Reduced Graphene Oxide Based Composites: Carrier Transport Properties, Photoinduced Charge Transfer under Continuous and Ultrafast Irradiation

Synopsis of the Thesis to be Submitted in Partial Fulfillment
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by

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1 Abstract

Electrically conducting network comprising of graphene-based materials are immensely versatile and have a broad area of potential applications. Chemically functionalized graphene and their composites with organic (π-conjugated molecule) and inorganic (metal chalcogenides) counterparts offer exceptional optical, electrical and mechanical properties which are recently being explored for advanced electronics, photonics, and energy harvesting applications. Therefore, clear understanding of the basic physical properties of these materials like charge carrier mobility, conductivity, trap density, charge transport mechanism etc. that can make an impact on the device performances are very crucial for potential applications. In this dissertation, charge transport as well as optoelectronic properties of reduced graphene oxide (RGO) and RGO based composites (RGO-zinc telluride (ZnTe), RGO-zinc tetra-tert-butyl phthalocyanine (ZnTTBPc)) have been investigated. The structural, morphological properties of the synthesized samples have been studied by various spectroscopic and microscopic techniques.

DC conductivity measurements indicate that the charge transport mechanism is consistent with variable range hopping (VRH) in RGO, RGO-ZnTe, and RGO-ZnTTBPc below some temperature around $\sim$280K, whereas at higher temperatures (290K-473K) the charge transport follows Arrhenius-like behaviour in RGO and RGO-ZnTe composite. RGO-ZnTTBPc, on the other hand, possesses VRH mechanism upto $\sim$320K above which the solid to liquid crystal mesophase transition intervenes. AC conductivity of RGO-ZnTe suggests Debye-like relaxation process caused by quantum mechanical tunnelling between localized sites distributed within the band gap in the whole temperature range. Moreover, magnetization measurements and electron paramagnetic resonance spectra show paramagnetic behaviour of RGO-ZnTe, despite the diamagnetism of pure RGO and ZnTe. Temperature dependent current density-voltage characteristics of RGO and RGO-ZnTTBPc in top-bottom electrode configuration show a transition from Ohmic to trap dominated space charge limited current conduction at higher applied bias voltages.

The synergistic effect between RGO and the semiconducting counterparts has been investigated by measuring photosensitivity, photocatalytic activity, photovoltaic performance, and ultrafast ($\sim$100 fs) nonlinear optical (NLO) responses. RGO-ZnTe and RGO-ZnTTBPc show one order higher P values compared to their semiconducting counterparts due to efficient charge transfer from semiconductor to RGO sheets. Comprehensive mea-

surements of nonlinear absorption by using open aperture z-scan technique on different RGO-ZnTTBPc heterojunctions show a significant enhancement in NLO properties compared to pure RGO and ZnTTBPc in 37 - 130 GW/cm^2 intensity range measured with 540 nm femtosecond pulses. Three times higher reduction rate constant in photoreduction of aqueous pollutant 4-nitrophenol were observed in RGO-ZnTe as compared to pure ZnTe. Moreover, RGO-ZnTTBPc heterojunctions have been used as an active layer in organic photovoltaic devices and show a maximum power conversion efficiency of 1.02%. These results suggest that RGO based donor-acceptor systems would provide a platform for manifold optoelectronic as well as photonic device applications.

2   Motivation

Silicon acts as the primary building block of electronic industry due to its excellent semiconducting behaviour, stability, and high device performances since last sixty years. In modern technology, the semiconductor industry is looking for minimized size of devices along with low cost, lighter weight, and flexibility [1]. But silicon based electronic devices have some operational difficulties on further minimization of device size like heating effect, leakage current etc. To find cost effective, easy to fabricate alternative to silicon, researchers have put tremendous effort to replace silicon with some semiconducting materials having tunable band gap, flexibility, and high charge carrier mobility. Carbon based materials such as graphene, chemically functionalized graphene derivatives, carbon nanotube etc. are considered to have high charge carrier mobility in comparison to silicon [2]. Furthermore, the energy band gap of graphene, chemically functionalized graphene derivatives, and organic semiconductors can be tuned by controlling the defect fraction or doping concentration present in the sample [3]. So, it can be visualized that carbon based materials and organic semiconductors can be used as efficient replacement of silicon in semiconductor industry.

It is validated in last one decade that carbon-based materials and its different composites are promising candidates for various applications like photodetector, biosensor, energy storage, photovoltaic, environmental etc. [4, 5]. On the other hand, organic semiconductor-based bulk heterojunction exhibits tremendous possibilities in different applications such as solar cell, light emitting diode, field effect transistor etc. [6, 7]. In

view of all these advantages, in this thesis, graphene-based composites have been chosen for detailed investigation in terms of charge transport processes, magnetic properties, ultrafast nonlinear optical behaviour, and possible optoelectronic applications of the systems.

3 Introduction

In early 1980 three major forms of carbon such as amorphous carbon, graphite, and diamond have been distinguished. At present time, researchers are working with a wide range of carbon allotropes consisting of different stable forms namely graphene, graphite, fullerene, carbon nanotube etc. Each of these stable forms exhibit different exciting properties. Buckyball was the first form of fullerene, discovered in 1985 in which sixty carbon atoms are arranged in the form of a soccer ball, known as C_{60} fullerene. In 1991, a Japanese scientist noted concentric hollow cylinders of carbon atoms which is termed as carbon nanotube [8]. Later in 2004, Novoselov *et al*. experimentally discovered another two dimensional, stable form of carbon, known as graphene [9].

Theoretically it was stated that two dimensional materials are not stable thermodynamically and cannot exist due to thermal fluctuation which causes change in interatomic distances [10]. But researchers experimentally discovered that the carbon atoms in graphene are strongly bonded to each other and the carbon-carbon bonds cannot be disrupted by thermal fluctuations even at room temperature. Since last 15 years graphene has been widely used and it has attracted a great attention of research community due to its excellent electrical [11], mechanical [12], and thermal [13] properties. Unlike other conventional semiconducting materials, it has a unique electronic structure which is the key to its exceptional properties. It is known that graphene has very high crystalline nature so that charge carriers can move several microns path in it without scattering which results in high charge carrier mobility.

Graphene sheet with different thickness can be obtained by using various techniques like mechanical exfoliation or peeling off layers from different graphitic materials, namely highly ordered pyrolytic graphite (HOPG), crystalline graphite, natural graphite etc. In the very first experiment, graphene sheets were mechanically exfoliated from HOPG and this remarkable work awarded the authors Nobel Prize in Physics in 2010 [9]. This

notable discovery was unique but it has limitation towards mass production. Later, researchers have developed many techniques to synthesize graphene of different dimensions like chemical exfoliation [14], epitaxial growth on silicon [15], chemical vapour deposition [16] etc. The synthesis techniques must be cost effective, easy to achieve, and there should be large scale production for application purpose. Among different synthesis methods, chemical exfoliation technique is more preferable for large scale production as well as different applicability aspects. On the other hand, the hydrophobic nature of pristine graphene prevent it to disperse in water which is one of the major shortcomings of this stable forms of carbon. However, despite having so many exciting properties, it is not suitable for optoelectronic device application due to its zero band gap [17]. To overcome these constraints, researchers have modified graphene sheets by functionalization with various oxygen functional groups (OFGs)/ different semiconductors – named as graphene derivatives/ graphene-based composites. A brief discussion on graphene derivatives and graphene-based composites are described below.

The chemical exfoliation of graphite causes the oxidation of graphene, known as graphene oxide (GO) which was synthesized by Hummers and Offeman by generating different oxygen functionalities on the graphene sheet [18]. The structure of GO can be seen as graphene-like structure decorated with various OFGs like hydroxyl (-OH), carbonyl (O-C=O), carboxyl (-COOH), epoxides (-O-) etc. on the surface or basal plane giving rise to different sp^2 to sp^3 hybridized carbon ratio (carbonyl, carboxyl are located at the sheet edge and hydroxyl, epoxides are at the basal plane). GO can be considered to be composed of two randomly distributed domains: (i) graphene like domains with sp^2 hybridized carbon atoms and (ii) oxidized domains having sp^3 hybridization due to the presence of OFGs. These oxidized domains destroy the long range conductivity of GO breaking the conjugated network of graphene domains and make GO electrically insulating [3]. The removal of these OFGs from GO can partially bring back the sp^2 conjugated network depending on degree of reduction which allows the creation of percolation pathways among intact graphene domains. This reduced from of graphene is known as reduced graphene oxide (RGO). There are many popular technique to reduce GO to RGO such as epitaxial growth [2], thermal treatment [19], chemical reduction [20], hydrogen or ammonia plasma treatment [21], infrared reduction [22] etc. Among these methods chemical reduction of GO to RGO is most widely used method due to its low

cost and easy processing [23].

The high electrical conductivity, excellent mechanical, and thermal properties of graphene make it an efficient filler material in graphene-based nanocomposite systems for multifunctional applications [24]. The incorporation of a semiconducting material into the filler leads to drastic change in different physical and electronic properties of the composite system compared to individual components. In last ten years, it is reported that RGO based composites like RGO incorporated nanorod, nanoparticle, nanofiber or conjuagated organic polymer are remarkably favourable for energy storage, optoelectronic, photovoltaic, environmental, sensing, and nonlinear optical applications [5, 25]. Researchers have developed different techniques to synthesis metal-based nanostructures. The methodologies can be broadly classified into two parts, namely (i) vacuum-based and (ii) solution-based. Vacuum-based techniques are primarily a deposition method which takes place under moderate to high vacuum. Typical examples of these methods are chemical vapour deposition, pulsed laser deposition, molecular beam epitaxy, sputtering etc. These are very powerful techniques to fabricate efficient devices but it requires expensive instruments. On the other hand, solution-based techniques are basically chemical reactions in liquid phase and it does not require costly instruments, easily achievable, and large scale of products can be obtained. Examples of this process are solvothermal, hydrothermal, sol-gel method, thermal treatment, etc. If in a reaction, water is used as the solvent then the process is termed as hydrothermal process whereas if the solvent is any organic solution then this method is named as solvothermal process. We have followed solvothermal method to synthesis RGO and RGO-ZnTe composite.

In modern technology researchers are interested in conducting composite materials of a polymer or semiconductor with a filler materials having good environmental stability and excellent electrical conductivity. It is reported that the incorporation of a conducting filler materials like RGO into the less conducting matrix creates percolating paths which allows charge carriers to move easily through the composite system giving rise to enhanced electrical conductivity [26]. Moreover, under illumination, electron can transfer from valence band to the conduction band of the material by absorbing photons by generating an electron-hole pair (called exciton). In pure semiconductor system, the electron-hole recombination rate is very high which leads to poor device performance. In case of a composite system, the strong interlayer coupling between the donor and acceptor material

reduces the electron-hole recombination probability owing to efficient charge transfer from conduction band of donor to that of acceptor. Consequently, optoelectronic responses (such as photocurrent generation, photocatalytic activity, and ultrafast nonlinear optical property) of the composites are enhanced compared to pure semiconductors [4].

Under the influence of an external electric field across a sample, charge carriers can be driven from one electrode to the other which gives a measure of the conductivity or resistivity of the sample. Though RGO and RGO-based composites are highly conducting, they exhibit semiconducting nature upon temperature change. At low temperature, charge carrier transport is governed by hopping mechanism because of the disorder or defect present in RGO consisting of short range graphitic domains (sp^2) along with oxygen functional groups (sp^3) which act as defect states and cause localization of charge carriers. But with increasing temperature, band conduction $i.e.$ electron conduction from valence to conduction band becomes more favourable due to available thermal energy [27]. There are many well established models to explain the charge transport processes in a disordered system like Mott-variable range hopping (VRH), Efros-Shklovaskii (ES)-VRH, nearest neighbour hopping (NNH), Arrhenius-like behaviour etc. In our work, temperature dependent charge transport processes of RGO and RGO-based composites/heterojunctions have been explained with the help of VRH and Arrhenius-like behaviour.

In last one decade, organic solar cells (OSCs) have gained increasing research interest and emerged as a competitive alternative to conventional silicon-based inorganic photovoltaic devices due to low cost, light weight, flexibility, and easy processibility . Organic solar cell was first fabricated by Kearns and Calvin in 1958 [28]. In recent years, power conversion efficiency (PCE) of OSCs has been improved and they already have achieved the milestone of 10% [29]. Despite of achieving a great progress in this field, the performance of OSCs are still far behind the inorganic cells and several issues like poor air stability and low efficiency of organic cells limit the feasibility for their commercial device applications. The PCE of OSCs has got a major boost with the introduction of bulk heterojunction (BHJ) concept which is composed of an interpenetrating network of organic semiconductor (donor) and an electron acceptor material. The donor-acceptor ratio, sample thickness, type of used solvent and even the postproduction treatment like thermal annealing make an impact on the performance of the OSCs. We have used ZnTTBPc-RGO heterojunction as an active layer in organic photovoltaic devices and the

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charge transport behaviour and optoelectronic properties have been investigated in detail above percolation threshold.

4 Thesis outline

4.1 Chapter1: Introduction: The first chapter of the thesis introduces brief discussion on carbon-based materials such as graphene, graphene derivatives (GO, RGO), and RGO based composites. Different properties of the nanomaterials which differ them from their bulk counterparts are then reviewed. The possible charge transport processes based on dc and ac measurements and various charge carrier mobility measurement techniques of the semiconductor systems are discussed. It includes a brief description about z-scan method to obtain third order nonlinear optical parameters.

4.2 Chapter 2: Synthesis and instrument details: In chapter 2, modified Hummer's method and solvothermal synthesis process (figure 1) have been discussed along with some of the experimental techniques used for structural and morphological characterization of the samples. As already mentioned, primarily the solution based methods were adopted for material synthesis. Among basic characterization methods, X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, UV-visible absorption, and scanning electron microscopy are to name a few. The synthesised materials are either drop casted or spin coated on suitable substrate for electrical characterizations.
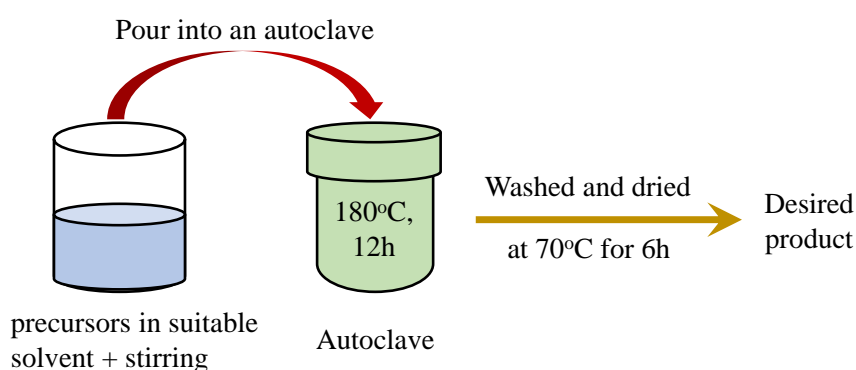

Figure 1: Schematic diagram of solvothermal synthesis route.

4.3 Chapter 3: Investigation of electrical transport processes and magnetic properties of RGO-ZnTe composite: The third chapter includes the electrical transport processes of RGO and RGO-ZnTe composite. It is ob-

served from dc measurements that the charge transport process is consistent with Mott two dimensional (2D)-VRH in RGO whereas RGO-ZnTe follows Mott three dimensional (3D)-VRH mechanism in 85K-280K, confirmed by resistance curve derivative analysis (RCDA) method. At higher temperatures (290-473K), charge transport mechanism is governed by Arrhenius-like behaviour for both RGO and RGO-ZnTe composite. A model where ZnTe nanoparticles are incorporated inside wrinkled RGO layers to facilitate interlayer connections, thus 3D charge transport, has been proposed as shown in figure 2. On the other hand, ac conductivity indicates Debye-like relaxation process caused by quantum mechanical tunnelling between localized sites in the whole temperature range. Magnetic measurements and electron paramagnetic resonance (EPR) spectra show paramagnetic behaviour of RGO-ZnTe composite in 5K-330K despite the diamagnetism of pure RGO and ZnTe at room temperature.
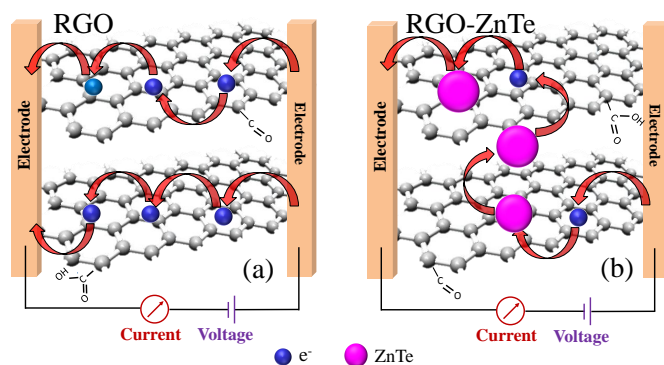

Figure 2: Proposed charge carrier transport mechanism of RGO (left) and RGO-ZnTe (right).

4.4 Chapter 4: Synergistic effect of ZnTe decorated RGO sheets:

This chapter presents the effect of ZnTe nanoparticle incorporation into RGO sheets in terms of photosensitivity (P) and photocatalytic activity towards the reduction of toxic water pollutant. Temperature dependent (100K-460K) P values of ZnTe and RGO-ZnTe show a decreasing trend with increasing temperature which is ascribed to enhanced scattering mechanisms at higher temperatures. One order enhanced photosensitivity along with three times higher reduction rate constant in photoreduction of aqueous pollutant 4-nitrophenol were observed in RGO-ZnTe as compared to pure ZnTe (figure 3). These significant enhancement in photocurrent and photoreduction efficiency is a signature of dispersion of ZnTe on the RGO surface indicating the synergy of ZnTe
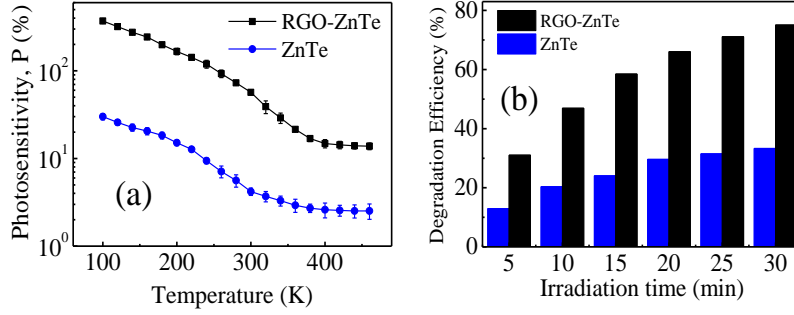
nanoparticles with RGO sheets.

Figure 3: (a) Photosensitivity of ZnTe and RGO-ZnTe different temperatures with error bars. Error bars are small compared to the dimension of points for some data. (b) Comparison of photo degradation efficiency with time for RGO-ZnTe and pure ZnTe.

4.5 Chapter 5: Charge transport mechanism and enhanced light-matter interaction of graphene induced ZnTTBPc above percolation threshold:

Chapter 5 focuses on the electrical conductivity (σ) of ZnTTBPc-RGO heterojunctions with different RGO concentrations (0 - 1 volume fraction). It shows a percolating behaviour with the percolation threshold of $\sim$0.167 vol. fraction of RGO which acts as a filler material in ZnTTBPc matrix. Resistivity data suggests that the charge transport process of ZnTTBPc-RGO is consistent with ES - VRH mechanism in 85-320K. A decreasing trend in photosensitivity values with increasing temperatures are observed in different ZnTTBPc-RGO heterojunctions. Moreover, the synergistic effect of ZnTTBPc with RGO sheets has been investigated by open aperture z-scan technique measured with a 540 nm femtosecond pulses. Open aperture z-scan measurements using 540 nm femtosecond pulses ($\sim$100 fs) indicate a significant enhancement in nonlinear absorption coefficient (NLA) of ZnTTBPc-RGO as compared to pure ZnTTBPc in 37 - 130 GW/cm^2 intensity range (figure 4). Comparative study on P values and NLA coefficient show that among different ZnTTBPc-RGO heterojunctions, $\sim$0.33 vol. fraction of RGO content performs better in those applicability aspects.

4.6 Chapter 6: Photovoltaic performance of ZnTTBPc-RGO bulk heterojunction:

Chapter 6 presents the correlation between minimum of trap density with maximum of photoconversion efficiency and charge carrier mobility for ZnTTBPc-RGO heterojunctions. The donor-acceptor blend has been used as active layer in organic photovoltaic devices and show a maximum power conversion efficiency
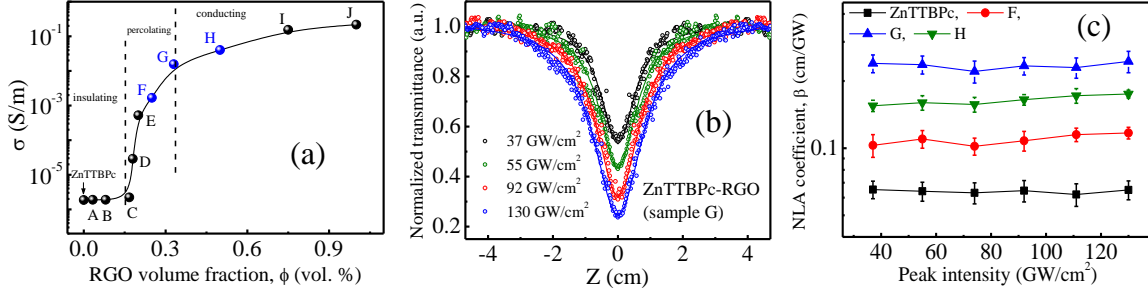
Figure 4: (a) Electrical conductivity of ZnTTBPc-RGO with different RGO concentrations at room temperature. (b) Open aperture z-scan curves ZnTTBPc-RGO (sample G) at different input intensities. Scattered points are the experimental data and the solid lines are the fitted plots. (c) Variation of nonlinear absorption coefficient (β) with intensity for pure ZnTTBPc and different ZnTTBPc-RGO heterojunctions (namely F, G, and H).

of 1.02%. Quantitative analysis on density of trap states indicates that the sample with 0.33 volume fraction RGO content shows the best photovoltaic device performance, also possess minimum trap density and highest charge carrier mobility, tabulated in table 1.

Table 1: Comparison of trap density (N_t), power conversion efficiency (PCE) and charge carrier mobility (μ).

Sample (ZnTTBc:RGO)	N_t (m^{-3})	PCE (%)	μ (cm^{2}V^{-1}s^{-1})
F (1:0.75)	11.60×10^{22}	0.40	2.05×10^{-4}
G (1:1)	1.78×10^{22}	1.02	4.32×10^{-4}
H (1:1.5)	5.62×10^{22}	0.53	2.86×10^{-4}

4.7 Chapter 7: Summary and future scope: Finally, chapter 7 contains conclusions and discussions for future scope.

5 Summary and future scope

In summary, RGO and RGO-ZnTe composite are synthesized by modified Hummer's method and chemical reduction technique. Highly soluble ZnTTBPc-RGO heterojunction has been prepared in DMF solvent with different RGO contents. Temperature dependent

dc conductivity measurements show a crossover of charge transport mechanism from VRH (85-280K) to Arrhenius like behaviour (290-473K) in both RGO and RGO-ZnTe. AC conductivity measurement of RGO-ZnTe composite indicates Debye-like relaxation of charge carriers caused by QMT process throughout the whole temperature range (90-473K). FTIR analysis of different samples suggest that the carbonyl functional group (C=O) is responsible for the paramagnetic behaviour of RGO-ZnTe composite despite the diamagnetic nature of pure RGO and ZnTe at room temperature. RGO-ZnTe composite exhibits enhanced photosensitivity and photocatalytic activity towards the reduction of toxic water pollutant compared to pure RGO and ZnTe which is a signature of synergy between ZnTe nanoparticles and RGO sheet. Comparative study on different optoelectronic properties of ZnTTBPc-RGO bulk heterojunctions with varying RGO contents reveal that the sample with 0.33 volume fraction of RGO content exhibits best photovoltaic device performance, highest photosensitivity along with maximum NLA coefficient. The calculated P values of ZnTe, RGO-ZnTe, and ZnTTBPc-RGO show a decreasing trend with increasing temperature which is attributed to enhanced phonon scattering mechanism at higher temperatures. Our studies provide detailed understanding about charge transport processes and optoelectronic properties of graphene-based materials which can be useful for device applications.

The following points can be addressed in future:

i) Composition dependent studies on different RGO-ZnTe composites can be done for further investigation on electrical transport and magnetic behaviour. The fraction of carbonyl group (C=O) in the sample can be optimized by changing the synthesis condition to tune the magnetic moment of RGO-ZnTe.

ii) AC conductivity measurements on ZnTTBPc-RGO bulk heterojunction can be performed to investigate the conductivity relaxation mechanism in the sample.

iii) In this thesis, the simplest device configuration (ITO/PEDOT-PSS/ZnTTBPc-RGO/Al) has been adopted for photovoltaic performances without no additional hole transport layer (HTL) or electron transport layer (ETL) and we could reach a PCE of 1.02%. The performances of this non-fullerene, cost effective, solution processable bulk heterojunction devices can be improved by introducing HTL/ETL, encapculation etc.

List of Publications

i) <u>A. Sarkar</u>, A. B. Rahaman and D. Banerjee, *J. Phys. D: Appl. Phys.*, (2018), **51**, 095602 (1–10).

ii) <u>A. Sarkar</u>, A. B. Rahaman, K. Chakraborty, T. Pal, S. Ghosh and D. Banerjee, *Applied Surface Science*, (2019), **493**, 279-–286.

iii) <u>A. Sarkar</u>, A. B. Rahaman, K. Chakraborty, T. Pal, S. Ghosh and D. Banerjee (under review).

iv) <u>A. Sarkar</u>, A. B. Rahaman, K. Chakraborty, T. Singha, T. Pal, S. Ghosh and D. Banerjee (under preparation).

v) A. B. Rahaman*, <u>A. Sarkar</u>*, K. Chakraborty, J. Mukherjee, T. Pal, S. Ghosh and D. Banerjee, *J. Phys. Chem. C*, (2019), **123**, 15441–15450 (*equal controbution).

vi) A. B. Rahaman, D. Giri, <u>A. Sarkar</u>, S. K Patra and D. Banerjee, *Mater. Res. Express.*, (2019), **6**, 115114 (1–8).

vii) A. B. Rahaman, S. Bhattacharya, <u>A. Sarkar</u>, T. Singha, D. Banerjee and P. K. Datta, (in press, Journal of Applied Physics).

viii) A. B. Rahaman, <u>A. Sarkar</u>, T. Singha, K. Chakraborty, T. Pal, S. Ghosh, P. K. Datta and D. Banerjee (under review).

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