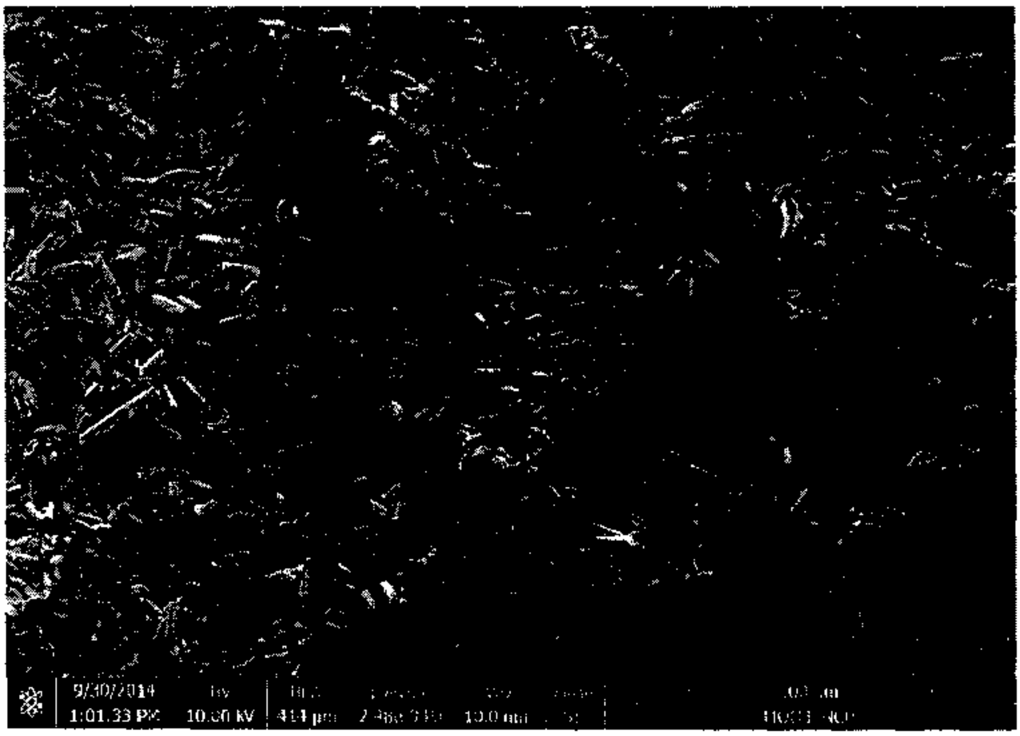


Fig 4.10 SEM image for MoO_3-Go composites deposited over ITO.

4.5.1 Sample 2 SEM images for MoO_3-GO Thin film.

In the fig the SEM images can be seen at different magnification to observe the exact morphology of the nano composites.

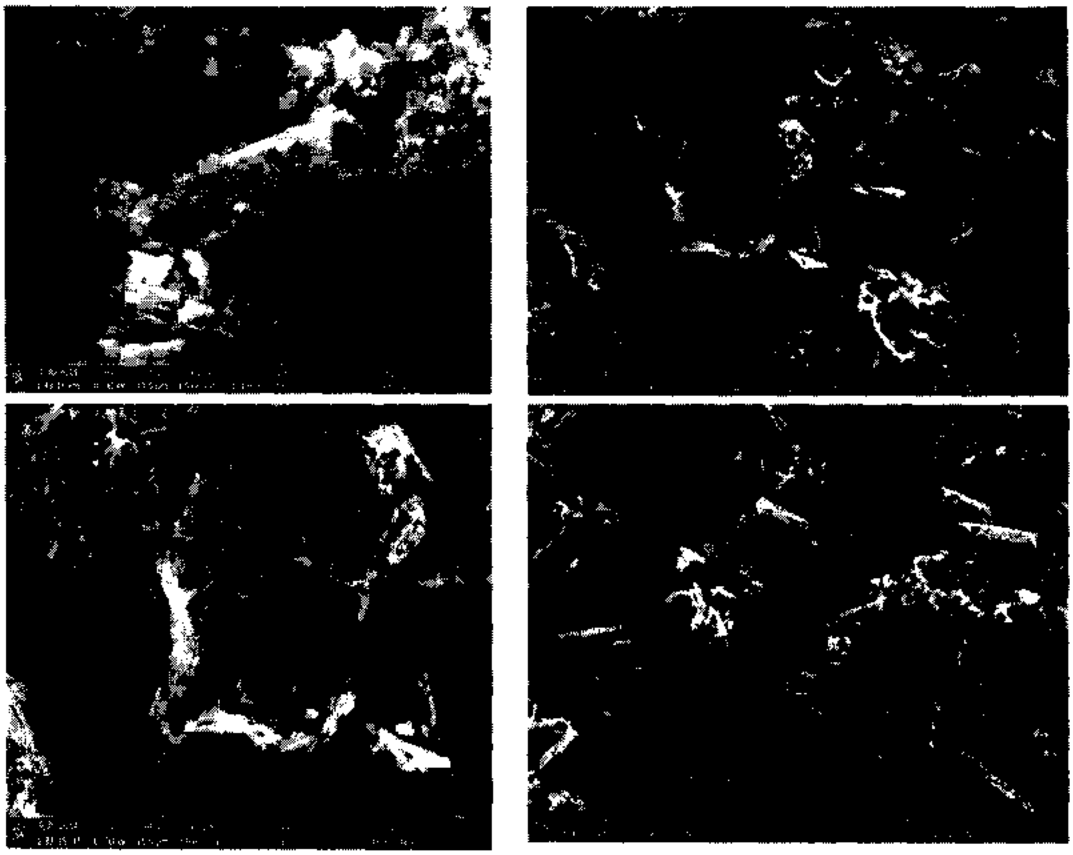


Fig4.11SEM image of MoO_3-GO composites.

SAMPLE 3(THIN FILM)

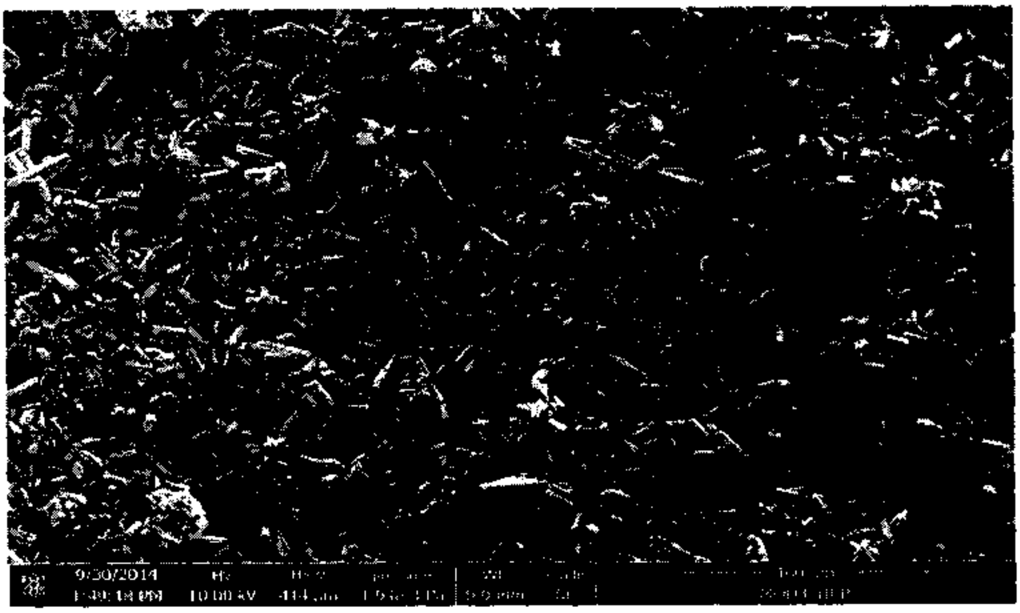


Fig 4.12 SEM image for MoO_3-GO composites

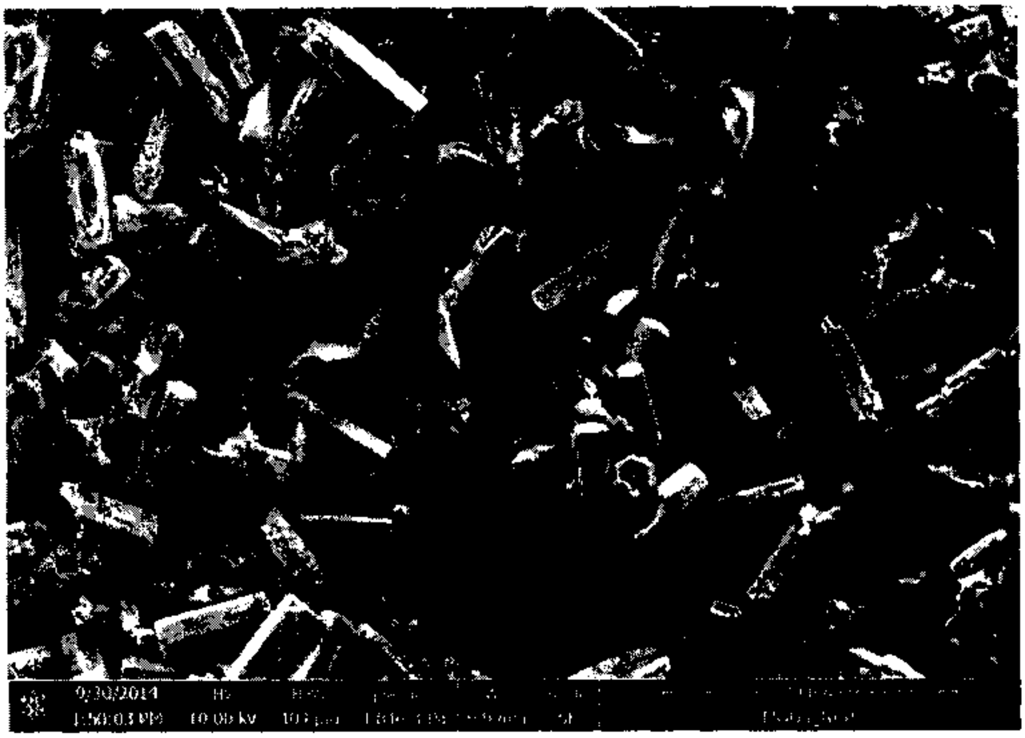


Fig 4.13SEM nanocomposites (MoO$_3$-Go)

SEM POWDER FORM .S1(100mg/20ml of GO water).

The below image can be seen for the MoO$_3$-Go composites in powder form at high temperature of 160-180Ċ. With the hexagonal structures and different magnification nono rods as well as nano tubes can be seen clearly synthesized hydrothermally. A certain amount of graphene has been added. It showed that the graphene sheets are not only deposited on the surface of the MoO$_3$ but also went through the inner surfaces as well.

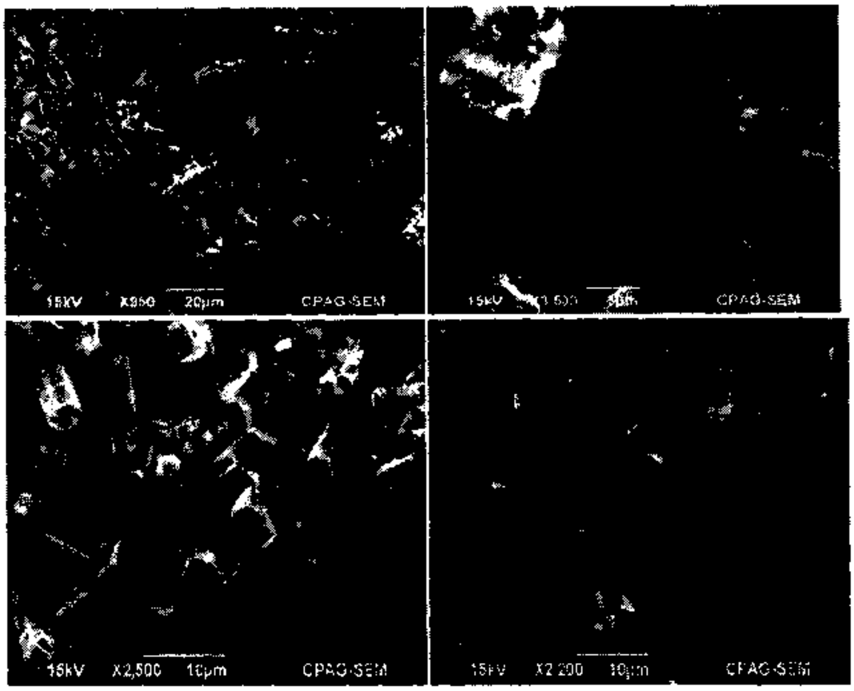


Fig4.14 SEM image of Powder MoO3-G0 composites

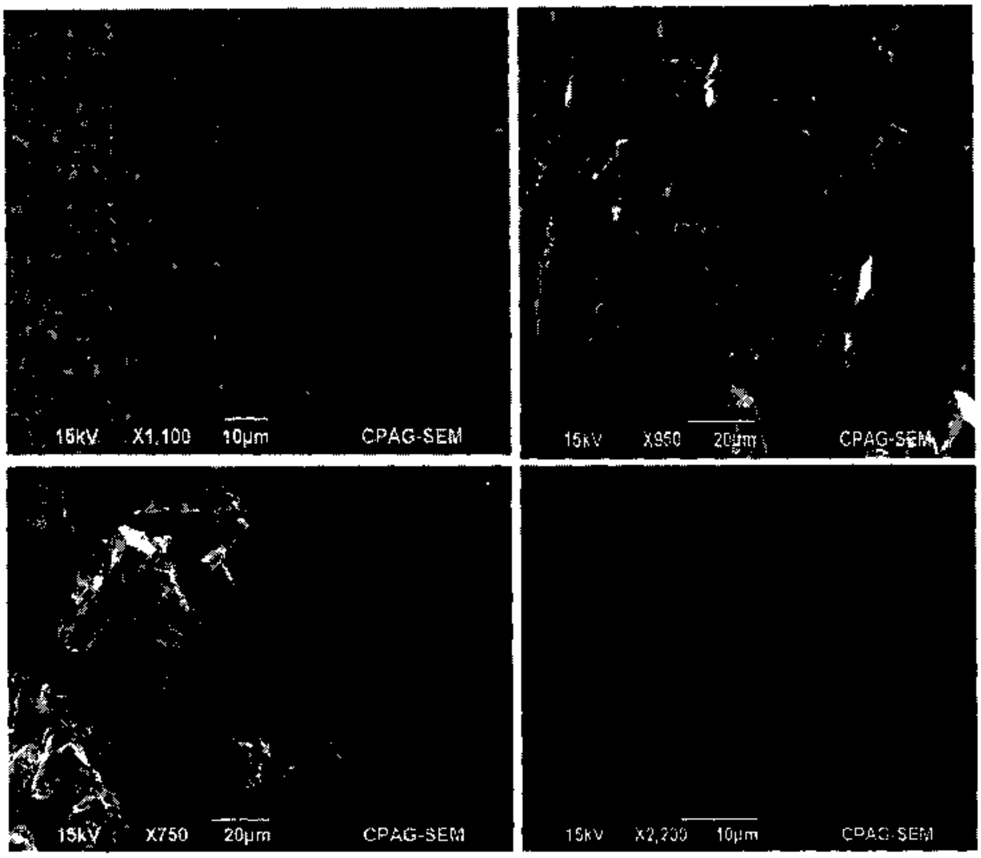
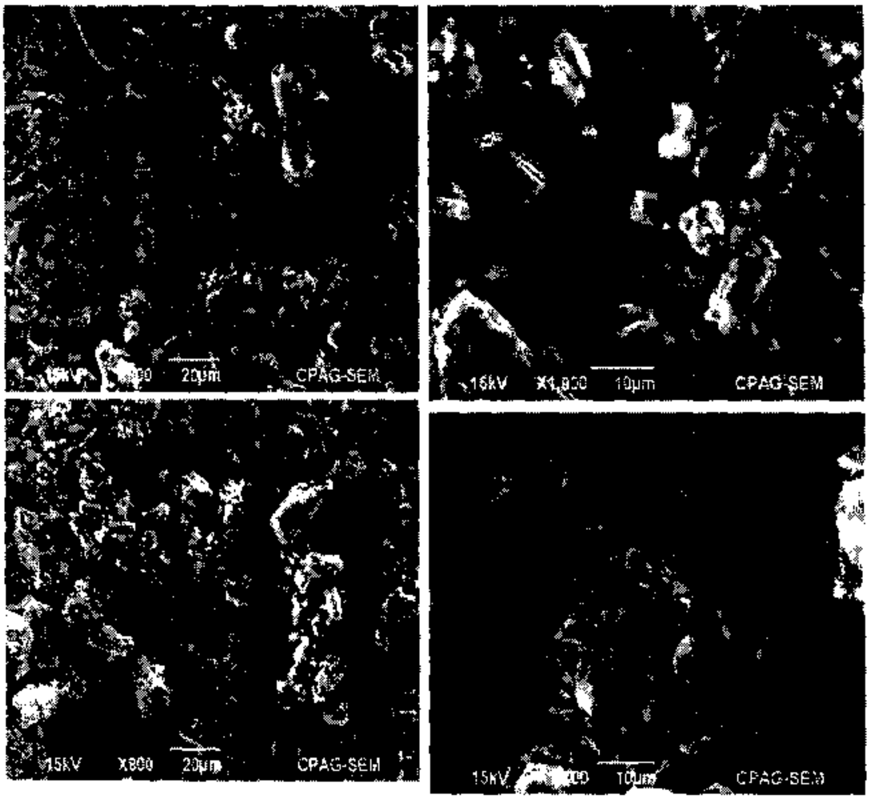


Figure 4.15 MoO3-GO Nanocomposites at different magnification.

Sample 3 Low Temperatures.(135-140Ċ)

The given SEM image given below shoes the composites form of the nanostructures synthesized at comparatively low temperature for about130-140Ċ.

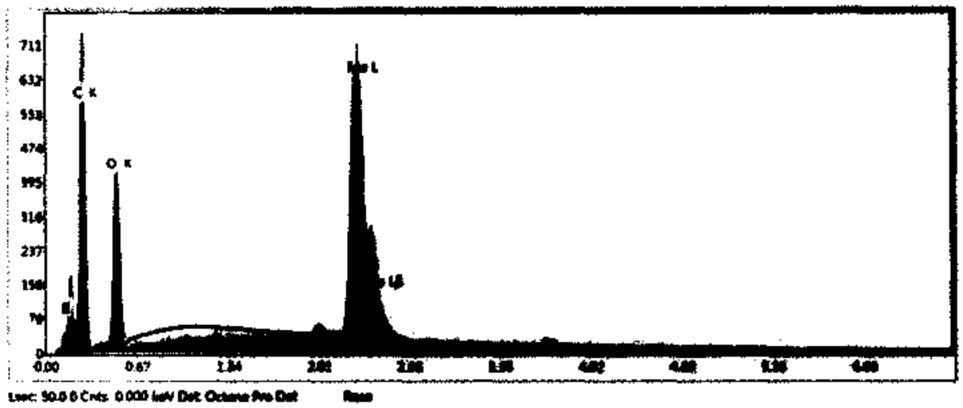


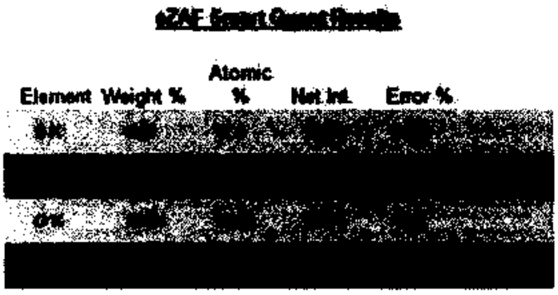
4.16SEM image for MoO3-Go nano powder at low temperature.

4.7 EDX ANALYSIS.

EDAX analyses were carried on to get the appropriate information and elemental analysis of the nano composites of MaoO$_3$ –GO nano composites thin film.

The spectra show the presence of the different essential elements in the composite form. The corresponding peaks in the EDAX data confirm the presence of Mo, C&O respectively. This observation do supports the presence of MoO$_3$ and GO phases in the composites oxides thin film used as an electrode for the PEC cell.

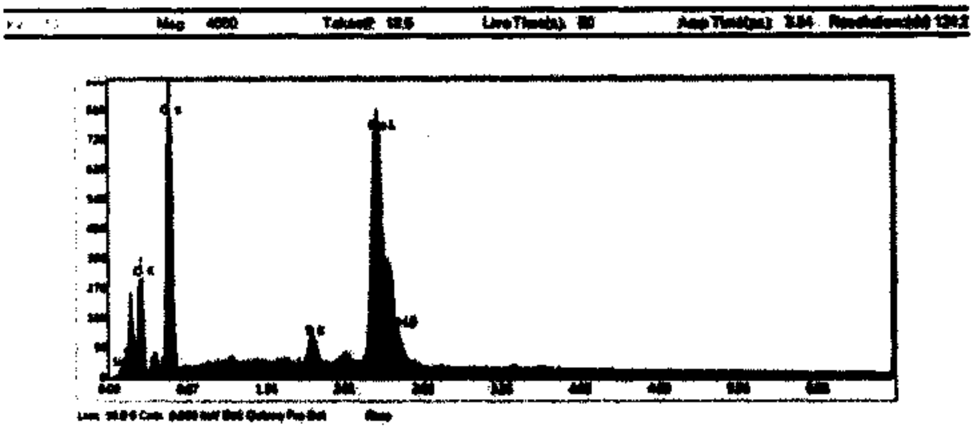



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

4.17 EDX analysis of MoO$_3$-GO nanostructured thin films.

From the SEM images the presence of graphene layers were not very much visible .EDAX TEM was used to verify the existence of the Composite materials in thin film. Similarly the second sample was studies under EDXA and about 51 weight % of Molybdenum and 14 weight % of carbon was visible in the EDXA elemental analysis.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

4.18 EDX Analysis of MoO_3-Go sample 2

The below image show the area selected for the EDAS analysis that was investigated for the existence of the MoO_3 and GO deposited on the film. For the 3rd sample the EDAX elemental analysis was carried on through the same way to get the clear existence of MoO_3 and GO in the materials deposited on the ITO coated thin film.

In the second check of the area under observation it was found that 41weight % of MoO_3 along with the Graphene were present in the composites form. These images ABCD given below indicate the selected areas for the checking of the existence though EDAX. The respective figure of the selected area has is given on the next page.

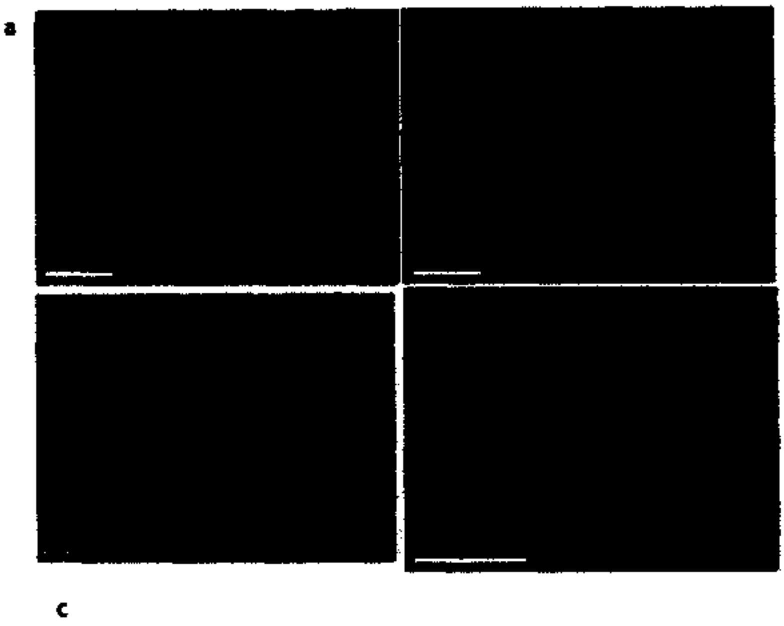


Figure 4.19 selected areas of EDX sample

4.8 Electro chemical behavior.

The below figures exhibits the electrochemical behavior of the electrodes upon which the MoO_3-GO composites were deposited .The linear sweep and cyclic Volta grams were obtained in 1M NaOH solution at comparatively different scan rates.

4.8.1 Linear Sweep Voltametry.

The results under discussion were obtained in the dark condition in 1M NaOH in a three electrodes beaker type cell. The figure abcd given below were the linear sweep volt grams obtained within the potential; ranges of 0.1-0.7Ev, 0.2 -1.2EV , 0-0.6 EV and 0.2 -.9 ev at a scan rate of 50Mv/s.

In the figure at 47.8mv the current amounted at 72.64µA which followed the linear increase ahead showing the electrochemical response. In the figure b at 911.6 mV the current leap was recorded at 210.7µA .the trend is followed ahead up to the specified limits which showed a good response of the electrode.

In the next run the photocurrent response was shown at 292.7Mv where the current response was 14µA. In case of d the response was given at 449.6Mv for about 123µA but as reaction takes place and it goes down to 110µA at 493Mv/s. similarly at 706 mV the current response is 176mA that goes on increasing linearly by showing good photo electrochemical response.

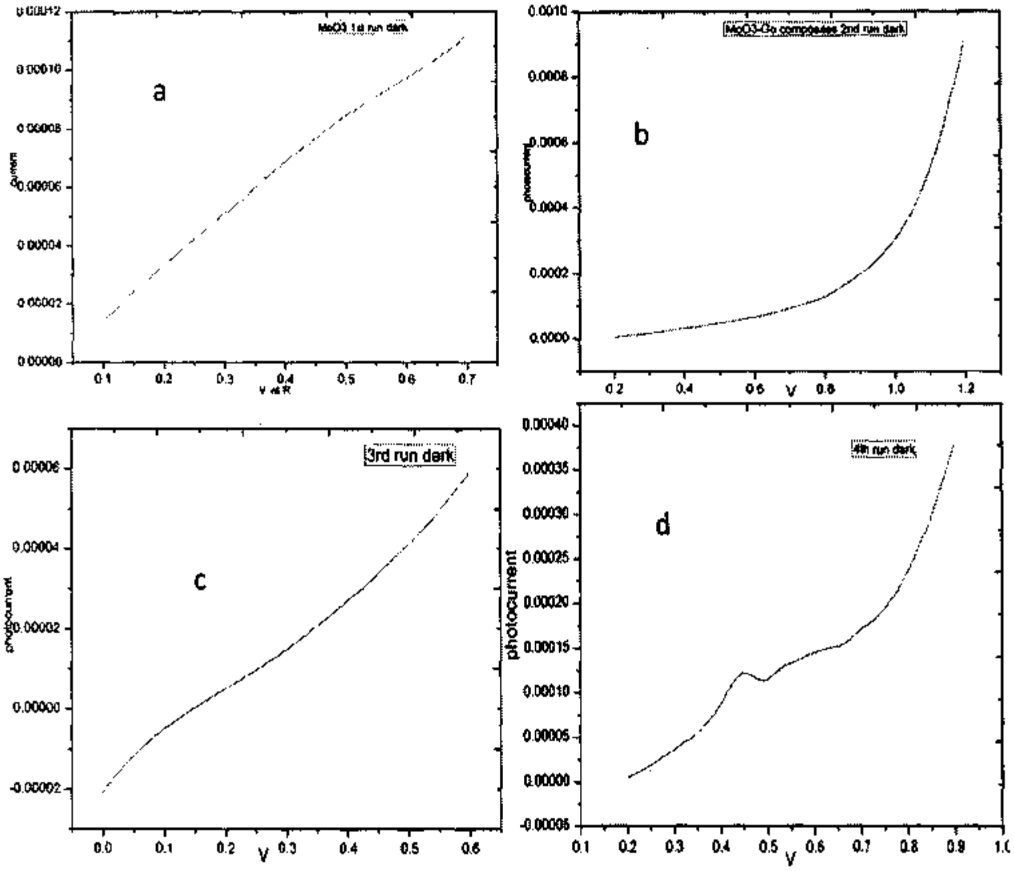


Figure 4.20 LSV curves of MoO_3-GO nano electrodes sample 1.

LSV's Sample 2

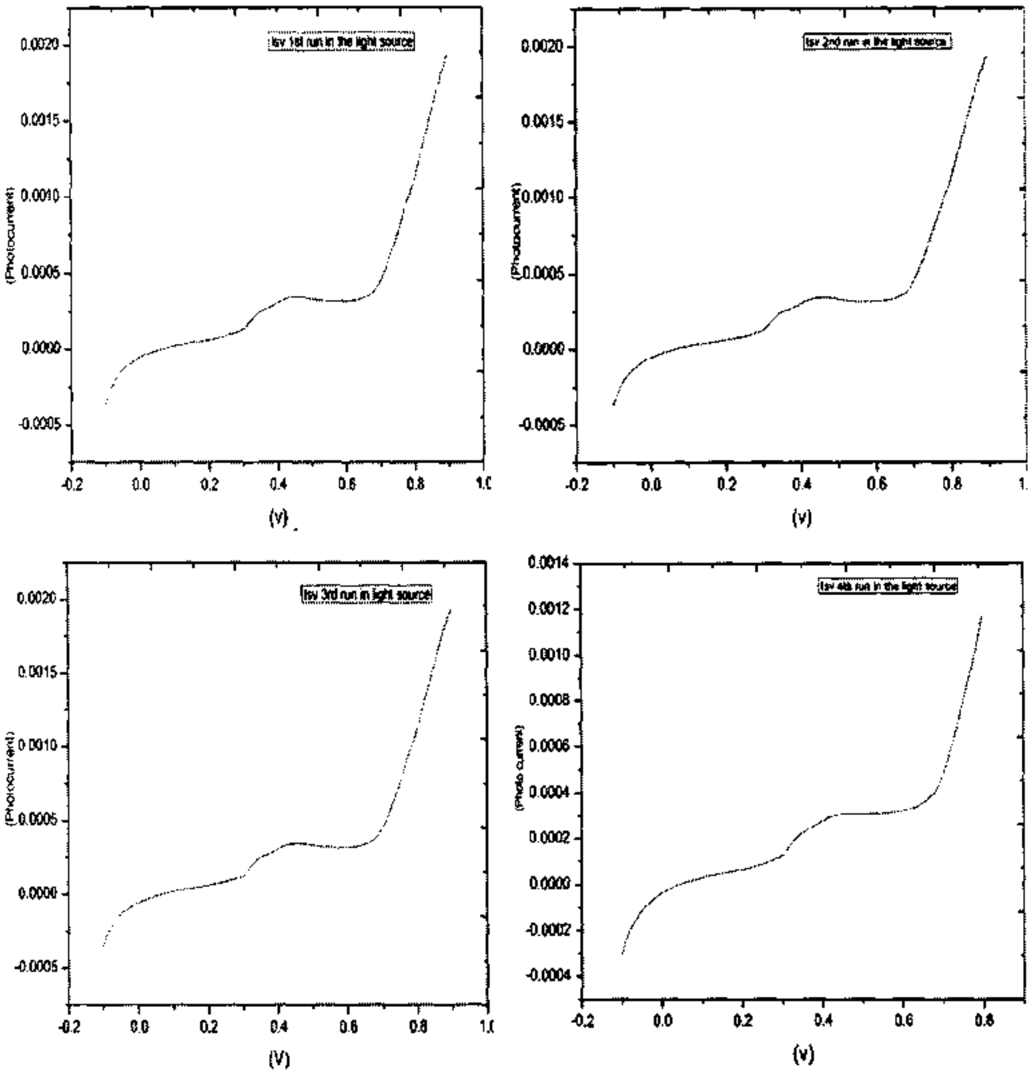
The same fashion was followed for the second sample as well and promising photo electrochemical response was observed.

4.8.2 LSV curves of electrodes under the source of light.

While studying the electrochemical behavior of the prepared electrodes, artificial sun light source was used as well. The purpose was to see the comparative performance of the electrodes in the presences of the light as well. In the first run at the potential of 419mv, the current of amount 250.6μA was recorded under the sun light which remained stable till the potential grad of 605 mv that responded 318μA current and followed the increasing fashion.

In the second run under the light source at 330mv the increasing behavior of the current was shown which was 207μA that increased up to 1.6 m.A.

In the 3rd and 4rh run of the sample under the light source the electro chemical response was considerably good. In the 3rd run at 446 mV potential the current response was 329 μA that increased sharply up to 1.9m.A .Similarly in the 4th run under the illumination at 310 m.V the response was 268μA that followed comparatively stable fashion electrochemically. The current –voltage response has been shown in the figure on the next page in detail.



LSV curves for the electrodes under the source.

4.9CyclicVoltametery.

To check the cyclic behavior of the prepared electrodes, the cyclic Voltametery was performed by arranging the cell structure while having a reference electrode in 1M NaOH solution. . The CV was performed for 10 cycles at comparative scan rates on 10 mv/s, 20mv/s 30mv/s, 40mv/s 70mv/s 80mv/s and 100mv /s as well. In the very first cycle the charging response was not as linear as to be observed. But in the rest of the cycles both the charge –discharge behavior was good enough. The figure given below shows the cyclic response of the first electrode.

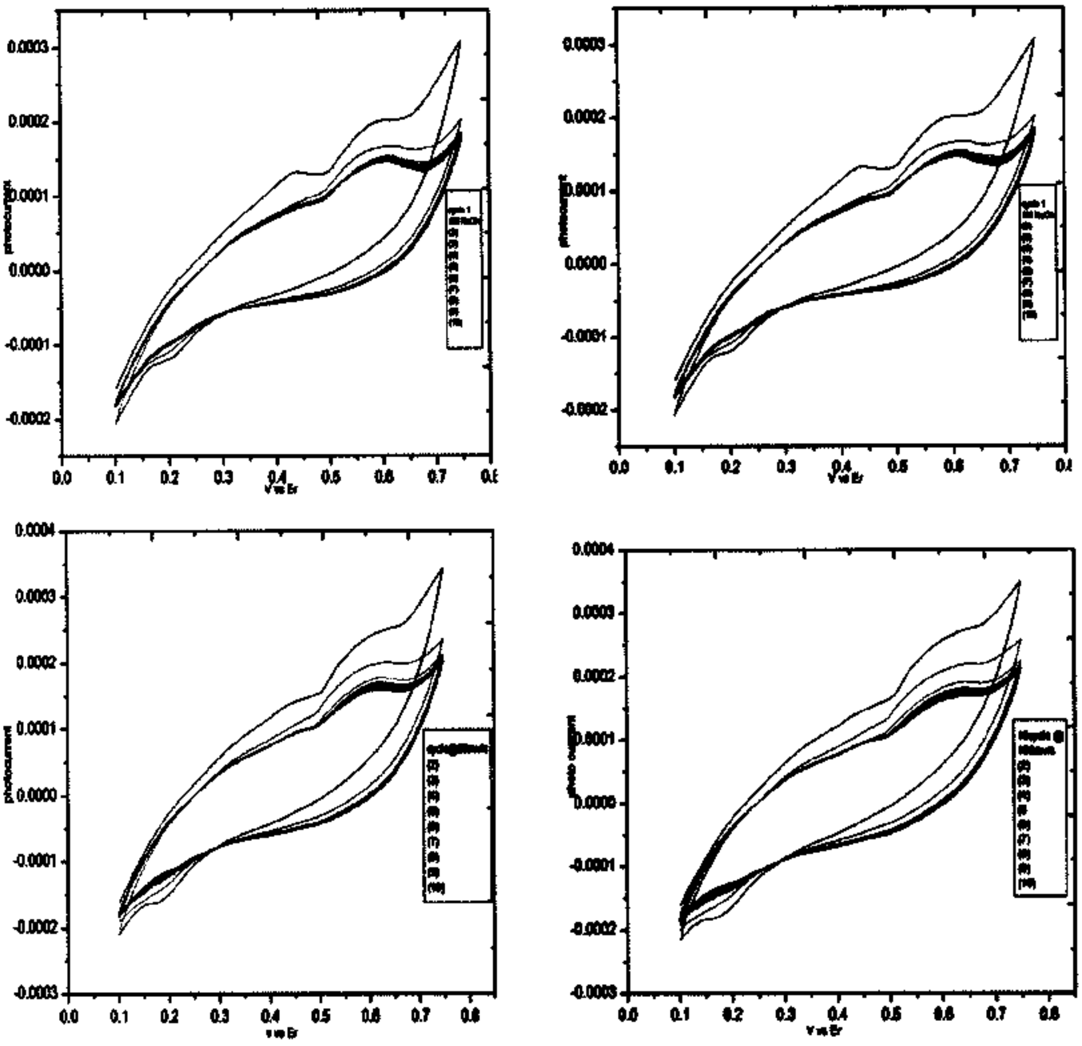


Figure 4.21 CV curve for MoO$_3$-GO 1st electrode

4.9.1 CV curves for2nd ELECTRODE.

For the second electrode the cyclic response is shown below. The response of 10 specified cycles at variable scan rate is considerably balanced one which shows the good cyclic behavior of the prepared electrodes. The scan rate was from 10 mv/s to 100 mv /s respectively. The reading was taken in the absence of the light source.

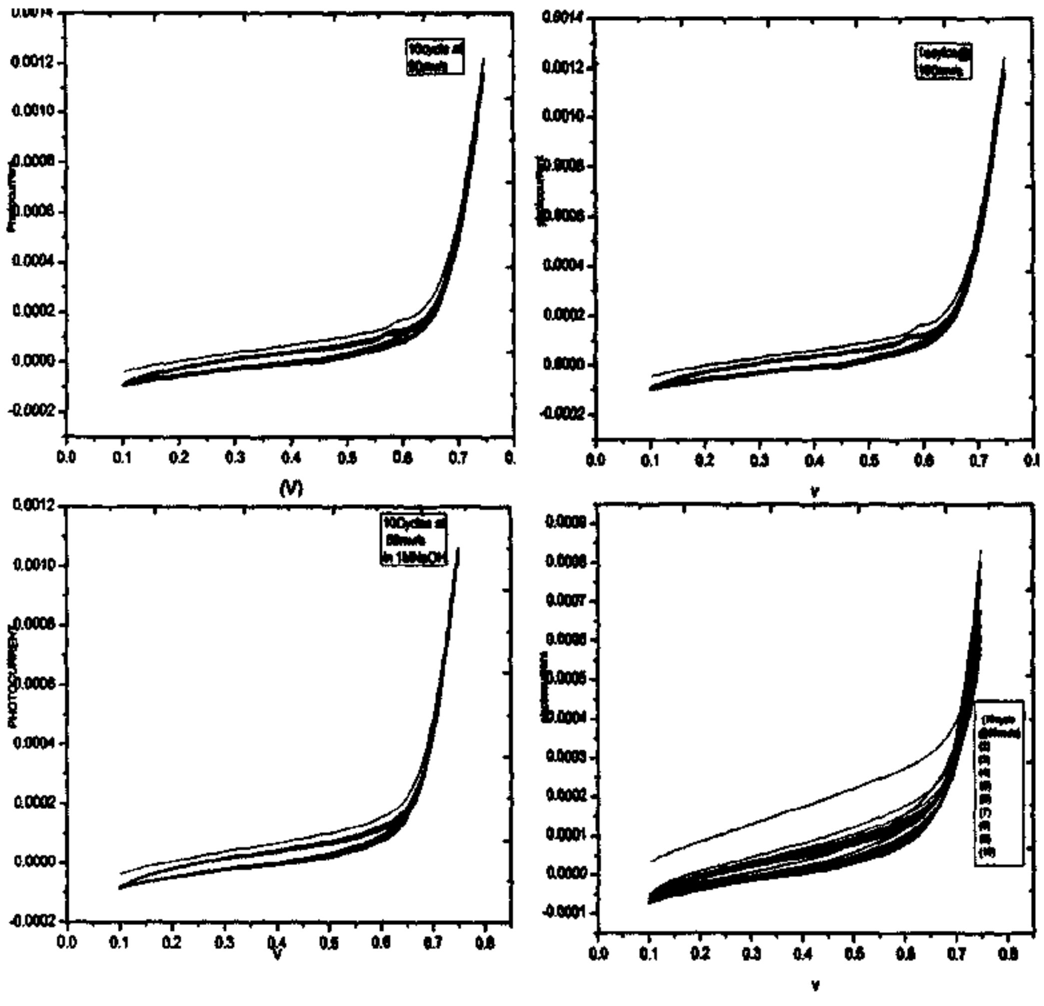


Figure 4.22 **CV CURVE OF 2nd electrode**

4.9.2 CV curves for 3rd Electrode.

The same method was followed to check the cyclic nature of the 3rd sample at variable scan rate. At 10mv/s the first run was not as stable as to be but the cycles ahead shows comparatively stable response of charging and discharging behavior.

The below figure shows clear presentation of the cyclic properties of the 3rd electrode based upon the MoO3- Go nanocomposites.

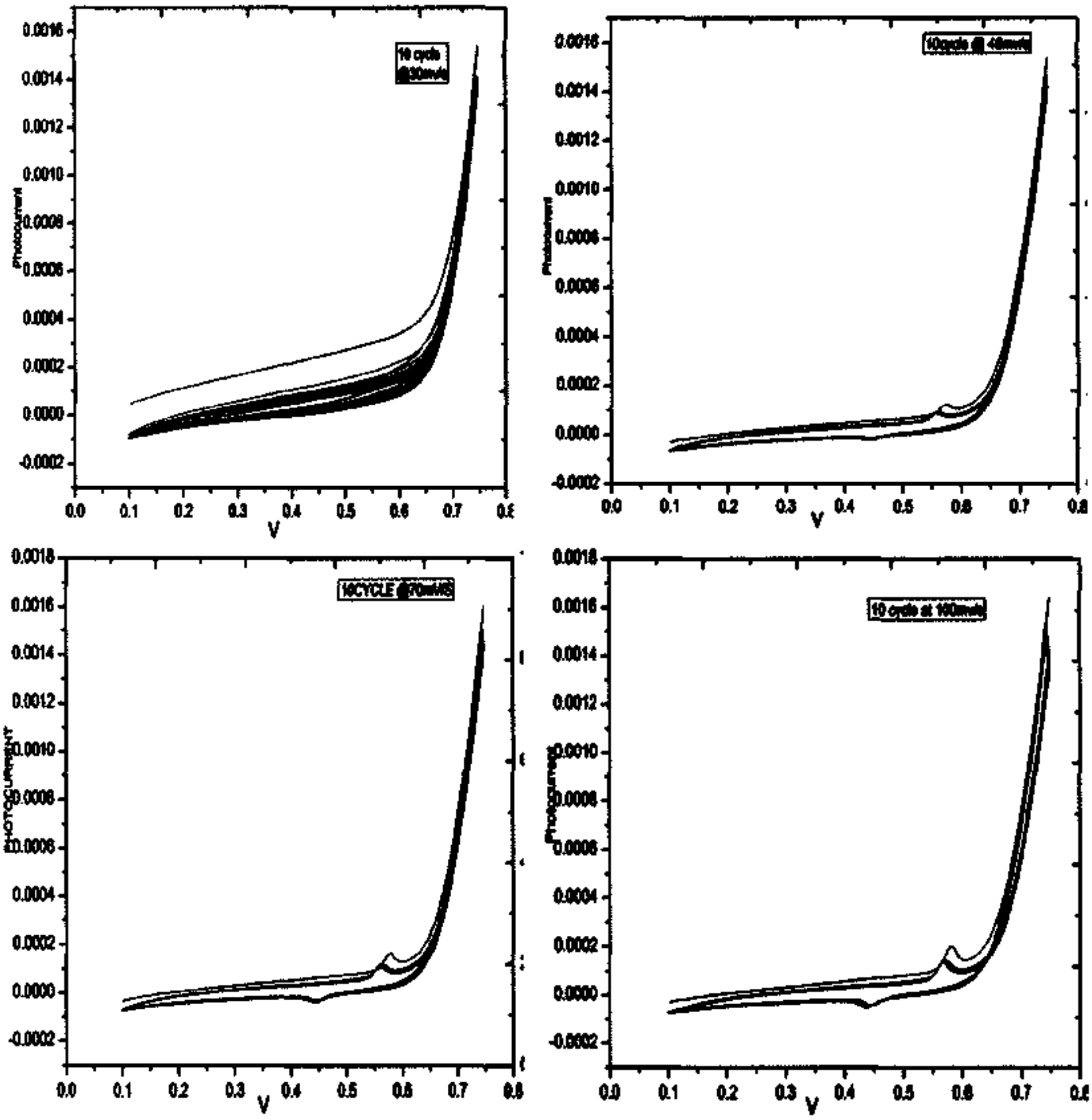


Figure 4.23 **CV curve for 3rd Electrode**

Conclusion.

The new energy materials have taken a quantum leap in the present day R&D .Following the concepts graphene nanoparticles were synthesized hydrothermally. To conclude, the work has resulted in the fabrication of composite photo anodes fabricated from hydrothermally prepared MoO_3 and GO that shows a significant increase in the photocurrent response upon illumination under solar radiation. Compared to around 300 micro ampere currents, the composite photo anodes registered photocurrents up to 1.9mA. The structural study of the Go-r GO was carried on through XRD. The band gap was calculated by caring on the UV-DRS techniques. In the second phase of the experimental work, MoO_3 nanoparticles were synthesized solo thermally. The MoO_3-GO nanocomposites were synthesized in different compositions for which all the necessary techniques were followed. The 3rd phase of the work comprised of deposition of nanocomposites on ITO to get photo anode as energy storage and conversion material. The result was promising for the fabricated electrodes with considerable charging and discharging potentials. The outcome of the work in shape of electrode material can be used for Li ion batteries, super capacitors and anode for Phoroelectro chemical cell used for solar water splitting.

Future Planes

- Synthesizing well isolated nanoparticles with feasible grain size.
- Reutilizing the already fabricated electrodes for prototype photo electrochemical cell.
- To check the STH efficiency of cell for solar water splitting and electrodes for Li ion batteries and supercapacotors.
- Investigating known and exploring unknown catalysts for the purpose of energy storage and conversion material.

References.

1. Chithambararaj, A. and A.C. Bose, *Investigation on structural, thermal, optical and sensing properties of meta-stable hexagonal MoO3 nanocrystals of one dimensional structure.* Beilstein journal of nanotechnology, 2011. **2**(1): p. 585-592.