Chapter-7

7.1 Conclusion

In this thesis work, photovoltaic redox couple mechanism have been developed by using thermoplastic polyurethane ionomer gel in Quantum dots sensitized solar cell. Thermoplastic polyurethanes are containing hard and soft segments in their polymeric chains. Electrochemically active pendant group (sulfonate group) have been introduced on the hard segment contents of the polymeric chains. Semiconducting characteristic of polyurethane ionomer was observed by the variation of extent of functionalization and various kinds of tagging of nanomaterials on the polymeric backbone chains. Electrolyte active redox groups played an important role in photovoltaic reactions. For the conversion of solar energy via quantum dots sensitized solar cells the functionalized redox active urethane linkage behaves as redox mediator during the photovoltaic reaction. The incorporation of the sulfonate pendent group at hard segment with the various degree of functionalization the functionalized polyurethane polymer exhibited ionic conductivity. In this thesis work we have focus on the functionalization of the hard segment and attachment of nanomaterials on the main polymeric backbone chains to improves the ionic conductivity of polymer. The photovoltaic redox active mediator has been developed with different extent of functionalization of the hard segments and the chemical tagging of nanomaterial with polymeric chains to improve the ionic conductivity. Functionalized thermoplastic polyurethane has more attention due to good adhesive character, corrosion resistant ability and high electrochemical stability. The incorporation of the pendent ionomeric group (sulfonate group) on the hard segments, polyurethane semiconducting nature was observed. Thus, various types of polyurethane have been studied through structural modification and different extent of the functionalization at the hard segments contents to investigate the solar characteristic photovoltaic performance. The major concluding remarks of the thesis are explained below chapter wise.

In ***Chapter 3*** thermoplastic polyurethane have been synthesized by the reaction of the MDI, PTMG and butanediol at hard segment contents of 30 %. The polyurethane hard segments have been functionalized through sulfonating agents (NaH, propane sultone) to generate the mono-negative charge in polymeric chains. The degree of hard segment functionalization increases with increases the weight ratio of the sulfonating agents. To confirmed the structural and functional change in polymeric chains the different kinds of spectroscopic techniques was used. Thermal resistant capability was enhanced due to presence of covalently linked ionic group segments. The crystalline characteristic of polyurethane ionomers was observed due to introduction of the ionic pendent group in polymer. UV-visible absorption spectroscopy was used to confirmed the variation of the functionalization. The red shifted absorption peaks were observed for the functionalized polyurethane polymer and these peaks were shifted due to variation of the energy gap between the HOMO-LUMO energy levels and the for optimized the HOMO-LUMO energy levels and their gap ware controlling the extent of functionalization. The pure polyurethane is inactive in electrochemical response due its insulating behavior. While after the introduction of ionomeric pendent group at hard segment of the polymeric chains, the ionic segment offers charge redox active center at polyurethane and the redox active behavior and intense sign of reduction and oxidation peaks was observed. the hydrophilic ionic pendent group generate the electrical regions on the surface of the polymeric chains. The ionic conductivity has been studied in solution phase by tuning the composition of the electrolytic active anionic pendent moiety across the polymer hard segments. The highly polar organic solvent was used to prepared the ionomer gel. The CdSe quantum dots was synthesized with different particles size by using the selenium precursor through hot injection method. And CdS quantum dots are synthesized through solution mixing method and to stabilized the surface structure of the CdS quantum the Disodium salt of ethylene diamine tetraacetic acid was used. The blue shifted UV- visible absorption spectra of CdS and CdSe of synthesized quantum ware used to investigate the quantum confinement effect. The cosensitization effect was also observed through the measurement of light harvesting efficiency. The light harvesting efficiency was high in case of CdS/ CdSe loaded quantum dots as compared to single loaded CdS either CdSe quantum dots. The particle sized of CdS and CdSe quantum dots was estimated by using the TEM measurements. The average particle size for CdS and CdSe quantum dots are 5 and 4 nm respectively. The band gap of the synthesized quantum dots is calculated by using the Tauc's plots and the calculated optical band are 2.23 and 2.16 eV for the CdS and CdSe synthesized quantum dots. The photovoltaic device was fabricated with layer structure by using the doctor blade and spin coating techniques. The photovoltaic characteristic curve and photovoltaic reaction was realized with the measurement of the photocurrent density and open circuit voltage of the fabricated QDSSCs devices. The electrolyte characteristics was observed with the open circuit voltage range (0.46 – 0.74 V) in the fabricated QDSSCs. The photovoltaic power conversion efficiency 1.51 % was achieved as hole transport carrier.

In ***Chapter 4*** graphene oxide was chemically tagged on polymeric chain of the thermoplastic polyurethane polymer with varying the lengths via chain extenders such as butanediol. Polyurethane was functionalized by attachments of sulfonate group to the main chain. 1HNMR, FTIR and UV spectroscopic measurements was used to confirmed the chemical tagging of GO in polymer chain. The electrical resistance was decreases due to presence of graphene sheet. And the enhanced the conductivity of GO-tagged polyurethane by incorporation of ionic polar moiety and a suitable semiconducting gel was developed for the QDSSCs. The HOMO – LUMO energy levels are depend upon the extent of functionalization, ware measured by using the cyclic voltammetry measurements. The active materials such as CdS and CdSe quantum dots synthesized by using the suitable capping agent and their dimension ware measured through TEM bright field images. The optical band gaps ware calculated from Tauc's plots of the synthesized quantum dots by using the UV-visible measurements and the cosenitized effect was observed in case of CdS/CdSe loaded quantum dots by measuring the light harvesting efficiency of prepared quantum dots was measured for have been synthesized via in- situ polymerization reaction with contents 30 % hard segments contents. Chemically GO-tagged functionalized polyurethane ionomer shows the higher ionic conductivity, good thermal stability, and high corrosion resist ability. The electrolytic activity was explored through structural and functional change in polyurethane ionomers.

In ***Chapter 5*** The successful functionalization was carried out of the MWCNTs and further tagged with the main chain of the polyurethane polymer. The sulfonation of the MWCNTs tagged polyurethane polymer was takes places by using the propane sultone as a sulfonating agent. The all functionalization was confirmed through ^{1}HNMR, FTIR and UV-vis spectroscopic measurements and Raman spectroscopic technique was also used the confirmed the functionalization of polymer. The thermal stability measured through the using the thermogravimetric analysis measurements and the melting temperature was estimated through differential scanning calorimetry. The carbon nanotubes increase the electrical conductivity of the thermoplastic polyurethane due to presence of π-framework in tubes which provide the medium for the transportation of the charge carries. The ionic polar pendent moiety was further enhanced the conductivity of the CNTs-tagged PU (SPU-CNT) and electrical conductivity of the prepared polymer is 1.367×10^{-4} S cm^{-1}, hence, the developed polymer is suitable for the preparation of gel electrolytes (hole transport materials) for QDSSCs. The CV measurements was used to calculate the HOMO and LUMO energy levels of the functionalized polymer. The active materials $CuInS_2$ QDs was synthesized by using the DDT as a capping agent and their particles sized was measured through TEM bright field images. The optical band gap of the synthesized QDs and relatives light harvesting efficiency of photoanode was calculated by using the light absorption measurements. Three type of the counter electrode was used in QDSSCs such as platinum, nickel and gold. The fabricated devices by using the SPU-CNT polymer gel electrolytes with gold as a counter electrode shows the better performance and the power conversion efficiency 0.81 % was obtained. The devices show the high performances is due to suitable matches of the HOMO energy levels of the developed polymer electrolytes with the energy levels of the gold counter electrode.

In ***Chapter 6*** The graphene oxide is successfully tagged with polyurethane chains through three stages of polymerization technique and prepared the gels in organic solvent and studied the effect of chemical tagging on gelation behavior. Dramatic enhancement of gelation rate is observed when graphene is chemically tagged with polymer. Pure PU forms a weak gel while graphene tagged-PU formulate a strong gel as evident from high gel melting and better solvent retention properties. Graphene oxide interact nicely with polyurethane chains as evident from the UV and FTIR peak shifting as compared to physical mixture of the two components. The structure formation and homogeneity of morphology alter considerably when GO is chemically tagged with PU chains. The details rheological studies have been measured to understand the effect of chemical tagging of GO in polyurethane. The gel strength significantly increases in chemical tagging of GO in PU while viscosity enhances considerably as compared to pure PU and physical mixture gel. The stress relaxation modulus as a function of time has been measured to understand the elastic effect caused by the chemical tagging of GO with PU.

7.2 Scope of the Future Work

- Explore the polymer / quantum dots hybrids materials for solar cells application.
- Explore the new polymer gel electrolytes with high electrical conductivity for improve the devices performance.
- Using the suitable alloy of quantum dots as an active material in solar cells application.
- Doping of the metal in green quantum dots.