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Optical Properties of Solar Cells Based on Zinc(hydr)oxide and its Composite with Graphite oxide Sensitized by Quantum Dots

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Optical Properties of Solar Cells Based on Zinc(hydr)oxide and its Composite with Graphite oxide Sensitized by Quantum Dots

by

S.M. Zakirul Islam

A dissertation submitted to the Graduate Faculty in Electrical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy,

The City University of New York

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This manuscript has been read and accepted for the Graduate Faculty of Electrical Engineering in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

Optical Properties of Solar Cells Based on Zinc(hydr)oxide and its Composite with Graphite oxide Sensitized by Quantum Dots

by

S.M. Zakirul Islam

Advisor:

Professor Robert R. Alfano

This thesis research focuses on developing a hybrid form of solar cell based on zinc(hydr)oxide and its composites with graphite oxide, TiO₂, quantum dot, electrolyte and . This work expands upon the Gratzel solar cell with a dye in TiO₂.

Due to various structural and optical characteristics, zinc(hydr)oxide (Zn(OH)₂) and its porous composites with 2% and 5% graphite oxide(GO) can be used for various applications including the manufacture of various , protective elements in electric and electronic appliances, as gas-sensors, catalysts, in cosmetics a UV light absorber, and solar cells.

In this research, both TiO₂ and zinc(hydr)oxide (refer as Zn(OH)₂ ) and its porous composites with 2% and 5% graphite oxide(GO) (refer as ZnGO-2 and ZnGO-5 respectively) have been studied with photoactive quantum dots (QDs). The goal of this research was to understand the optical properties of Zn (OH)₂, ZnGO-2 and ZnGO-5 (i.e. We determined the band gap of these three materials using absorptions, photoluminescence and photo-conductivity), structural characterizations of these three samples (i.e.We determined critical points transitions), time resolved fluorescence of these three materials, (i.e. We determined the lifetime of the carrier, the rise time of the carrier, relaxation, and carrier density using new model) and application in the Gratzel like quantum dots (QDs) sensitized hybrid Zn(OH)₂/ZnGO solar cells compared with TiO₂ which made with QD(CdSe and PbS ).The main objective of this thesis was
to develop hybrid solar cell with Zn(OH)/ZnGO material and TiO$_2$ to make alternative designs for the fabrication of quantum dots sensitized Zn(OH)/ZnGO hybrid solar cells that can enhance the efficiencies as well as reduce the cost by making it more amenable to large scale production.

**Figure (abstract A):** (left) the exciton generation process is presented in a band diagram. NIR QD multi-exciton generation scheme (C-conduction band, V-valence band, $E_F$ -Fermi level, NR-non-radiative process, NIR-near infrared, UV-ultraviolet, QD-quantum dots, e-electron, i-current). (Right) summarizes the dominate exciton process in the hybrid solar cells. Roles of different wavelength-dependent exciton generation processes are shown with respect to the solar spectrum.

In hybrid solar cells, the role of the conductive glass substrate with the performance of Zn(OH)$_2$/ZnGO/QD(CdSe and/or PbS) /Electrolyte or Perovskite based photovoltaic devices, as well as fabricate new photovoltaic devices, to improve the efficiencies in power. The focus of this doctoral thesis was to introduce new composite material such as Zn(OH)$_2$ with QDs CdSe(visible), PbS(UV and NIR) for their applications in new solar cells which incorporate energy transfer processes in order to improve light harvesting. The basic idea to obtain maximum energy efficiency is to absorb most of the solar spectrum in the 3 zones: UV, visible and NIR.
light. The photoexcitation and processes involved with carriers excitons and multiexcition
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I want to use this opportunity to thank all those people who have supported and helped me both in this work and on my path to this point. Most importantly, I am sincerely grateful to my thesis advisor, Professor Robert R. Alfano, for his kindness, advice, and excellent supervision throughout the course of this research works. He took me in and showed me the light. His exceptional insight and broad view knowledge led me to the wonderful field of the semiconductor, laser, and solar cell devices, and helped me avoid so many detours during the progress of my research. In addition, his impressive carefulness and diligence have showed me how to work as a fruitful scientist, which will be my greatest asset in the future.

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Dedications

To the memory of my father and mother
Optical Properties of Solar Cells Based on Zinc(hydr)oxide and its Composite with Graphite oxide Sensitized by Quantum Dots

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Chapter 1

1. Introduction

Without semiconductor compounds, our life would be very different today and would be based on tubes. The electrons in the semiconductor created today’s electronics. Without it, there would be no television, computers, cell phones and other appliances to make our lives easier. With the advent of photo-detectors and lasers, light will have a major impact in the upcoming world and in the future. Most of all, light from the Sun lights up the world and sends us energy. Solar energy is a relatively free source. One needs ways to convert it to useful forms for our use. Photodetectors convert light to electrons as a form of energy. Again, worlds of electrons and photons are used to produce an excellent combination of electronics and Photonics for the possible energy source of the future, much attention during the past two decades focused on novel optical materials with structural and transport properties which have great potential for many optoelectronic applications. Silicon is the material of choice with 24% energy solar conversion. The research is to get better conversion efficiencies using many semiconductors and different mechanisms to convert energy for the purpose of the work as is with the heart of transistors in computers. Theoretically, using many semiconductors one can envision energy conversion up to about 80%. One of the major concepts used to convert Solar energy cheaply was developed by M. Gratzel using dyes and semiconductor TiO$_2$ in Potassium Iodide electrolyte. The search is on to make cheap solar cells that use the entire solar spectra without losing any carriers in the cell. The key for increasing the efficiency of solar conversion is to use most of the solar spectrum from 300nm to 2000nm and to not lose any photogenerated carriers due to non-radiative processes. The use of hybrid Gratzel –like solar cells are the focus of this thesis. In my thesis research Zn(OH)$_2$, ZnGO-2, ZnGO-5, and TiO$_2$ used for solar cells because
they are promising materials for electronic and optoelectronic applications such as solar cells, gas sensors, liquid crystal displays, heated mirrors, etc.

Due to the large band gap of Zn(OH)$_2$ and its composites (2% graphite oxide doped (ZnGO-2), and 5% graphite oxide doped (ZnGO-5)), we have applied them as quantum dots in sensitized solar cells called Gratzel cells. In our version, these composites replace TiO$_2$. The band gap of these materials is close to TiO$_2$. There is another TiO$_2$ solar cell made using CdSe quantum dots for comparison with ZnGO solar cells. My research focuses on how to generate higher efficiency solar cells using compact hybrids of new meso/micro porous materials with the QDs of CdSe and PbS to cover the UV, visible and NIR portion of the Solar spectrum.

1.1 Organization of dissertation

In chapter 1 is a brief description of the introduction.

In chapter 2 is a brief description of the absorption coefficients of materials. Band gap energies of Zn(OH)$_2$, ZnGO-2, and ZnGO-5 were determined by fitting absorption curves, nonlinear polynomial algorithm. Band gap energies were found in the range of 2.88 eV. to 3.00 eV. Free carrier absorptions and interband transitions are discussed.

In chapter 3, the reflectivity and its derivative, critical point energies, band structure and density of the states are discussed. The wavelength modulation technique was applied to find the band gap and critical point energies. Interband transitions show how the energy transits in the band structure.

The semiconductor can be 3D, 2D, 1D or 0D. In this research, 3D is the bulk, 2D is a quantum well, 1D is quantum wire and 0D are quantum dots. The band structures of bulk semiconductor, quantum well, and quantum dots are shown in figure 1.1 with photon $h\nu$ absorption following:
Fig. 1.1: (a) band structure of bulk of ZnGO materials, (b) band structure of the quantum well, (c) band structure of quantum dots, (d) band of MEG (multiexciton generation)

The above figure 1.1 shows the band structures of bulk materials, quantum wells, quantum dots and multi-exciton carrier generation (MEG). One of the potential approaches to increase solar energy conversion efficiency is carrier multiplication (CM), or multiple excitation generation (MEG). The idea is illustrated in figure 1.1(d). One phonon can generate only one pair of excitons. The excess photon energy ($h\nu - E_g$) is dissipated as heat via phonon emission and therefore is wasted. In this idea we can get a higher conversion efficiency as well as quantum efficiency from solar cells. In order to increase the efficiency up to 20% it is challenging to design quantum dots that absorb more broadly than CdSe QD based solar cell. A CdSe quantum dot based solar cell absorbs visible light (400 nm-700nm) shown in figure 1.2, therefore it is necessary to look at designing new sensitizing PbS and PbS/CdSe QDs that are capable of absorbing in the UV and NIR-portion of the spectrum.
In chapter 4 briefly describes the photoluminescence and photoconductivity to determine the band gap energies of these three composite materials. The band gaps of the three samples (Zn(OH)$_2$, ZnGO-2, and ZnGO-5) were found to be in the range between 2.90 eV to 3.05 eV.

In chapter 5, structural characteristics of Zn(OH)$_2$, ZnGO-2, and ZnGO-5 are described. There were several experiments performed for analysis these three materials. Two photon image (TPF), transmission electron microscopy (TEM), and X-ray diffraction (XRD) images are discussed in this chapter.

In chapter 6, the time-resolved fluorescence technique is described. Lifetime and rise time were determined using fitting curves. Fitting curves are based on new formula and a new model that is discussed in this chapter. The reasons behind the change in life time is also discussed in this chapter.

In chapter 7 briefly describes the background and operations of dye/QD sensitized solar cells. Power conversion, quantum efficiencies, open circuit voltage, and short circuit current are also described in this chapter.
In chapter 8 describes the QD sensitized ZnGO solar cell, QD sensitized TiO2 solar cell, two photon fluorescence images of these solar cells, the fabrication temperature effect on ZnGO solar cells and internal structures.

In chapter 9 describes a new model for the solar cells. This chapter describes a new designed black silicon hybrid solar cell. This solar cell is based on black silicon, QD, ZnGO and . The chapter shows the results of hybrids with multi QDs, CdSe and PbS with Zn(OH)$_2$ doped with graphite oxide (GO). This solar cell portrays a new design where energy relay QDs unattached to the black silicon and ZnOH-GO absorbs high energy photons and transfer their energy to the sensitizing quantum dots via electrolytes.

In chapter 10 describes multiple exciton generation of carriers, electron-holes pairs multiplication in QDs, A multi exciton generation (MEG) excitation of the ZnGO solar cell is also described in this chapter using PbS QDs. The PbS QD creates carriers from absorption of the NIR and UV portions of the solar spectrum. Super-linearity was found of $J_{sc}$ vs $P_{in}$ showing the higher efficiency with light power.

In chapter 11 is the last chapter and describes our conclusions and future work.
Chapter 2

2. Optical properties of materials

This chapter describes the optical properties, such as optical absorbance, free carrier absorptions and interband transitions. We have determined these optical properties and found the relationship between those properties for the three materials (Zn(OH)$_2$, ZnGO-2 and ZnGO-5). As a part of research on materials for solar energy and photovoltaic, we are evaluating the optical properties and solar cell applications and compared with TiO$_2$ based solar cells. Here we show optical absorbance and absorption coefficient of the above three materials.

2.1 Semiconductors and its background

A semiconductor is usually defined rather loosely as a material with electrical resistivity lying in the range of $10^{-2}$ to $10^9$ (cm. Alternatively, it can be defined as a material whose energy gap for electronic excitations lies between zero and about 4 electron volts (eV) [3].

The well known semiconductor is undoubtedly silicon (Si). However, there are many semiconductors besides silicon. In fact, many minerals found in nature, such as zinc-Blende (ZnS) Cuprite (Cu2O) and galena (PbS), to name just a few, are semiconductors. Including the semiconductors synthesized in laboratories, the family of semiconductors forms one of the most versatile classes of materials known to man. Semiconductors occur in many different chemical compositions with a large variety of crystal structures. They can be elemental semiconductors, such as Si, carbon in the form of C$_{60}$ or nanotubes and selenium (Se) or binary compounds such as gallium arsenide (GaAs). Many organic compounds, e.g. polyacetylene (CH)$_n$, are semiconductors. Some semiconductors exhibit magnetic (Cd$_{1-x}$Mn$_x$Te) or ferroelectric (SbSI)
behavior. Others become superconductors when doped with sufficient carriers (GeTe and SrTiO3)[1].

2.1.1 Growth/composition Zn (OH)₂ / ZnGO Semiconductor materials:

The samples used in this thesis were prepared by Prof. Teresa J. Bandosz Group synthesis according to reference [1] by Dr. Mykola Seredych. GO was synthesized by oxidation of graphite (Sigma-Aldrich) using the Hummers method [2]. The composites were prepared by dispersing GO powder (2wt. % or 5 wt. %) of the final mass of the material in 1.0 L zinc chloride solution (0.05 M). The results of well-dispersed suspension was stirred for four hours. Sodium hydroxide solution (0.05 M) was then added (2.0 L) with a rate of 2.0 mL min⁻¹ using a Titronic Universal (SCHOTT) method. Afterwards, the obtained composites were extensively washed with distilled water until neutral pH and no traces of chloride ions were found. Finally, the suspension was centrifuged and a gel formed was dried at 100°C over 48 hours. Zinc (hydr) oxide was prepared in the same way, without the GO in ZnCl₂ solution. Prior to the chemical synthesis of ZnGO composites, the structure of the precursor materials was investigated. Some details on Zn(OH)₂ are discussed in reference [1].

Zn(OH)₂ and its porous micro-composites materials with 2% graphite Oxide (GO) (referred as a ZnGO-2) and 5% graphite oxide (referred as ZnGO-5), and TiO₂ are a new type of semiconductors came to our research attention. Zinc hydroxide Zn(OH)₂ is an inorganic chemical compound. It also occurs naturally as three rare minerals: wülfingite (orthorhombic), ashoverite and sweetite (both tetragonal) [4]. 2% and 5% graphite oxide synthesized with Zn(OH)₂.

Over the past four decades III-IV group semiconductors have been more attraction due to their attraction. GaAs is one of them popular materials [5]. In general, oxide semiconductors are
not well understood with regard to their growth processes, so they have limited potential for applications at present. One exception is the II–VI compound zinc oxide (ZnO), and Zn(OH)$_2$ which has found application as a transducer and as an ingredient of adhesive tapes and sticking plasters. However, this situation has changed with the discovery of superconductivity in many oxides of copper [5]

In this thesis the band gap of Zn(OH)$_2$ is $\sim$2.97 eV while ZnO is 3.2 eV. ZnGO-2, ZnGO-5, and TiO$_2$ are 2.93 eV, 2.84 eV, and 3.2 eV respectively have been recorded in this research. The next chapter gives these results.

2.2 Absorption coefficients semiconductor materials

Measurement of the absorption of light is one of the most important techniques for optical measurements in solids. The absorption coefficient, $\alpha$, is a property of a material which defines the amount of light absorbed by it. The inverse of the absorption coefficient, $\alpha^{-1}$, is the average distance traveled by a photon before it gets absorbed. The inverse of the absorption coefficient, $\alpha^{-1}$, also is the distance at which its intensity of light is reduced to a value $1/e$ ($\sim$36%) of its original intensity. The light intensity as a function of distance $z$ is given by, [6]

$$I(z) = I_0 e^{-\alpha z} \quad (2.1a)$$

where, the absorption constant is shown schematically in fig. 2.2. Since the intensity $I(z)$ depend on the square of the field variables, it immediately follows that [7]

$$\alpha = \frac{2k\omega}{c} = \frac{4\pi k}{\lambda} \quad (2.1b)$$

where, the factor of 2 results from the definition of $\alpha(E)$ in terms of the light intensity, which is proportional to the square of the fields. This expression tells us that the absorption coefficient is
proportional to k, the imaginary part of the complex index of refraction (extinction coefficient), so that k is usually associated with power loss. We note that Eq. 2.1b applies to free carrier absorption in semiconductors in the limit $\omega \tau >> 1$, and $\omega >> \omega_p$.

We classify materials as opaque, translucent and transparent according to the absorption strength of these materials. Glass, for example a window pane, is transparent, while a silicon wafer is opaque to visible-spectrum light. A transparent material has a smaller absorption coefficient than an opaque material.

![Graph showing absorption coefficient $\alpha(E)$ vs photon energy $E$ with a tangent intersecting the energy line called band gap $E_G$.](image)

**Figure 2.2:** Photon energy dependence of the absorption coefficient near a threshold for interband transitions. The tangent intersects the energy line called band gap.

### 2.3 The absorption coefficient of composites $\text{Zn (OH)}_2$ materials

The amount of absorption depends on the wavelength, the amount of absorbing material in the radiation path, and the absorption of that material at that wavelength. Materials that absorb some visible wavelengths appear colored. In a solid absorbing media, excitation energy is dissipated with release of heat (vibrations of particles) or light (spontaneous emission).

In spectroscopy the observance is defined as:

$$ A = \varepsilon |c| , $$  \hspace{1cm} (2.2a)
Where $\varepsilon$ – extinction coefficient (characteristics of a material that is a sum of absorption coefficient and scattering coefficient), $l$ – the distance that the light travel through the material, $c$ – concentration of absorbing atoms in the material.

The intensity of an incident beam drops exponentially as it passes through the absorbing media. This is expressed as Beer’s law:[7, page.6]

$$\frac{I_1}{I_o} = 10^{-OD} \quad \text{(2.2b)}$$

where, $I_o$ is the intensity of incident light, $I_1$ the intensity of the light after passing through the absorbing material, OD- optical density of a material. As an example of Zinc(Hydr)Oxide (ZnOH$_2$) materials and its composite with 2% (ZnGO-2) and 5% graphite oxide(ZnGO-5) materials which Absorbance are measured in the range of 300 nm to 800nm shown in fig.2.3.

**Fig. 2.3:** Absorption of spectra of Zn(OH)2 and its composites as a function of wavelength in the range of 300nm to 800nm
The absorption measurements were carried out at room temperature using Varian’s Cary 500 Scan (UV-VIS-NIR) Spectrophotometer. A beam of light with a spectral range between 300nm and 800 nm from a broadband light source was passed through an aperture of six (6) mm in diameter and was allowed to impinge upon the samples.

2.4 Optical gaps characterization by absorption spectroscopy

In the absorption spectra, there appear several common features on the absorption edge commonly shown in amorphous, non-crystalline, and crystalline semiconductor materials [8]. The main features of the edges are direct edge and Urbach tail. The characteristic slope of the exponential part of the absorption edge, commonly referred as the Urbach edge, is found to be proportional to kT for temperatures above the Debye temperature [9] and is believed to be associated with the disorder caused by thermal fluctuations of the electronic structures [10]. The weak portion of the absorption region, a measure of the width of the defect state, depends on the structural properties of the materials. The fundamental absorption edge follows the exponential law, and the absorption coefficient has the following spectral dependence [11]

\[ \alpha(E) = \alpha_0 (E - E_g)^n \]  \hspace{1cm} (2.4a)

where \( \alpha(E) \) is the absorption coefficient, \( E = \hbar \omega \) is the photon energy, \( E_g \) is the band gap energy, \( \alpha_0 \) characteristic parameter of the material, and finally, \( n = \frac{1}{2} \) for direct band-gap and \( n = 2 \) for indirect band gap materials. The optical absorption edge in the exponential Urbach region, having its dependence on photon energy and temperature, can be given by [12]

\[ \alpha(E,T) = \alpha_0 \exp \left( \frac{E - E_{\infty}}{E_n} \right), \]  \hspace{1cm} (2.4b)
Where, $\alpha(E,T)$ is the temperature dependent absorption coefficient, $E = h\omega$ is the photon energy, $E_{op}$ is the optical band gap energy, $E_u$ is the characteristic Urbach energy. Here the optical band gap energy is defined as the energy at which the extrapolated absorption coefficient reaches $\alpha_g$, which is one of the Urbach bundle convergence points coordinates [12]. Combining the two key processes of absorption makes use of equations (2.4a) and (2.4b), a form that has been used for simulation for absorption vs. energy is given by:

$$\alpha(E) = \alpha_1(E) + \alpha_2(E) \quad (2.4c).$$

The diameter (~ 8±0.01 mm) and thickness (~150 ± 5 µm) of the samples for absorption spectroscopy, fluorescence spectroscopy and photocurrent experiment were measured by Accupro dial thickness gauge measurement tool.

The absorption measurements were carried out at room temperature using Varian’s Cary 500 Scan (UV-VIS-NIR) Spectrophotometer. A beam of light with a spectral range between 250 and 800 nm from a broadband light source was passed through an aperture of 6 mm in diameter and was allowed to impinge upon the samples. The absorption started at 400 nm (~3.1 eV), as shown in fig. 2.4 (a-c).
Fig. 2.4. Plots from absorption data for determining the band gap energies and absorption-coefficients for three different materials: (a) porous Zn(OH)$_2$; (b) composite ZnGO-2; and (c) composite ZnGO-5. In fig.2.4(a), the left vertically slanted line intersecting with the horizontal(energy) axis denotes edge and the right one intersecting the energy axis denote $E_{op}$.
A very good agreement is seen between the experimental data and the data obtained by a numerical method. Using the least square fitting technique for a third order polynomial function, this simulation method involved equations (2.4b) and (2.4c) to find the optical band gap energy $E_{\text{op}}$ and direct energy-gap energy $E_g^D$ (fig. 2.4(a)) and Urbach energy $E_u$. The values along with fitting parameters are listed in Table 2.4. The investigated materials are micro-porous and they lack any long-range order and are considered to be amorphous. In characterizing optical band gap parameters of such materials, three (high, medium, and low) spectral regions have been

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption</th>
<th>Photoluminescence</th>
<th>Photocurrent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (OH)$_2$</td>
<td>$E_\text{m}^\alpha = 2.97$</td>
<td>$E_\text{m}^{\text{re}} = 2.93$</td>
<td>$E_\text{m}^{\text{re}} = 3.06$</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{op}} = 3.00$</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>$E_{\text{ur}} = 0.36$</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$\alpha_0 = 330$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_g = 58$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_\text{g}^\alpha = 2.93$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnGO-2</td>
<td>$E_{\text{m}} = 0.85$</td>
<td>$E_\text{m}^{\text{re}} = 2.87$</td>
<td>$E_\text{m}^{\text{re}} = 2.88$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_0 = 480$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_g = 130$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_\text{g}^\alpha = 2.84$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnGO-5</td>
<td>$E_{\text{m}} = 0.80$</td>
<td>$E_\text{m}^{\text{re}} = 2.84$</td>
<td>$E_\text{m}^{\text{re}} = 2.85$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_0 = 440$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha_g = 140$</td>
<td></td>
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</tr>
</tbody>
</table>

- Photoluminescence and Photocurrent have been described on the chapter 4.
identified. The absorption coefficient (i.e., $\alpha = 330$ cm$^{-1}$, 480 cm$^{-1}$, and 440 cm$^{-1}$) for the direct-gap region for the samples of Zn(OH)$_2$ and its composites ZnGO-2 and ZnGO-5, respectively are estimated. Absorption-coefficient for one of the Urbach convergence point coordinates (i.e., $\alpha_s = 58$ cm$^{-1}$, 130 cm$^{-1}$ and 140 cm$^{-1}$) for the Urbach tail region for the above-mentioned samples are also estimated. The absorption coefficient for the lowest region that depends on the structural properties of the materials is not reported here. The characteristic direct-gap energy, lying below the optical gap region, depends on phonon beating, has been obtained after taking off the thermal energy contribution due temperature fluctuation even at room temperature. The thermal fluctuations that are occurring even at the short-range orders are the basic attributes that these materials exhibit. The detailed analysis of the dependence of Urbach energy on various factors, such as, structural feature, aggregate state, crystal lattice dimensionality, types of phase transitions are beyond the scope of this article. One more important point is that the absorption coefficient below 10 cm$^{-1}$ has not been included in the simulation scheme, because the data below those values are more sensitive to the approximations in the model calculations and uncertainties associated with the subtraction of the low-energy absorption.

### 2.5 Algorithm of fitting curves:

The least-squares fit technique was applied for curve fitting. This algorithm has divided by both polyfit and polyval methods. Specifically, the polyfit method is used to generate the $n + 1$ coefficients $a_j$ of the $n$th-degree polynomial,

$$P_n(x) = a_n x^n + a_{n-1} x^{n-1} + \cdots + a_1 x + a_0 \quad (1)$$
used for fitting the data. The basic structure requires that the vectors x and y be submitted to polyval along with the desired degree of polynomial fit n. To fit a line (n = 1) through the data, the structure, use the command pcoe=polyfit(x,y,1);

The output of this function call is a vector pcoe which includes the coefficients a1 and a0 of the line fit p1(x) = a₁ x+a₀

xp=0:0.1:7;
yp=polyval(pcoeff,xp);

The polyval command uses the coefficients generated from polyfit to generate the y−values of the polynomial fit at the desired values of x given by xp. In our technique we took the 3rd order polynomial of lambda. Where, lambda substitutes as in xp. And then we took the exponential form of 3rd order polynomial lambda.

2.6 Free carrier Absorption

Free-carrier absorption is an optical absorption process that does not generate electron-hole pairs; instead, the photon energy is absorbed by free-carriers in either the conduction or valence band, moving the carrier to a higher energy state within that band via phonons. Free-carrier absorption has only a small impact on the total power output for most photovoltaic devices, but because it is heavily dependent on wavelength, it may still significantly affect the spectral response. This has implications for device characterization [13].

Free carrier absorption occurs when a material absorbs a photon and a carrier is excited from filled state to an unoccupied state (in the same band). This is different from interband absorption in semiconductors because the electron being excited is a conduction electron (i.e. it can move freely). In interband absorption, the electron is being raised from a valence (non-conducting) band to a conducting one.
It is well known the optical transition of electrons and holes in the solid state is a useful clue to understand the physical properties of the material. However, the dynamics of the carrier are affected by other carriers, not only the periodic lattice potential. Moreover, the thermal fluctuation of each electron should be concerned so that the statistical approach is needed. To predict the optical transition in an appropriate precession, we should choose some approximation, called assumption of quasi-thermal distributions of the electrons in the conduction band and of the holes in the valence band. In this case, the diagonal components of the density matrix become negligible after introducing thermal distribution function.

Here is an example of sample Zn(OH)\(_2\) and its composite with 2\% GO (ZnGO-2)'s free carrier absorption spectra measure in the range of 400nm to 3000nm.

**Fig. 2.6a:** Free carrier absorption of Zn (OH) \(_2\) taken at room temperature in the range of 400 nm to 3000 nm for carrier concentration of 1.37 \times 10^{16} \text{ cm}^{-3} with a low power of incident light.
**Fig. 2.6b**: Free carrier absorption of ZnGO-2 taken at room temperature in the range of 400nm to 3000nm for carrier concentration of $1.4 \times 10^{16}$ cm$^{-3}$ with a low power of incident light.

Free carrier absorption is found between 700nm to 2700nm for Zn(OH)$_2$ and between 1800nm to 2400nm for ZnGO-2. Typically, good free carrier absorption can be found 2 microns to 15 microns, but in our lab carrier absorption measure tool has a maximum range up to 3000nm. There is more free carrier absorption may be found after 2400nm.

### 2.7 Direct interband transitions

Two types of interband transitions (i.e. direct and indirect) occur in semiconductor materials. Zinc(hydr)oxide (Zn(OH)$_2$) and its composite materials (ZnGO-2 and ZnGO-5) play direct interband transitions. Since our materials behave direct interband transitions, here is the following summary of these materials describing;

(a) Form absorptions coefficient [11]
\[ \alpha_i(E) = \alpha_v(E - E_v)^{1/2} \quad 2.7a \]

(b) Conservation of crystal momentum

(c) Relation between \( m^* \) and momentum matrix element

(d) Form absorptions coefficient for direct forbidden transitions [11]

\[ \alpha_i(E) = \alpha_v(E - E_v)^{1/2} \quad 2.7b \]

To calculate the absorption due to direct interband transitions we go back to the definition for the absorption coefficient \( \alpha(E) \) which is defined as the power removed from the incident beam per unit volume per unit incident flux of electromagnetic energy:[6]

\[ \alpha(E) = \frac{E \times \text{No. of transitions / unit volume / unit time}}{\text{Incident electromagnetic flux}} \quad 2.7c \]

where, \( E \) is energy in eV.

Electromagnetic flux is calculated from the Pointing vector;

\[ \vec{S} = \frac{c}{8\pi} \text{Re}(\vec{E}^* \times \vec{H}) \quad 2.7d \]

where,

\[ \dot{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} = \frac{i\omega}{c} \vec{A} \quad 2.7e \]

\[ \mu \vec{H} = \nabla \times \vec{A} \quad 2.7f \]

\[ \vec{A} = \vec{A}_0 e^{i(\vec{K} \cdot r - \omega t)} \quad 2.7g \]

Substitute equation 2.7(e,f,g) into 2.7d; \( S \) can be calculated as;
\[
\hat{S} = \frac{c}{8\pi} \text{Re} \left[ -\frac{i\omega}{c} \vec{A}^* \times (i\vec{K} \times \vec{A}) \right] \quad 2.7h
\]

\[
= \frac{\omega}{8\pi} \text{Re} \left[ (\vec{A}^* \cdot \vec{A})\vec{K} - (\vec{A}^* \cdot \vec{K})\vec{A} \right] \quad 2.7i
\]

Transverse plane wave, \( \vec{A}^* \cdot \vec{K} = 0 \), we obtain,

\[
\hat{S} = \frac{\omega}{8\pi} \frac{\hbar^2}{c} |\vec{A}|^2 \hat{k} \quad 2.7j
\]

Using all of the above equation, thus we got direct interband transitions;

\[
\alpha(E) = \alpha_0 \left( E - E_g \right)^{1/2} \quad 2.7k
\]

where,

\[
E = \hbar \omega
\]

Fig. 2.4 (a-c) shows the plot of the absorption coefficient of Zn (OH)_2, ZnGO-2, and ZnGO-5 as a function of energy \( \hbar \omega \) showing the linear dependence of \( \alpha(\omega) \) on \( \hbar \omega \). The intercept with the x-axis defines the direct energy gap.

2.8 The band gap shrinks of composite Zn(OH)_2 materials

The data by optical characterization techniques and simulations methods strongly suggest that the band gap narrowing occurs for composites in comparison to zinc (hydr) oxide. Moreover, the energy-gap (~2.97 eV) of Zn(OH)_2 is found to be smaller than that of zinc oxide (~ 3.2 eV). The physics of band gap shrinkage in materials, ranging from nanocrystals to composites have been investigated [14-19]. The energy band gap narrowing has been attributed to the followings phenomena: lattice disorder with the appearance of mid-gap electronic states[14], the electron-impurity interaction and coulomb-interaction between carriers [15], nature and location of defects [16], the change in the nature and strength of the interaction potentials.
between donors and host materials [17], oxygen vacancies and interstitial sites [18], and disordered semiconductors [19].

Based on the surface properties of the studied materials [4], we link a decrease in the energy gap in the composites with an increase in GO content, an increase in the amorphousness level of the zinc (hydr)oxide phase, relatively high level of impurity (chlorine), and the presence of hetero-junctions/bonds between the graphene carbon and zinc(hydr)oxide lattice [4]. It has been shown that the bonds also increase the conductivity, which also suggests the phenomenon of energy-gap narrowing.

The defects in the lattice affect the interactions between electrons and phonons. Besides electron-phonon interaction effects, phonon-confinement due to the addition of graphite-oxide phase and nano-sized particles of Zn(OH)₂ might have played a key role in down shifting the band gap energies in the composites. The larger size particles in the composites may be the cause of lower band gaps due to weaker confinement. The decrease in the band gap energy in Zn(OH)₂ compared to pure ZnO can be linked to the defects in the lattice of the material resulting in porous texture, larger particles, accompanied by weaker confinement.

Reflectivity and critical points have been described in chapter 3.
Chapter 3

3. Reflectivity and critical points

Past few decades, the subjects of band structures of semiconductors have attracted much attention. The results have had a strong impact on the recent advance in band-structure calculations. The subject of energy band structures and critical points of porous micro-composites have attained renewed interest because of the potential applications of these new optical materials in sensors and solar energy converters [20].

The determination of the optical band gap energies and transitions between critical points (i.e., between valence and conduction bands) are important because they not only control the efficiency of solar conversion and the shape of the optical emission spectrum, but also manifest the effect of structural and thermal disorder on the electronic properties of the composite materials [21]. Direct interband transitions are believed to be responsible for the peaks observed in the derivative of reflectivity with respect to energy of a number of semiconductors and composite materials in the spectral energy range between 1 and 12 eV [22]. Identification of these critical points would provide insight into the band structure of these materials over a wide spectral-range of energies, as indicated in [22]. Wavelength modulation techniques using derivatives of normalized reflectance spectra (i.e., (1/R)(dR/dE)) have been identified as two most robust methods in the measurement and analysis of band gap energies and pores and light-emitting regions.
Fig. 3.0: The figures show the reflectivity of six samples (GaAs, Zn(OH)2, ZnGO-2, ZnGO-5, ZnO power, and ZnO –C shaped crystal) as a function of energy(eV). The samples of Zn(OH)2, ZnGO-2 and ZnGO-5 were compared with the references GaAs, ZnO powder and ZnO crystal. From the curves show reflectivity of three samples are between 15% to 20% which are suitable for solar energy.

In this chapter we have determined critical points transitions energies as well as band gap energies of Zn(OH)2, ZnGO-2, and ZnGO-5 using the reflectivity and its modulation technique.

3.1 Modulated reflectivity

Many different modulation schemes have been invented for derivative spectroscopy. For measurements of reflectivity spectra of solids, electroreflectance, piezoreflectance, thermoreflectance, and wavelength modulation methods have been most successful. In all these schemes except the wavelength-modulation method, modulation of the light beam is obtained through application of a direct AC perturbation on the solid, and, hence, interpretation of the derivative spectrum depends very much on how the solid responds to the perturbation. Thus, in electroreflectance, we must know how the band structure of the solid changes with an applied electric field. Since, the fact that no perturbation on the solids is needed makes the wavelength-
modulation method most attractive. The wavelength-modulation spectrum is simply the derivative of the normal spectrum; there is no ambiguity in the interpretation. However, unlike the other modulation schemes, the wavelength-modulation method requires careful construction of the experimental system in order to eliminate the huge background in the derivative spectrum. This background appears as a result of wavelength modulation on the spectra of various optical components in the system. In particular, because of the many narrow spectral lines in the arc source, it is difficult to apply the scheme to the UV region. For this reason, the wavelength-modulation method has not been as popular as the other modulation schemes. Work done with wavelength modulation has usually been limited to a narrow region in the visible or near infrared [23].

The first order derivative of reflectance, a modulation technique, as a function of photon energy has been employed to determine the band gaps and critical transition energies for Zn(OH)$_2$, and its composites with 2% and 5% graphite-oxide(GO) as zinc-graphite-oxides (ZnGO-2 and ZnGO-5, respectively).

Using reflectance spectroscopy GaAs, Zn(OH)$_2$, ZnGO-2, and ZnGO-5 were studied in the energy range from 1.0 eV to 6.1 eV. The band gaps for ZnO and GO are reported to be 3.3 eV [24] and 2.4 eV [25], respectively. The reflectance spectroscopy method has proven to be efficient, as no perturbation is necessary. The interpretation of data poses no ambiguity, but it demands careful elimination of background contributions and the sensitivity of the spectrometer needs to be maintained at a value of $\Delta R / R \geq 10^{-4}$. Using the energy-derivative of normalized reflectance data, effects of surface conditions on
Fig. 3.1: Reflectance spectra and their derivatives which used for determining the critical point energies of different materials: (a) GaAs; (b) porous Zn(OH)$_2$; (c) ZnGO-2; and (d) ZnGO-5. For clarity, two vertical lines that intersect the derivative curves identified as $E_0=E_g$ and $E_1$ are shown in fig.3.1 (b-d.).

[Ref. 46 Islam et al, Vol. 38, issue. 6, 962(2013)]

reflectance measurements are greatly minimized. The reflectance data were obtained at room temperature.

The reflectance spectra and their derivatives for the three samples, Zn(OH)$_2$, ZnGO-2, and ZnGO-5 shown in fig. 3.1(b-d) are very much alike, reflecting the similarity of their band structures. Similar groups in different semiconductors or materials are believed to come from transitions in the similar general areas of the band structures.
The band gap energies of the three samples Zn(OH)$_2$, ZnGO-2, and ZnGO-5 have been labeled with $E_0$ and $E_1$ only. Critical points of transition that have been labeled as $E_0$, $E_0+\Delta_0$, $E_1$, $E_1+\Delta_1$, $E'_0$, and $E_2$ were obtained using $(1/R)dR/dE = 0$ for GaAs in [3,6,22] and are compared with results reported in [22].

The critical point at $E_0$ (i.e., $E_g$) is identified as the direct band gap energy, while the critical point at $E_0+\Delta_0$ corresponds to a transition from the split-off valence band at $k = 0$ which arises through the spin orbit interaction. The transitions at $E_1$ and $E_1+\Delta_1$ corresponding to $\Lambda$-point and L-point transitions are also due to spin-orbit splitting. Although the detailed band structure and notation given to GaAs are obtained from ref [3], the values of pertinent interband transitions are given in Table 3.1 for GaAs (as a reference), Zn(OH)$_2$, ZnGO-2 and ZnGO-5.

The band gap and the critical point energies for a new class of optical micro composite materials (ZnGO-2 and ZnGO-5) have been investigated using reflectance spectroscopy and the derivatives of such data shown in fig. 3.1 and table 3.1. Our experiment was performed in room temperature 300K.
Table 3.1. Show the critical point energies (eV) of a few materials. Previous studies on band gap energies for GaAs are reported in Ref. [3] and Ref. [22].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Previous Results (eV)</th>
<th>Present Results (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>(E_0=1.5192)</td>
<td>(E_0=E_g=1.50)</td>
</tr>
<tr>
<td></td>
<td>(E_0+\Delta_0=1.859)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(E_1=3.017)</td>
<td>(E_1=2.99)</td>
</tr>
<tr>
<td></td>
<td>(E_1+\Delta_1=3.245)</td>
<td>(E_1+\Delta_1=3.20)</td>
</tr>
<tr>
<td></td>
<td>(E_0=3.8^*)</td>
<td>(E_0=3.80)</td>
</tr>
<tr>
<td></td>
<td>(E_1^<em>+\Delta_1^</em>=4.659)</td>
<td>(E_1^<em>+\Delta_1^</em>=4.60)</td>
</tr>
<tr>
<td></td>
<td>(E_2=5.11)</td>
<td>(E_2=5.11)</td>
</tr>
<tr>
<td>Zn(OH)(_2)</td>
<td>(E_0=E_g=2.97)</td>
<td>(E_0=E_g=2.98)</td>
</tr>
<tr>
<td></td>
<td>(E_1=3.5)</td>
<td></td>
</tr>
<tr>
<td>ZnGO(_2)</td>
<td>(E_0=E_g=2.93)</td>
<td>(E_0=E_g=2.90)</td>
</tr>
<tr>
<td></td>
<td>(E_1=3.40)</td>
<td></td>
</tr>
<tr>
<td>ZnGO(_5)</td>
<td>(E_0=E_g=2.84)</td>
<td>(E_0=E_g=2.88)</td>
</tr>
<tr>
<td></td>
<td>(E_1=3.60)</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Critical points of energy

Critical points transitions are mathematically defined as[6]:

\[
\rho_{ev}(\hbar \omega) = \frac{2}{8\pi^3} \iint \frac{ds}{|\nabla_k (E_c - E_v)|_{E_c - E_v = \hbar \omega}} \quad \text{(3.2)}
\]

Of special interest are those points in the Brillouin zone where \((E_c - E_v)\) is stationary and \(\nabla_k (E_c - E_v)\) vanishes. At such points, called joint critical points, the denominator of the integrand in Eq. 3.2 vanishes and especially larger contributions can be made to \(\rho_{ev}(\hbar \omega)\). This can be understood on the basis of physical considerations. Around critical points, the photon energy \(\hbar \omega = (E_c - E_v)\) is effective in inducing electronic transitions over a relatively larger region of the Brillouin zone.
than would be the case for transitions about non-critical points. The relatively large contributions to the transition probability for critical points give rise to “structure” observed in the frequency dependence of the optical properties of solids. Critical points generally occur at high symmetry points in the Brillouin zone, thought i is is not necessarily the case.

As our experiment critical points are determined from the derivative of reflectivity equal to zero that shown in figure 3.1. The critical point at $E_0$ (i.e., $E_g$) is identified as the direct band gap energy, while the critical point at $E_0+\Delta_0$ corresponds to a transition from the split-off valence band at $k = 0$ which arises through the spin orbit interaction. The transitions at $E_1$ and $E_1+\Delta_1$ corresponding to $\Lambda$-point and $L$-point transitions are also due to spin-orbit splitting. Although the detailed band structure and notation given to GaAs are obtained from ref [3], the values of pertinent interband transitions are given in Table 3.1 for GaAs (as a reference), Zn(OH)$_2$, ZnGO-2 and ZnGO-5.

### 3.3 Dependence of reflectance on the band structure

The number of transitions is defined in the Brillouin zone with density [26],

$$W(\omega) = \frac{2\pi}{\hbar} \left( \frac{eA_0}{mc} \right) \sum_{v,c} \int_{BZ} \frac{2dk}{(2\pi)^3} |\varepsilon.M_{c,v}(k)|^2 \delta(E_c(k) - E_v(k) - \hbar\omega)$$

3.3a

Where, the integral extend over the first Brillouin zone and the fraction 2 arises from in the integration of spin variables.

The reflectance $R$ is given by the following relationship [7,11];

$$R = \frac{(\bar{n} - 1)^2 + k^2}{(\bar{n} + 1)^2 + k^2}$$

3.3b

Where $n$ is the real part of the index of refraction and $k$ is the extinction co-efficient. This reflectance depends on both $n$ and $k$. 
The optical intensity of a light wave is proportional to square the electric field, namely $I \propto \varepsilon^2$.

We can deduce from equation $\varepsilon(z,t) = \varepsilon_0 e^{-k\omega z/c} e^{-i(\omega t - kz)}$ that intensity falls of exponentially in the medium with the decay constant equal to $2(k\omega/c)$ on comparing this to Beer’s law given in equation $[I(z) = I_0 e^{-\alpha z}]$ [7]. We have,

$$\alpha = \frac{2k\omega}{c} \quad 3.3c$$
$$\alpha = \frac{\omega}{nc}\varepsilon_2 \quad 3.3d$$

where $\alpha$ is the absorption coefficient. Near and below the energy gap, $k$ is usually small compared to $(n-1)$; therefore, $R$ is dominated by $n$;

$$R = \left(\frac{n-1}{n+1}\right)^2 \quad 3.3e$$

The average density $u$ is a medium of radiation field described by the vector potential ;

$$u = \frac{n^2 A_0^2}{2\pi c^2} \omega^2$$

Using the equation 3.3a, obtain microscopic absorption co-efficient and other optical constant,

$$\alpha(\omega) = \frac{\hbar\omega W(\omega)}{u(c/n)}$$

we thus obtain for the absorption co – efficient,

$$\alpha(\omega) = \frac{4\pi^2 c^2}{ncm^2} \sum_{v,c} \int_{BZ} \frac{2dk}{(2\pi)^3} \left| \tilde{M}_{c,v}(k) \right|^2 \delta(E_c(k) - E_v(k) - \hbar\omega) \quad 3.3f$$

$$\varepsilon_2(\omega) = \frac{4\pi^2 c^2}{m^2 \omega^3} \sum_{v,c} \int_{BZ} \frac{2dk}{(2\pi)^3} \left| e \tilde{M}_{c,v}(k) \right|^2 \delta(E_c(k) - E_v(k) - \hbar\omega) \quad 3.3g$$

the absorption coefficient is by definition the energy absorbed in the unit time in the unit volume divided by energy flux, This is the basic expression which connects band structure with optical
properties. The quantum expression for $\varepsilon_1(\omega)$ can be obtained using the dispersion relation of Kramers-Kronig [7]:

$$
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \omega' \varepsilon_2(\omega) \frac{1}{\omega'^2 - \omega^2} d\omega' \quad 3.3h
$$

Where, $P$ is the principal part. By direct substitute $3.3g$ into $3.3h$,

$$
\varepsilon_1(\omega) = 1 + \frac{8\pi e^2}{m^2} \sum_{v,c} \int_{BZ} \frac{2dk}{8\pi^2} \frac{[\varepsilon \tilde{M}_{c,v}(k)]^2}{[E_c(k) - E_v(k)]/\hbar \left[\frac{E_c(k) - E_v(k)}{\hbar - \omega^2}\right]} \quad 3.3i
$$

Equation 3.3g and 3.3i allows in principle of computation of all optical constants once the band structure is known.

### 3.4 Structure of the optical constants at critical points

We shall now discuss the specific case and will show that a structure in optical constants results with peaks at critical points. The matrix element $|\varepsilon \tilde{M}(k)|^2$ between a given couple of the valence and conduction bands are shown to be smooth functions of $K$, except near special $k$ vector where $|\varepsilon \tilde{M}(k)|^2$ vanishes because of symmetry.

Modify the equation 3.3a and we have,

$$
J(\hbar \omega) = \int_{BZ} \frac{2dk}{(2\pi)^3} \delta(E_c(k) - E_v(k) - \hbar \omega) \quad 3.4a
$$

Which is called the density of states, because it gives the density of pair states-one occupied and other empty separated by energy $\hbar \omega$.

Using the delta function properties, we integrate of equation 3.4a
\[ J_{c,v}(E) = \frac{2}{(2\pi)^2} \int_{E_c(k)-E_v(k)=E} \frac{dS}{|\nabla_k [E_c(k)-E_v(k)]|} \]  

3.4b

Where \( dS \) represents the element of surface in \( k \) space defined by the equations \( E_c(k) - E_v(k) = E \)

The joint density of states for interband transition as a function of \( E \) shows strong variations in the neighborhood of particular values of \( E \) which is called critical points of energies. From equation 3.4b, we have

\[
\nabla_k E_c(k) = \nabla_k E_v(k) = 0 \quad 3.4c \quad \text{or} \quad \nabla_k E_c(k) - \nabla_k E_v(k) = 0 \quad 3.4d
\]

Critical points of types 3.4c will occur in general at high symmetry points of the Brillouin zone, while critical points of type 3.4d occur in any vector \( k \).

Limiting the expansion of quadratic term and denoting the wave vectors along the principal axes with the origin at the critical points by \( k_x, k_y, k_z \),

\[
E_c(k) - E_v(k) = E_0 + \frac{\hbar^2}{2} \left( \frac{k_x^2}{m_x} + \frac{k_y^2}{m_y} + \frac{k_z^2}{m_z} \right) \quad 3.4e
\]

With \( m_x, m_y, m_z \) positives quantities and \( \varepsilon_x, \varepsilon_y, \varepsilon_z \) equal to +1 or -1. We obtained four types of singularities depending on the sign of \( \varepsilon_x, \varepsilon_y, \varepsilon_z \), the critical points are called;
Table 3.2: Summary of the joint density of states for a 3D system near each of the distinct types of critical points. [Ref. 6]

<table>
<thead>
<tr>
<th>Type of singularity</th>
<th>Number of negative $\alpha_i$’s</th>
<th>Joint density of states</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_0$ minimum</td>
<td>0</td>
<td>$\rho_{nc}(\hbar\omega)$, $\hbar\omega$</td>
</tr>
<tr>
<td>$M_1$ saddlepoint</td>
<td>1</td>
<td>$\rho_{nc}(\hbar\omega)$, $\hbar\omega$</td>
</tr>
<tr>
<td>$M_2$ saddlepoint</td>
<td>2</td>
<td>$\rho_{nc}(\hbar\omega)$, $\hbar\omega$</td>
</tr>
<tr>
<td>$M_3$ maximum</td>
<td>3</td>
<td>$\rho_{nc}(\hbar\omega)$, $\hbar\omega$</td>
</tr>
</tbody>
</table>

3.5 Summary

In this chapter we have discussed the reflectivity and critical points of energy as well as theoretical parts of critical point energies. Critical points of energy of three sample $\text{Zn(OH)}_2$, $\text{ZnGO-2}$ and $\text{ZnGO-5}$ were determined using wavelength modulation techniques. From the table 3.1 shows we got two critical points of energy of each sample, which indicates our sample is composite materials of $\text{ZnOH}$ and $\text{GO}$. It may be one band gap for $\text{Zn(OH)}_2$ and another band gap for $\text{GO}$ (graphite Oxides). Reflectivities of these three samples were between 15% to 20% that is suitable for photovoltaic energies.
Chapter 4

Luminescence and photoconductivity

Since our purpose is to use Zinc(hydr)oxide and its composites with 2% and 5% Graphite Oxides (GO) as a solar cell material, photovoltaic properties are an important properties of these materials. In this chapter, we will discuss about luminescence, photoconductivity and enhancement of photoconductivity of ZnGO materials. Enhancements of photoconductivity treatment were performed by the ICG dye that soak by materials at least 12 hours.

Luminescence is basically a non-equilibrium phenomena, it requires excitation by light, electron beams, current injection, which generally act as to create excess electrons, holes, or both. The effects of electron-hole recombination give rise to recombination radiation or luminescence [6]. The atom emits light by spontaneous emission when electrons in excited states drop down to a lower level by radiative transitions. In solid the radiative emission process is called luminescence [7].

One classification of luminescent processes is based on the source of the excitation energy. The most important excitation sources are;

1. **photoluminescence** by optical radiation,
2. **electroluminescence** by electric fields or currents,
3. **cathodoluminescence** by electron beams (or cathode rays),
4. **radioluminescence** by other energetic particles or high energy radiation.
Fluorescence and Photoluminescence are luminescence where the energy is supplied by electromagnetic radiation (such as light). In generally Photoluminescence means "luminesce from any electromagnetic radiation", while fluorescence is often used only for luminescence caused by ultraviolet, although it may also be used for other photoluminescences. Photoluminescence is distinguished such that the light is absorbed for a significant time, and generally produces light of a frequency that is lower than, but otherwise independent of the frequency of the absorbed light [27].

**Fig. 4:** Energy transition diagram of fluorescence.

Fluorescence molecules also called fluorophores or simply fluors respond distinctly to light compared to other molecules, as shown fig.4. A photon of excitation light is absorbed by an electron of a fluorescent particle, which raises the energy level of the electron to an excited state. During the short excitation period, some of the energy is dissipated by molecular collision or transfer to a proximal molecule, and the remaining energy is emitted as a photo to relax the electron back to the ground states. Because the emitted photon usually carries less energy and
therefore has a longer wavelength than the excited photon, the emitted fluorescence can be distinguished from the excitation light.

4.1 Excitation of photoluminescence

The band diagram corresponding to the photoluminescence (PL) process of in a direct and indirect gap material are given in fig. 4.1. The shaded states at the bottom of the conduction band and the empty states at the top of the valence band respectively represent the electrons and holes created by the absorption of photons with energy $\hbar \omega_{exc} > E_g$. The cascade of transitions within the conduction and valence bands represents the rapid thermalization of the excited electrons and holes through phonon emission. In a direct gap material (left), the conduction band minimum and the valence band maximum occur at the same $k$ values.

Both the photon absorption and emission (i.e. the electron-hole recombination) processes can conserve momentum without the assistance of phonons, since the momentum of the absorbed or emitted photon is negligible compared to the momentum of the electron. We therefore represent photon absorption and emission processes by vertical arrows on $E$-$k$ diagrams. In an indirect gap material (right), the conduction band minimum and the valence band maximum occur at different $k$ values. As a result, to conserve momentum, the photon absorption process must involve either absorption (indicated by a "+" sign) or emission (indicated by a "-" sign) of a phonon, while the Photoluminescence (PL) process requires the emission of a phonon [28]. While the PL process requires the emission of a phonon. Since the energy of a phonon (~ 0.01 eV) is much smaller than the energy of the PL photon for an indirect gap material, the peak energy of the PL also roughly reflects its band gap.
4.2 Photoluminescence spectroscopy of Zn(OH)$_2$ and its composites

Photoluminescence spectra is mainly used a diagnostic and development tool in semiconductor research. The goal of our research is to develop solar cell device as a light emission mechanism have been studied in details by photoluminescence spectra.

Fig 4.2(a) : Photoluminescence spectra of (a) Zn(OH)$_2$, (b) ZnGO-2
In photoluminescence experiment, the samples were excited by energy above the optical band gap energy. This experiment exhibits both radiative and non-radiative relaxation. The photoluminescence experiments were carried out at room temperature using a Perkin-Elmer LS-50 fluorescence spectrometer. The Perkin-Elmer Models LS-50 Luminescence Spectrometer measure the fluorescence intensity of samples in either a continuous scan over a range of wavelengths or at selected excitation and emission wavelength pairs.

The samples were excited with a beam of light at 300 nm (~4.13 eV) and fluorescence was collected between 320 nm and 760 nm. The first peak, for Zn(OH)$_2$ sample, appears at 400 nm (~3.1 eV) and the highest intensity peak appears at around 420 nm (~2.95 eV), as shown in fig. 4.2 (a). The subsequent peaks visible on the spectrum are attributed to phonon assisted recombination at lower photon energy in regions where materials are more transparent as reported in the case of some semiconductors [29]. It is recognized that there might be impurity-assisted non-radiative transitions for which band broadening can be attributed [29]. The optical band-gap energies for samples were found from using the following equation:
\[ E_{op} = E_{g}^{PL} + 0.5k_B T, \]  

(4.2)

The \( E_{g}^{PL} = 2.93eV \) was obtained after subtracting the contribution due to the Boltzmann factor \((0.5k_B T)\) from optical band gap energy \( E_{g} \) (i.e., energy corresponding to the highest peak). Likewise, \( E_{g}^{PL} = 2.87eV \) for ZnGO-2 and \( E_{g}^{PL} = 2.84eV \) for ZnGO-5 were recorded.

More fluorescence radiative and non-radiative has been discussed in chapter 6.

4.3 Photoconductivity

Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation such as visible light, ultraviolet light, infrared light, or gamma radiation [30].

When light is absorbed by a material such as a semiconductor, the number of free electrons and electron holes increases and raises its electrical conductivity. To cause excitation, the light that strikes the semiconductor must have enough energy to raise electrons across the band gap, or to excite the impurities within the band gap. When a bias voltage and a load resistor are used in series in the semiconductor, a voltage drop across the load resistors can be measured when the change in electrical conductivity of the material varies the current flowing through the circuit.

Photoconductivity is observed when light is incident on a poorly conducting material, (e.g., an insulator or semiconductor), and the photon energy is sufficiently high to excite an electron from an occupied valence state to an unoccupied conduction state. In such interband transitions both the electron and hole will contribute to the electrical conductivity if a voltage is applied across the sample as shown in the schematic experimental arrangement in fig. 4.4. Since
the threshold for photoconduction occurs at $h\nu = E_g$, measurement of the photoconductivity can be used to determine the band gap for non-conducting materials. Photoconductivity is often the concept used for the design of practical optical detectors [6].

![Diagram](https://via.placeholder.com/150)

**Fig. 4.3**: Schematic diagram of the experimental arrangement for measuring the photoconductivity.

The photoconduction process increases the electrical conductivity $\Delta \sigma$ due to the increase in the density of electrons ($\Delta n$) and ($\Delta p$) resulting from photo-excitation [6];

$$\frac{\Delta \sigma}{\sigma} = \frac{\Delta n \mu_n + \Delta p \mu_p}{n \mu_n + p \mu_p}$$

(4.3)

in which $\mu_n + \mu_p$ are respectively, the electron and hole mobilities. Since the carriers are generated in pairs in the photo-excitation process $\Delta n = \Delta p$.

### 4.4 Photoconductivity spectroscopy of $\text{Zn(OH)}_2$ and its composites

A photocurrent due to photon induced electron–hole pair generation and subsequent charge separation by an electrical field was found flowing through the sample upon light illumination [30].

To measure photocurrent, photo-excited carriers are collected at the external electrodes. In the steady state, free carriers are continually created by the incident light. At the same time,
they annihilate each other through electron-hole recombination. To produce a large photocurrent, it is desirable to have a long free carrier lifetime $\tau$ or a slow recombination time. If $G$ is the rate of generation of electrons per unit volume due to photo-excitation, then the photo-excited electron density in the steady state will be given by [31]:

$$\Delta n = G\tau, \quad (4.4)$$

The generation rate $G$ will in turn be proportional to the photon flux incident on the photoconductor. Whereas slow recombination rates are essential to the operation of photoconductors, rapid recombination rates are necessary for luminescent materials.

In the recombination process, an electron and hole annihilate each other, emitting a photon in a radiative process. In real materials, the recombination process tends to be accelerated by certain defect sites. When such defects tend to be present in relatively greater concentrations at the surface, the process is called surface recombination. In bulk, the density of recombination centers can be made low for a very pure and “good” crystal. A typical concentration in a high quality ZnGO crystal would be $\sim 10^{12} \text{ cm}^{-3}$.

The photoconductivity experiments were carried out using a Triax 320 monochromator to select the wavelength of light from a Quartz Tungsten Halogen Lamp in a wide spectrum ranging from 300 nm to 1200 nm. Photocurrent spectra were recorded by a SR 830-DSP Locking Amplifier. The light beam coming out from monochromator was focused onto an area in between electrodes over the samples. Lamp spectrum emerging from monochromator was measured by a UV enhanced silicon detector. A grating with blazing wavelength of 500 nm was used for all measurements. Fig. 4.4 (a-c) shows photocurrent curves for all three samples. All photocurrent spectra cover a spectral range from 300 nm to 800 nm. The photocurrent peak for Zn(OH)$_2$...
appears at 405 nm \( (i.e., E_{g}^{pc} = 3.06 eV) \). Likewise, for ZnGO-2 and ZnGO-5, the photocurrent peaks appear at 430 nm \( (i.e., E_{g}^{pc} = 2.88 eV) \) and 435 nm \( (i.e., E_{g}^{pc} = 2.85 eV) \).

The photocurrent measurement has been of very practical use, as this technique provides direct band gap energy for non-conducting materials and which has also been proven to be very useful information in designing the practical photo detectors. All band gaps related energies and absorption coefficients, obtained by three optical characterization techniques are compiled in Table 2.4 (Ch.3, page 14) show a close correspondence with one another and those values obtained by a numerical method.

**Fig.4.4(i):** Photocurrent spectra of (a) Zn(OH)$_2$; and its composites (b) ZnGO-2, (c) ZnGO-5. Photocurrent (PC) as a function of wavelength (nm).
Highest photocurrent of these three samples are found 0.5 μA to 3.5 μA at the spectral ranges of 375 nm to 475 nm. There are some big pores inside these samples (shown in fig. 4.6) reasons of low photoconductivity.

![Image](image_url)

**Fig. 4.4(ii):** Two Photon image of ZnGO-2 shows big pores at inside the samples.

Electrons are trapped in pores and gets low rate of electron-hole recombination may affect the low conductivity.

The next section discusses about the enhancement of photoconductivity.

**4.5 Conductivity enhancement of ZnGO by ICG dye**

Since our goal is to increase photoconductivity which can enhance solar cell energy conversion efficiency. In this section, we have discussed conductivity of ZnGO-2 (Zinc(hydr)oxide with 2% graphite oxide) which has been enhanced using indocyanine green
(ICG) dye. The photovoltaic properties of the cells with and without treatment of the porous ZnGO photocurrent were compared. From the photocurrent measurements, it was shown that the cells with treated ZnGO layers have higher value compared to cell with untreated ZnGO layers.

4.5 (i) Preparation of samples

Preparation of samples discussed in section 1.3 (page 4) of this research paper without dye treatment. For dye treatment, the sample was dipped into an ICG dye solution at least 10 hours at room temperature and then it was dried at least one hour at room temperature before using in two photon fluorescence tools. The concentrated dye solution is made by accurately diluting 1mL of the 5mg/mL dye with 7mL of distill water.

\[ \text{Indocyanine Green} \]

**Fig. 4.5 (i):** Structural formula of indocyanine green (ICG) dye [32].

4.5 (ii) Indocyanine dye

**Indocyanine green** (ICG) is a cyanine dye used in medical diagnostics. It is used for determining cardiac output, hepatic function, and liver blood flow, and for ophthalmic angiography [33]. It has a peak spectral absorption at about 800 nm [33]. ICG is a fluorescent dye which is used in medicine as an indicator substance (e.g. for photometric hepatic function
diagnostics and fluorescence angiography) in cardiac, circulatory, hepatic and ophthalmic conditions[34]. In here our purpose is to increase photoconductivity using ICG dye.

**Fig. 4.5 (ii):** (a) Absorption of ICG dye and (b) Fluorescence of ICG dye.
The absorption and fluorescence spectrum of ICG is in the near infrared region. Both depend largely on the concentration and solvent used [35]. ICG absorbs mainly between 600 nm and 900 nm and emits fluorescence between 750 nm and 950 nm (shown in fig. 4.6(ii)). The large overlapping of the absorption and fluorescence spectra leads to a marked re-absorption of the fluorescence by ICG itself. The fluorescence spectrum is very wide. In combination with fluorescence detection, lasers with a wavelength of around 780 nm are used. At this wavelength, ICG still absorbs very well and yet it is still technically possible to suppress the excitation light in order to detect the fluorescence.

4.5 (iii) Results and discussions

The micro/meso porous structure of ZnGO materials were investigated using two photon fluorescence image (2PF) shown in fig. 4.6 (iii). Two photon fluorescence (TPF) imaging was performed with the Ultima Multi-Photon-Microscope (Olympus BX-51 of Prairie Tech.Inc.,WI,USA).

An excitation energy between 1.82 eV (680 nm) and 1.15 eV (1080 nm) was used to conduct TPF imaging. In particular, the samples were excited with 100-fs laser pulses with an energy of 1.569 eV (i.e., 790 nm) using the Ti-Sapphire (Chameleon Ultra II laser, Coherent Inc.) laser, and the fluorescence emitted from the specimen was collected by the photomultiplier tubes (PMTs) after passing barrier filters (450~490 nm). 2P images have been described details in Chapter 5.

A photocurrent due to photon induced electron–hole pair generation and subsequent charge separation by an electrical field was found flowing through the sample upon light illumination [30].
Effective charge separation between dye’s and a wide band oxide semiconductor can be achieved by fitting the conduction band of the oxide and the size-dependent electron level of the dye’s. Photoexcited electron transfer from the dye to the oxide, while the holes remain trapped in the Dye(fig. 4.5(iii)). The electron injection rate increases strongly with the energy difference between the oxide conduction band and the electron level of the dye, as shown by transient photocurrent measurements.

**Fig. 4.5(iii):** Two photon images of zinc(hyd)oxide with 2% graphite (ZnGO-2) (a): without dye and (b-d): with dye. Images (b-d) show dyes were filled in pores looking like black spots.

**Fig. 4.5 (iv):** Scheme of electron transfer between an ICG dye and a ZnGO-2 grain.
Among other wide band semiconductor oxides, ZnGO has the maximal electron affinity that should result in a maximal electron injection rate. The photoconductivity of the sensitized films/materials was investigated in a cell shielded from background light. The photocurrent was registered using a lock in amplifier SR 830 electrometer as a change of the sample conductivity under illumination. Photoconductivity vs. Wavelength (nm) dependence during periodic switching of illumination was recorded. The sample was pumped by 3.9 watt input DC power supply.

![Graph of ZnGO-2 without dye](image1)

![Graph of ZnGO-2 with dye](image2)

**Fig. 4.5(v):** Photoconductivity of ZnGO-2, (a) without dye, (b) with dye
Maximum photocurrent was 0.25 µA at 450 nm without using dye and 2.75 µA at 450 nm with dye that is ~11 times higher than without dyes shown Fig. 4.5 (vi). Due to dye treatment of ZnGO sample, micro/ meso porous were filled up by the ICG dye [fig. 4.5 (iii) b-d], photoconductivity were increased 11 times higher than without dye using the data may reason of higher photocurrent.
Chapter 5

Structural characterization of materials

Amorphous micro/meso-porous materials are gaining importance in solar energy conversion and as sensors due to their low cost, high accessible surface area, and wide band gap energies [36-37]. As possible key components in solar converters and detectors, it is of great importance to describe structural properties micro/ meso-porous materials. A new class of micro/meso-porous material is zinc (hydr)oxide and its composites with graphite oxides. Bandosz and co-workers [4] have shown that such materials exhibit the photo-activity in the visible light [38-39]. The shape of the optical emission spectrum, manifests the effects of structural and thermal disorders on the electronic properties of the micro-composites [40]. The unique characteristics, such as improved structural [41] and electrical properties [42], stem from the layered structure of the micro-composites with chemically active oxygen groups at the basal planes of graphite oxide (GO) [44]. GO is found to be a promising material for a large scale graphene processing, as its chemical and thermal reductions are proven to produce a material with properties comparable to those of chemical vapor deposition (CVD)-grown graphene. The presence of increased GO phase in the final micro-composites formed is reported to increase electrical conductivity, and this feature is particularly important for energy storage and sensor applications [4]. These micron-sized pores can be impregnated with quantum dots and dyes to enhance conversion of energy from solar spectra.

The properties of materials are determined by their structure which depends on composition and growth conditions. The formation and development of defects of the crystal structure and their
influence on the material properties is also essential to be studied. Thus, it is necessary to characterize both composition and microstructure at the highest levels of resolution possible in order to understand materials behavior and to facilitate the design of new improved materials. Such a characterization requires advanced methods of analysis using microscopics, diffraction, and spectroscopic techniques, two photon fluorescence image.

Structural characterization is one of which important chapter of my research. Because, structural properties describe the surface properties of materials, chemically bonding of molecules, chemical composition, phase composition, defects of materials, composite materials, size of particles etc. which is more or less importance using in semiconductor industries.

In this chapter, the structural properties of zinc(hydr)oxide with 2% and 5% graphite oxide (ZnOH2, ZnGO-2 and ZnGO-5 respectively) were investigated by the two photon fluorescence (2PF) image, Tunneling Electron Microscopy (TEM) and X-Ray diffraction (XRD) pattern. Develop of surface of material layer were also discussed.

5.1 Two photon image of materials

Two-photon excitation microscopy is a fluorescence imaging technique that allows imaging up to a depth of approximately one millimeter. The application of two-photon excitation fluorescence microscopy has become a powerful tool for studying biological functions in live tissues and offers many advantages over conventional imaging techniques. Two photon fluorescence (TPF) is a technique in which a fluorophor is excited by the simultaneous absorption of two photons. The familiar one photon fluorescence process involves exciting a fluorophor from the electronic ground state to an excited state by a single photon.
This process typically requires photons in the ultraviolet or blue/green spectral range. However, the same excitation process can be generated by the simultaneous absorption of two less energetic photons (typically in the infrared spectral range) under sufficiently intense femtosecond pulse laser illumination [43-44]. TPF imaging identifies light emitting regions. It also identifies the pores and void regions of samples. Using this imaging technique, particle size and distribution can be estimated.

**Fig. 5.1**: Jablonski diagram for (a) one-photon (b) and two-photon excitation. Excitations occur between the ground state and the vibrational levels of the first electronic excited state. One-photon excitation occurs through the absorption of a single photon. Two-photon excitation occurs through the absorption of two lower-energy photons via short-lived intermediate states. After either excitation process, the fluorophore relaxes to the lowest energy level of the first excited electronic states via non-radiative processes. The subsequent fluorescence emission processes for both relaxation modes are the same [43-44].
Two-photon excitation is a fluorescence process in which a fluorophore (a molecule that fluoresces) is excited by the simultaneous absorption of two photons (figure 5.1). The familiar one photon fluorescence process involves exciting a fluorophore from the electronic ground state to an excited state by a single photon. This process typically requires photons in the ultraviolet or blue/green spectral range. However, the same excitation process can be generated by the simultaneous absorption of two less energetic photons (typically in the infrared spectral range) under sufficiently intense laser illumination. This nonlinear process can occur if the sum of the energies of the two photons is greater than the energy gap between the molecule’s ground and excited states. Since this process depends on the simultaneous absorption of two infrared photons, the probability of two-photon absorption by a fluorescent molecule is a quadratic function of the excitation radiant. Under sufficiently intense excitation, three-photon and higher photon excitation is also possible and deep UV microscopy based on these processes has been developed.

Here is an example of three materials such as Zn(OH)\(_2\), ZnGO-2, and ZnGO-5 whose two photon fluorescence image has been taken by Ultima Multi-Photon-Microscope (Olympus BX-51 of Prairie Tech.Inc.,WI,USA). An excitation energy between 1.82 eV (680 nm) and 1.15 eV (1080 nm) was used to conduct TPF imaging. In particular The samples were excited with 100-fs laser pulses with an energy of 1.569 eV (i.e., 790 nm) using the Ti-Sapphire (Chameleon Ultra II laser, Coherent Inc.) laser, and the fluorescence emitted from the specimen was collected by the photomultiplier tubes (PMTs) after passing barrier filters (450~490 nm). The 2-D images (239.1 \(\mu\)m×239.1 \(\mu\)m) produced on the screen (512×512 pixels) were recorded as shown in Fig.5.2. For 3-D images, we collected Z-series image stacks with defined ranges for the start position, stop position, and step size. The image stacks were analyzed using Image J software (National
Institutes of Health). After importing images into image J, image properties of pixel width (0.467 µm) and height (0.467 µm) in the X and Y directions, and voxel depth (1 µm) in the Z-direction was provided. They were then converted into 8-bit images to reconstruct the 3-D images. The clearest images were chosen for analysis.

**Fig. 5.2:** Two photon fluorescence images showing voids and light-emitting regions: (a) A 2-D image for Zn(OH)$_2$ with the pore size ranging from 20-µm to 63 µm; (b) A 2-D image for ZnGO-2 with the pore size ranging from 25-µm to 255 -µm; and (c) A 2-D image for ZnGO-5 with pore sizes ranging from 20-µm to 232 -µm; a 3-D image for each sample is shown in the insets on the upper-left-corner of each figure. Upper right corner of the images shows intensity bars of emitted regions of samples, where a white color denotes region of maximum emitted light whereas light blue color denotes region of no light. The arrows shown in fig. (a-c) show that the holes are almost hexagonal in shape.
TPF images shown in fig. 5.2(a-c) are very similar. These three samples indicate the presence of holes between the aggregates of particles. These holes are almost hexagonal in shape, and these three images also show light-emitting regions that are nothing but the aggregates of nanoparticles. Particle size distribution of the luminescent average area of Zn (OH)\textsubscript{2}, ZnGO-2, and ZnGO-5 were 143 µm\textsuperscript{2} [Average size, \(\sim(11.94 \pm 3.21)\ \mu m\), min 4.5\(\mu m\), max 17.0\(\mu m\)], 318 µm\textsuperscript{2} [Av. Size, \(\sim(17.83 \pm 4.52)\ \mu m\), min 4.5\(\mu m\), max 21.0\(\mu m\)], 551 µm\textsuperscript{2} [Av. Size, \(\sim(23.48 \pm 5.18)\ \mu m\), min 5.0 \(\mu m\), max 45.0 \(\mu m\)], and area of pores 498 µm\textsuperscript{2} [min 20.0\(\mu m\), max 63.0\(\mu m\) diameter], 982 \(\mu m^2\) [min 25.0 \(\mu m\), max 255.0 \(\mu m\) diameter], and 827 µm\textsuperscript{2} [min 20.0 \(\mu m\), max 232.0 \(\mu m\) diameter] respectively.

The light emitting regions, observed via TPF imaging technique, that are aggregates of micro-particles vary in size in the studied samples and this unique imaging technique shows the structural details of the composites that are reported for the first time. The current studies on these micro-composites have proven to be very useful as Zn(OH)\textsubscript{2}, ZnGO-2 and ZnGO-5 hold promise as new materials for their unique capacities in harvesting solar energy and their storage purposes. The pore sizes are possibly suitable for doping with dye molecules and quantum dots to enhance solar conversion energy and their storage purposes. The pore sizes are possibly suitable for doping with dye molecules and quantum dots to enhance solar conversion.
5.2 Structural properties enhancement by ICG dye

Structural properties play the important role of materials that increase photoconductivity of solar cells. Since their structure which depends on composition and growth conditions. The formation and development of defects of the crystal structure are necessary to increase conductivity. In order to big holes / pores of ZnGO materials, electron are trapped in holes reason of low conductivity. Crystal structure was improved by the using in Indocyanine (ICG) dye and two photon fluorescence image technique were applied to characterize this property.

Indocyanine dye used for developing structural crystal layer. The properties of indocyanine dye have been described in the sections 4.5 (II) chapter 4 and the preparation of samples were discussed also in sections 4.5 (I). Fig. 4.5 (iii) shows the structure of two photon fluorescence image of ZnGO-2 before and after dye treatment. ZnGO-2 materials absorbed the dye molecules and filled up some parts of pores and others empty reason due to dip the sample into dye solution.

The materials were exposed to dye to evaluate their suitability as adsorbents of toxic industrial compounds at ambient conditions. The highest dye adsorption capacities were found on Zn(OH)$_2$ and its composite with graphite oxide either in an as-received from [fig. 4.5 (iii) b-d] at room temperature. ICG dye is shown in fig. 4.5 (ii) absorbs electromagnetic radiation over UV to NIR regions that enhance amazing responds of photoconductivity of ZnGO-2 [fig. 4.5 (v)].

5.3 Light emitting of materials

Light can be produced by matter which is in an excited state and as its excitation can come from a variety of sources as Chemiluminescence, Bioluminescence, Electroluminescence, Photoluminescence [47]. The atoms and molecules that make up matter typically emit light at characteristic energies. The light emission can be spontaneous or stimulated. In spontaneous
emission matter at a sufficiently high energy level can relax by emitting photons of a characteristic energy, this is the process which occurs in flames, or discharge lamps. Stimulated emission occurs when matter in an excited state is perturbed by a photon of light and gives rise to a further photon of light, typically at the same energy and phase as the perturbing photon. This phenomenon is the process which gives rise to laser emission where you have many photons at the same wavelength and in phase with each other. Light emitting samples were characterized by the two photon image technique.

Fig. 5.3: TPF images showing voids and light-emitting regions: (a) A 2-D image for Zn(OH)$_2$ with the pore size ranging from 20-µm to 63 µm; (b) A 2-D image for ZnGO-2 with the pore size ranging from 25-µm to 255 -µm; (c) A 2-D image for ZnGO-5 with pore size ranging from 20-µm to 232 -µm; Upper right corner of images show intensity bars of emitted regions of samples, where white color denotes region of maximum emitted light whereas light blue color denotes region of no light.

5.4 Particle size distribution

The particle-size distribution (PSD) of Zinc(hydr)oxide and its composite (ZnGO-2 and ZnGo-5) powder is a mathematical function that defines the relative amount, typically by mass, of particles present according to size. PSD is also known as grain size distribution [48]. The PSD of a material can be important in understanding its physical and chemical properties. Particle size
can be measured by various techniques such as sieve analysis, Air elutriation analysis, Photoanalysis, Optical counting methods, Electroresistance counting methods, Sedimentation techniques, laser diffraction methods. Two photon fluorescence image is a new type of technique that measure the size of particles and pores. Particle size distribution data can be presented numerically (tabular format) or graphically. When presented graphically, there are two types: differential and cumulative. They are related. If one differentiates the cumulative distribution curve, the differential distribution is obtained. If one integrates the differential distribution curve, the cumulative distribution is obtained [49].

The goal of particle size measurement in two photon fluorescence image is the size determination of the zinc(hydr)oxide particles. Using the two photon fluorescence technique, a particle that was analyzed by the image-j 3D software. We conducted the imaging experiment with an Ultima Multiphoton Microscopy system with excitation wavelength between 680 – 1080 nm (Prairie Tech., Inc., WI, USA) to get the TPF images. For samples of Zn(OH)2, ZnGO-2% and ZnGO-5%, we set 100 fs laser pulse at 790 nm from Ti Sapphire (Chameleon Ultra II laser, Coherent Inc.) and observed them with a 40× lens (NA=0.8, water immersion, Olympus). The fluorescence emitted from the specimen is collected by the Photomultiplier tubes (PMTs) after the barrier filters (450~490). When the image showed on the screen (512×512 bins), we recorded the 2-D images (239.1 µm×239.1 µm) by using Prairie View Software (Prairie Tech., Inc.). For 3-D images (shown in figure 5.2 page 52) we collected Z-series image stacks with the defined ranges for the start positions, stop positions and step size.

The image stacks were analyzed using a software named Image J (National Institutes of Health). After importing them into image J, we input the image properties for their pixel width (0.467 µm) and height (0.467 µm) in X-Y direction, and voxel depth (1 µm) in Z direction, then
converted them into 8-bit images to reconstruct the 3-D images. We rotated to view them at different angles and saved the best one for analyzing.

Fig. 5.4 (i): Zn(OH)$_2$, particle count image (left) and particle size distribution (right) of Zn(OH)

Fig. 5.4 (ii): ZnGO-2, particle count image (left), Particle size distribution (Right) of ZnGO-2

Fig. 5.4 (iii): ZnGO-5, particle count image (left), Particle size distribution (Right) of ZnGO-5
Table: 5.4 (Particle size distribution)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PSD</th>
</tr>
</thead>
</table>
| Zn(OH)\textsubscript{2} | Most of particles are found below 50 µm\textsuperscript{2} area  
Av. Size of particle \~50 µm\textsuperscript{2}  
Smallest particle \~21 µm\textsuperscript{2}  
Largest particle \~300 µm\textsuperscript{2}  
Particle count: 42 (Whole area) |
| ZnGO\textsubscript{-2}  | Most of particles are found below 50 µm\textsuperscript{2} area  
Av. Size of particle \~40 µm\textsuperscript{2}  
Smallest particle \~20 µm\textsuperscript{2}  
Largest particle \~450 µm\textsuperscript{2}  
Particle count: 60 (Whole area) |
| ZnGO\textsubscript{-5}  | Most of particles are found above 100 µm\textsuperscript{2} area  
Av. Size of particle \~113 µm\textsuperscript{2}  
Smallest particle \~25 µm\textsuperscript{2}  
Largest particle \~2000 µm\textsuperscript{2}  
Particle count: 40 (Whole area) |

Figure 5.4 (i-iii) shows the particle size distribution (PSD) over a range of number of particles. The range of particle is called particle size distribution (PSD) and it can be represented by the table 5.4.

Particle size distribution of the luminescent average area of Zn (OH) \textsubscript{2}, ZnGO-2, and ZnGO-5 were 143 µm\textsuperscript{2} [Av. Size, \~(11.94 \pm 3.21) µm, min 4.5µm, max 17.0µm], 318 µm\textsuperscript{2} [Av. Size, \~(17.83 \pm 4.52) µm, min 4.5µm, max 21.0µm], 551 µm\textsuperscript{2} [Av. Size, \~(23.48 \pm 5.18) µm, min 5.0µm, max 45.0 µm], and area of pores 498 µm\textsuperscript{2} [min 20.0µm, max 63.0µm diameter], 982 µm\textsuperscript{2} [min 25.0 µm, max 255.0 µm diameter], and 827 µm\textsuperscript{2} [min 20.0 µm, max 232.0 µm diameter] respectively.
5.5 Transmission Electron microscopic (TEM) image of materials

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEM images, fig. 5.5, show that the texture Zn(OH)$_2$ as consisting of loosely attached, small irregular particles. In micro-composites, ZnGO-2 and ZnGO-5, the particles of the inorganic phases deposited on graphene sheet look smaller than those in for Zn(OH)$_2$ [50], structural and thermal analysis of these materials are described in reference [4] in details. The textural differences are confirmed in fig. 5.5 (a-b) where the small particles of zinc hydr(oxide) are seen either highly dispersed between the layers of ZnGO or between the large flakes of the graphite derived materials. The TEM images for all samples Zn(OH)$_2$, and the composites heated at 600 °C.

![TEM images](image)

**Fig. 5.5:** Structure and thermal analysis of the composites Zn(OH)$_2$. Transmission electron microscopy (TEM) images for the (a) zinc (hydr) oxide Zn(OH)$_2$; (b) ZnGO-2; and (c) ZnGO-5.
Ogata et al [51], the texture of ZnGO does not resemble those of the parent components. It appears that the Zn(OH)$_2$ phase creates a web-like network connecting GO particles, resulting in a highly mesoporous material. The carboxylic groups at the edges of GO layers are likely involved in the formation of “seeds” for that web-like network. The involvement of the GO oxygen groups in the formation of the composite was shown previously [52-53].

In these composite materials, ZnGO-2 and ZnGO-5, the particles of the inorganic phases are smaller in size than those in the parent material Zn (OH)$_2$ and they are clearly seen in fig. 5.5(b-c) as they are deposited on the graphene sheet as a thin layer. The measured surface area of Zn(OH)$_2$, ZnGO-2 and ZnGO-5 are 72, 64, and 64 m$^2$/g, respectively, and the total pore volume increases with an increase in the amount of GO present in the composites. The band gap and critical points of transition for a new class of optical micro composite materials (ZnGO-2 and ZnGO-5) have been investigated using reflectance spectroscopy and the derivatives of such data. TPF-imaging technique reported herein for the first time in investigating these composite materials, ZnGO-2 and ZnGO-5, show the presence of voids and their increase in size as the percent of GO increase in the composites.
5.6 STEM and X-Ray diffraction (XRD) image of materials

Scanning Tunneling Electron Microscopy (STEM) images of ZnGO-5 (fig. 5.6(i)) show more details on the dimensions of zinc species particles. With an increasing magnification, it is seen that the deposition of particles on the graphene sheets as a first layer is followed by the subsequent deposition of particles of similar sizes (between 2 nm and 4 nm, as seen from the 12 nm x 12 nm image in fig. 5.6(i)).

![Fig. 5.6(i): STEM images of ZnGO-5 sample. The imaging areas from left to right are: 520 x 520 nm, 24 nm x 24 nm and 12x 12 nm. The crystal lattice of small deposited particles of Zn (OH)$_2$ with sizes of 2 nm are seen on the GO layers.](image)

The measured surface areas of Zn(OH)$_2$, ZnGO-2 and ZnGO-5 are 72, 64, and 64 m$^2$/g [36], respectively, and the total pore volume increases with an increase in the amount of GO present in the composites. The X-Ray diffraction patterns presented in fig. 5.6 (II) indicate that zinc hydroxide and zinc hydroxychloride, Zn$_5$ (OH)$_8$Cl$_2$, are present in the structure of ZnGO-5 [37]. The latter species is the only crystalline phase detected in ZnGO-2. The presence of chloride introduces surface heterogeneity and it may affect the band gap. Interestingly, the zinc (hydr)oxide particle sizes calculated from X-Ray diffraction patterns (fig. 5.6(ii)) using Scherrer equation [54-55];
\[ L = \frac{KL \cos \beta}{\lambda}, \]  

(5.6)

where, \( L \) is the size of crystallite, \( K \) is a constant dependent on the crystallite shape (0.89), \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width at half maximum (FWHM), and \( \Theta \) is the scattering angle.

Particle sizes calculated from X-Ray diffraction patterns are larger than those seen in STEM images and similar true for all three materials (Table 5.6).

**Fig. 5.6 (ii):** X-ray patterns for three different materials: (a) Zn(OH)\(_2\); (b) ZnGO-2; (c) ZnGO-5.

This may suggest that they exist as rods or oval particles. The results of Energy Dispersive X-ray (EDX) analysis indicate that much more zinc chloride is present in ZnGO-2 than in ZnGO-5. Moreover, the higher Zn/Cl ratio in the former sample than that in Zn\(_3\)(OH)\(_6\)Cl\(_2\) for points out the presence of zinc hydroxide but it must be in amorphous form or its particles are too small to be detected using X-ray diffractions.
Table 5.6: Crystallographic structures, sizes of crystallites, and surface contents of Zn, O, and Cl in atomic% evaluated using EDX.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallographic structure detected</th>
<th>Crystal size $L_c$ [nm]</th>
<th>Zn</th>
<th>O</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(OH)$_2$</td>
<td>ZnO/Zn(OH)$_2$</td>
<td>19.6</td>
<td>47.4</td>
<td>52.6</td>
<td>ND</td>
</tr>
<tr>
<td>ZnGO-2</td>
<td>Zn$_5$(OH)$_6$Cl$_2$nH$_2$O</td>
<td>20.3</td>
<td>54.0</td>
<td>24.2</td>
<td>8.2</td>
</tr>
<tr>
<td>ZnGO-5</td>
<td>ZnO/Zn(OH)$_2$</td>
<td>21.7</td>
<td>32</td>
<td>32.0</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Zn$_5$(OH)$_6$Cl$_2$onH$_2$O</td>
<td>17.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

STEM aberration corrected [56] images were obtained using Nion Ultra-STEM-100, equipped with a cold field emission electron source and a corrector of 3$^{rd}$ and 5$^{th}$ order aberrations. The microscope was operated at 60 KV accelerating voltages, which is below the knock-on radiation damage threshold in graphene.
Chapter 6

Time-resolved fluorescence of materials

Time-resolved photoluminescence is used to determine the carrier recombination through radiative and non-radiative processes in zinc hydroxide Zn(OH)$_2$ and its porous composites with graphite oxide (GO). The decay times, measured by a streak camera, are found to be larger for zinc hydroxide (~1215±156 ps) than its composites (~976±81 ps for ZnGO-2 and 742±59 ps for ZnGO-5), but no significant changes in rise times (from 4.0 ps to 5.0 ps) are recorded. The dominant mechanism for the radiative process is attributed to free carrier recombination, while micro-porous networks present in these materials are found to be the pathways for non-radiative recombination process via multiphonon emission.

The study of relaxation processes of photo-generated excess carriers (i.e., electrons and holes) in micro/meso-porous composite materials are important both from the basic physics point of view and its applications in solar and photodetector devices [4, 57-58]. The radiative process involves exciton and free carrier recombination and the non-radiative (NR) processes involve carrier-phonon and carrier-carrier interactions, and the mechanisms for NR processes include carrier capture via defect levels (such as, pores, voids, stacking faults, etc.), carrier escape through multiphonon emissions (MPE). It has great importance to determine not only the band gap energies and absorption coefficients of zinc hydroxide, Zn(OH)$_2$ and its composites with graphite-oxide (GO), but also their radiative and non-radiative relaxation processes. The composites of Zn(OH)$_2$ studied herein are ZnGO-2 (with 2 wt. % GO) and ZnGO-5 (with 5 wt. % GO). Bandosz and co-workers [57] have shown that such materials exhibit photo-activity in
the visible light, which suggests their applications as sensors and solar energy harvesting components [58].

The new composites, obtained via an in situ precipitation method, involve synthesis of oxygen-containing functional groups from GO and a zinc hydroxide precursor, leading to the formation of an interface bond between the inorganic and graphene-based phase [4]. This interface decisively determines the texture and porosity of the heterogeneous composite materials. The porous structure of the composites significantly influences the carrier relaxation processes. The unique characteristics, such as improved structural and electrical properties stem from the layered structure of the composites with chemically active oxygen groups at the basal planes of GO. The micro/meso size pores of the composites can accommodate photo-active units (i.e. Quantum dots, dye molecules) and offer versatile applications. The quantum efficiency and operating lifetime of the sensors and solar energy converters depend strongly on NR recombination processes, as the functional nonlinearity of devices has been attributed to the loss mechanisms associated with NR recombination processes [59]. No work of time-resolved photoluminescence (TRPL) has yet been reported on these micro/meso-porous composite materials despite their potential applications as solar absorptive and sensing devices.

In this chapter, room-temperature TRPL technique is used to characterize radiative and non-radiative recombination processes in zinc hydroxide Zn(OH)₂, and its composites ZnGO-2 and ZnGO-5. Build in the new model, longer and shorter life time, rise time, fall time are described.

6.1 Times Resolved Fluorescence Physics Model

Time-resolved fluorescence studies can provide direct relaxation information on various underlying physical processes on a molecular and macromolecular scale. The basic theory[60-61] is used here to show how to extract the radiative and nonradiative from fluorescence
dynamics. Direct picoseconds resolved techniques under 100 fs laser excitation enable the study of dynamics of relaxation in macromolecules, particularly biopolymers such as proteins and nucleic acids using the streak camera.

**Fig. 6.1(a):** Photo-physics processes in a simplified energy level diagram of a polyatomic organic molecule [61].

Femtosecond pulses provide $\delta(t)$ excitation to extract the rise time for the emission fluorescence. The photo-physics involved in the underlying dynamics first starts with an organic molecule being excited to $S^*_n$ by an ultra short delta $\delta(t)$ laser pulse in fs to ps range. The molecule relaxes from the excited state $S^*_n$, such as the vibrational excited state $S^*_1$ in figure 6.1a, to the lowest level of the singlet state $S_1$ through vibrational relaxation at a rate of $k_0$, which gives vibration thermalization time, $\tau_0 = k_0$. The fluorescence rate is a measure of radiative and non-radiative processes. The constant $k_R$ is the radiative decay rate (probability of radiative transition per second). Various other non-emission channels denoted as non-radiative decay processes are
described by the rate $k_{NR}$. These non-radiative decay processes may occur due to collision by diffusion, quenching of emission by another species, energy transfer with the fast rotational motion of the molecule, or transfer with diffusion while the molecule itself relaxes to the ground state. In general, if the molecular decay rates of internal conversion, intersystem crossing, and quenching are denoted as $k_{IC}$, $k_{IS}$, and $k_q$, respectively, then the non-radiative rate is given by

$$k_{NR} = k_{IC} + k_{IS} + k_q \quad \text{(1a)}$$

And the fluorescence decay rate is given as

$$k_F = k_R + k_{NR} \quad \text{(1b)}$$

Where, the fluorescence lifetime $\tau_F = (k_F)^{-1}$. The rate of change of a number of molecules in the emitting state $S_1$ can be expressed as

$$\frac{dn_{S_1}}{dt} = k_{rs} n_{S_1^*} - k_F n_{S_1} \quad \text{(2)}$$

where, $n_{S1}$ and $n_{S1^*}$ are the number of molecules at the $S_1$ and $S_1^*$ (vibrational excited state of $S_1$) levels, respectively. For a $\delta$-pulse excitation, substituting for the number of molecules in the $S_1^*$ state as $n_{S_1} = n_0 e^{-k_{is} t}$, one obtains

$$\frac{dn_{S_1}}{dt} = k_{rs} n_0 e^{-k_{is} t} - k_F n_{S_1} \quad \text{(3)}$$

$$d(n_{S_1} e^{k_{is} t}) = k_{rs} n_0 e^{(k_r - k_{is}) t} \quad \text{(4)}$$

Integrating (4), and get population at $S_1$

$$n_{S_1}(t) = \frac{k_{rs} n_0}{k_{rs} - k_F} (e^{-k_{is} t} - e^{-k_{is} t}) \quad \text{(5)}$$

and we get fluorescence intensity is proportional to $n_{S_1}$

$$I(t) = k_R n_{S_1}(t) \quad \text{(6)}$$

The time to rise to the peak $t_p$ gives a measure of rise and decay parameters. Taking the derivative $dI/dt=0$, the rise time is given as
The size of fluorescence signal and the temporal profile give a measure of the quantum Yield:

\[ Q = \frac{k_R}{k_R + k_{NR}} = \frac{k_R}{k_F} \]  

(8)

For an example, the parameters for Erythrosin in water are \( Q = 0.02 \) and \( \tau_F = 68 \) ps, and for Rh6G in ethylene glycol \( Q = 0.9 \) and \( \tau_F = 1.8 \) ns. Using these numbers \( k_{NR} \) and \( k_R \) can be obtained.

![Fig.6.1(b): Pictorial representation of the number of excited molecules and the fluorescence intensity with time [61]](image)

The solvent interaction can give rise to a more complicated time dependence of the relaxation rate due to diffusion and relaxation dynamics. Streak camera has various applications. Streak camera can be used for solar cells. The purpose of the streak camera for solar cell is to measure carrier life time for radiative or non-radiative decay rate. From the graph I-t which gives fluorescence time. Fluorescence time is the relaxation time. So we can measure relaxation time that shows how fast electron injects from QDs to semiconductors. The rise time is about 10 ps which measure the fed rate of the emitter. The decay can be from 10 ps to 1 ns. This measures the transfer rate out of the emitting state or to ground state.
6.2 A new model of fluorescence of composite materials

According to the theory of Ref. [62], two pathways of electron travels through these materials shown in figure 6.1. The first part of this equation 6.1a is the path of zigzag path and trapped electron and the second part of the equation 6.1a is for the regular equation for light traveling through this material.

\[
I(t) = A_1 \left[ e^{-kt \tau_0} - e^{-t/\tau} \right] + A_2 \left[ e^{-t/\tau_0} - e^{-t/\tau_1} \right], \quad \text{(6.1a)}
\]

taking, \(A_1 = A_2 = A\)

\[
I(t) = A \left[ e^{-kt \tau_0} + e^{-t/\tau_0} - 2e^{-t/\tau} \right], \quad \text{(6.1b)}
\]

where, \(I(t)\) is the PL intensity at time \(t\); \(A_1\) and \(A_2\) are the rate constants for hop-induced energy transfer among acceptors and trap-limited local dynamics, respectively.

\([A_1 \text{ and } A_2\text{ are defined as the rate constants associated with two types of paths for the acceptance in samples, where } A_1 \text{ is due to un-correlated hop-induced energy transfer among acceptors and } A_2 \text{ is trap-limited local dynamics. The models based on the assumption that the two energy pathways are of equal probability, hence, } A_1 = A_2 = A. ]\)

---

**Fig.6.2.** Two photon fluorescence (TPF) images show light-emitting regions (i.e., aggregates of particles) and distribution of pores (i.e., white areas) of different sizes in Zn (OH)\(_2\), ZnGO-2, and ZnGO-5; and pathways of light travelling and trapping.
and these two energy pathways are assumed of equal probability; k is the fast fluorescence diffusion acceptor to acceptor decay rate component at the onset of relaxation process which depends on the concentrations of acceptors and local environment; and \( \tau_1 \) is rise time of excited carriers. The TRPL decay phenomena in this material system are found to be consistent with Equation (6.1). The first exponential term in equation (6.1b) contains k related to 2-D diffusive decay rate constant, which is strongly influenced by its local environment. The PL lifetime (\( \tau_0 \)) reflects the competition between radiative and non-radiative recombination processes.

### 6.3 Experimental methods of TRPL

The details of TRPL (Time resolved fluorescence) set up have been reported in an earlier work [62-64]. The experimental arrangement of the time-resolved fluorescence measurements for Zn(OH)\(_2\) and its composites with Graphite Oxides are schematically shown in fig. 6.2. The 400 nm pulses obtained by frequency doubling the 800 nm, 100 fs, 82 MHz repetition rate pulses from a mode-locked Ti:sapphire laser in a Beta Barium Borate (BBO) crystal was used to excite the samples.

![Schematic diagram of the experimental setup used for time resolved photoluminescence measurements](image)

**Fig.6.3.** Schematic diagram of the experimental setup used for time resolved photoluminescence measurements, M: mirrors; BS: beam splitter; LP: long pass filter; SP: Short pass filter; BBO: second harmonic generator; L: lenses; SIT: silicon intensified target.
The time evolution of the luminescence was recorded by a streak camera (Hamamatsu model C5680) with a typical temporal resolution of 7 ps. After the second harmonic BBO crystal to block the 790 nm laser beam and a long pass filter was used in front of the streak camera to block the 395 nm laser beam reflected from the sample. A series of band-pass filters, with center wavelengths ranging from 400 nm to 450 nm and a full-width-at-half-maximum (FWHM) of 7 nm, were used to select the luminescence wavelength-range of interest. TRPL spectra of the three samples were measured at room-temperature by a streak camera.

The temporal profiles of fluorescence recorded by a silicon intensified target (SIT) vidicon camera were analyzed to obtain the temporal profiles of the fluorescence. The laser beam power-density just before impinging on samples was measured to be 34 W/cm².

Samples of zinc hydroxides and its composites, ZnGO-2 and ZnGO-5, used in this TRPL experiment were synthesized by a scheme reported elsewhere [4, 57-58]. GO was synthesized by oxidation of graphite (Sigma-Aldrich) following the Hummers method [65]. Some details on Zn(OH)₂ and its composites are discussed in Refs [57-58]. Room temperature PL spectra are found to be in the spectral range between 420 nm and 550 nm and have already been reported [46].

### 6.4 Fitting the curve with experimental data

In order to determine the rise time, life (decay) time, and fluorescence decay rate constant (k) of Zn(OH)₂, ZnGO-2, and ZnGO-5. The experimental TRPL data shown in figure 6.3 were fitted using equation 6.1b.
Fig. 6.4: Time-resolved fluorescence (TRPL) spectra of Zn(OH)$_2$, ZnGO-2, and ZnGO-5 are shown together in Fig. 6.3(a); and Zn(OH)$_2$; ZnGO-2; ZnGO-5 separately in Figs. 6.3(b-d). [Islam et al. Ref.46 Vol.38, issue, 13, 001 (2013)]

The fitting rise and decay profiles match perfectly well with the theoretical curves based on Equation 6.1. The PL decay time of Zn(OH)$_2$ is found to be much greater than its composites, ZnGO-2 and ZnGO-5. This indicates that the NR recombination is more dominant in composite materials than in Zn(OH)$_2$, which is attributed to the presence of voids and pores found more abundant in the composite materials than in Zn(OH)$_2$ resulting in the short lifetime. The pore-size and their area coverage in Zn(OH)$_2$, ZnGO-2 and ZnGO-5 have been reported [46, 62]. The areas of pores in ZnGO-2 and ZnGO-5 are found to be 827 µm$^2$ and 982 µm$^2$, respectively as opposed to much smaller area of 498 µm$^2$ in Zn(OH)$_2$(Figure 6.2). Likewise, average size (i.e., diameter)
of micro/meso-pores are found to be $\sim 11.94 \pm 3.21 \mu m$, $\sim 17.83 \pm 4.52 \mu m$, and $\sim 23.48 \pm 5.18 \mu m$, for Zn(OH)$_2$, ZnGO-2 and ZnGO-5 respectively.

### 6.5 Rise time and life (decay) time

By fitting TRPL curves of equation 6.1b we have obtained following rise times, decay times, average pore sizes, and fluorescence constant for materials of Zn(OH)$_2$, ZnGO-2, and ZnGO-5.

#### Table 6.5. Life times ($\tau$), rise times ($\tau_1$), average pore sizes, and fluorescence decay rate constant (k) of Zn(OH)$_2$, ZnGO-2, and ZnGO-5 provided best fit to fluorescence (TRPL) profiles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Av. Pore sizes ($\mu m$)</th>
<th>Life Time ($\tau_0$)ps</th>
<th>Rise Time ($\tau_1$)ps</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(OH)$_2$</td>
<td>$\sim 11.94\pm3.21$</td>
<td>1215±156</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>ZnGO-2</td>
<td>$\sim 17.93\pm4.5$</td>
<td>976±81</td>
<td>4.5</td>
<td>0.4</td>
</tr>
<tr>
<td>ZnGO-5</td>
<td>$\sim 23.48\pm5.8$</td>
<td>742±59</td>
<td>4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### 6.6 New model discussions

Based on TPF images (fig. 6.2) of the samples, a model is proposed following the work of Swenberg [62] where light upon emitting from light emitting regions can transfer either: (1) locally as an emitter or (2) non-locally, 2-D diffusive exciton where motion is a series of uncorrelated hops among acceptors. This model is suitable, as the materials studied herein are amorphous, marked by a lack of translational symmetry of the lattice, and is connected by a network of voids and pores. There have been attempts to explain energy transport, electron-scavenger reaction, and excitonic lifetimes in such materials in terms of hopping and trapping in fractal structures [66]. The decay phenomenon of excited carriers, having carrier density $\sim 1.6*10^{16} \text{ cm}^{-3}$, is an ensemble average over all possible configurations of the acceptors (i.e., voids and pores) distributed over the structure. At high pump intensities Auger [59] and
bimolecular relaxation [66] occurs. Using much lower pump-intensity in this study, the carrier dynamics did not conform to the other bimolecular model, as the laser intensity was rather low nor with Auger recombination model, as it was energy-intensity-independent study. The fast component of highly non-exponential term depends on the dimension and spatial arrangement of the acceptor arrays, which are voids and pores for this material system. The TPF images (fig. 6.2) show the pathways to trapping among the various pores and sites to quenching for PL spectra.

Larger pores in ZnGO-5 and ZnGO-2 give shorter lifetimes. Whether the pathways to trapping are coherent or incoherent depend on the concentrations as well as the separation distance among the acceptors [62]. The model adopted herein is similar to the “lake-model” [62] in photosynthesis where energy transfer is allowed to happen between different sites. An excitation-intensity-dependent study will shed more light both on the nature of energy transport and whether it is a diffusion-limited process. Fig. 6.6 shows time dependence intensity profiles

![Fig.6.6](image)

**Fig.6.6.** Fluorescence intensity profiles for different values of fluorescent decay rate constant (k).
with the variation of decay rate constants. Higher decay rate constant (k) shows an overall slower decay rate implying higher separation distances between acceptors and their lower concentrations.

6.7 Carrier density of life time

Time resolved absorption and luminescence spectroscopy of semiconductor provide direct information about the evaluation of the carrier density as well as the distribution function. The energy relaxation of low carrier density carrier in GaAs has been studied by Ulbrich by measuring the photoluminescence spectra under nanosecond laser pulse excitation [67]. Carrier density were determined here as manually. The output power measured before sample= 34 mW. The measured Intensity is I=34 W/cm\(^2\), \(\alpha=10^{-4}\) cm. Carrier density were calculated \(1.37 \times 10^{16}\) cm\(^{-3}\) at low temperature.

6.8 Intensity dependent time resolved kinetics of Zinc(hyd)oxide

Time resolved photoluminescence kinematic of Zn (OH)\(_2\) were measured by the streak camera system in order to determine the radiative and non-radiative recombination rates [59]. The photoluminescence spectra were measured as intensity dependent. These time resolved photoluminescence spectra(s) have measured by four different excitation powers \(1.61 \times 10^{16}\) W/cm\(^2\) (100%), \(1.13 \times 10^{16}\) W/cm\(^2\) (70%), \(0.81 \times 10^{16}\) W/cm\(^2\) (50%), \(0.401 \times 10^{16}\) W/cm\(^2\) (25%) respectively in room temperature using steak camera shown in figure 6.8(a).
Fig. 6.8: Time resolved photoluminescence (TRPL) spectra of Zn (OH)$_2$ is shown together in fig. 6.8(a); Zn(OH)$_2$ at different power(s) and normalization curves of 6.8(a) shown in 6.8(b).
In figure 6.8(b) show all four different powers when a normalized and didn’t much have differences between them.

Hence, we can conclude that our sample Zinc(hydr)oxide and its composites do not fit for biomolecular and Auger process.
Chapter 7

Gratzel (Dye Sensitized) solar cells

Dye-sensitized solar cells (DSCs) are based on a sensitizing dye attached to a wide band gap semiconductor [68]. Low-cost and high-efficiency dye-sensitized solar cells are regarded as an excellent candidate for exploiting solar energy, which is one of the most important alternative energies [69]. Quantum dots (QDs) sensitized solar cell is very similar to dye sensitized solar cell, with one type using QD instead of dye. Semiconductor Quantum Dots (QDs) can also serve as a sensitizer for light harvesting assemblies in solar cells [70]. The size quantization of dye or QDs leads to the capability of tuning visible-spectrum response and varying band offsets to modulate the vectorial charge transfer across dies or QDs with different sizes [71]. By anchoring different-sized QDs on mesoporous electrodes, the researchers hope to prepare rainbow solar cells which take advantages of both the faster electron injection of small QDs and the greater absorption range of large QDs [72]. Among other benefits of the use of QDs in solar cells, hot electrons can generate carrier multiplication in QDs [73].

Two technologies that have been garnering significant attention are based on organic materials. Dye-sensitized solar cells use an organic dye coating a porous electrode with high surface area to absorb light. Efficiencies of up to 11% have been achieved for dye-sensitized solar cells [74]; however, the use of a liquid electrolyte in the cells is presently a source of reliability issues. Another organic technology is thin-film solar cells based on solid-state organic semiconductors. Organic semiconductors can have their chemical and electrical properties tailored in numerous ways by modifying the chemical structures and can allow for new
processing methods. State-of-the-art DSCs based on iodide/tri-iodide redox couple in a liquid electrolyte have validated power conversion efficiencies of over 11\%6-8 while DSCs comprised of a solid-state hole conductor have achieved power conversion efficiencies of over 7\%. Nine companies have recently begun to manufacture DSC for residential installations as well as consumer electronics. In 2010, Sony announced that it had created a DSC module that has achieved power conversion efficiency over 9\%.

In this chapter, we will discuss the background of dye/QD solar cells, and electrical/photovoltaic properties of solar cells.

### 7.1 Formation and operation of Gratzel cells

Liquid based dye-sensitized solar cells are comprised of a fluorine doped SnO2 front contact (FTO) on glass, nano-particle/powder covered with a monolayer of sensitizing dye, a hole conducting electrolyte, and carbon coated /FTO coated back contact as shown in figure 7.1. The most well studied DSC is composed of mesoporous TiO2 fabricated from sol-gel processed nano-particles (e.g. 20 nm in diameter, 60\% porosity) which are screen printed on the FTO and sintered at 450\° C.

![Fig.7.1: Structural sketch of our CdSe QDs / dye sensitized micro/mesoporous TiO2 solar cell with KI as liquid state electrolyte.](image-url)
The nano-particles films have a surface area that is typically 1000 times greater than that of a flat junction and allows for high loading of the sensitizing dye, which is responsible for light harvesting. The electrolyte is typically comprised of a large concentration of iodide (0.5M) in the form of lithium iodide. The counter electrode of DSC is typically comprised with a carbon coated or platinum coated FTO glass which reduces tri-iodide, transferring holes to the counter electrode.

The Gratzel cell is the modern dye sensitized low cost solar cells shown fig.7.1. This cell has three main parts. On top is a transparent anode made of fluoride-doped tin dioxide (SnO2:F) deposited on the back of a (typically glass) plate. On the back of this conductive plate is a thin layer of titanium dioxide (TiO2), which forms into a highly porous structure with an extremely high surface area. TiO2 only absorbs a small fraction of the solar photons (those in the UV) [75]. The plate is then immersed in a mixture of a photosensitive dye (also called molecular sensitizer) [75] and a solvent. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the TiO2.

A separate plate is then made with a thin layer of the iodide electrolyte spread over a conductive sheet, typically platinum metal. The two plates are then joined and sealed together to prevent the electrolyte from leaking. The construction is simple enough that there are hobby kits available to hand-construct them. Although they use a number of "advanced" materials, these are inexpensive compared to the silicon needed for normal cells because they require no expensive manufacturing steps. TiO2, for instance, is already widely used as a paint base.

Sunlight enters the cell through the transparent SnO2:F top contact, striking the dye on the surface of the TiO2. Photons striking the dye with enough energy to be absorbed to create an
excited state of the dye, from which an electron can be "injected" directly into the conduction band of the TiO$_2$. From there it moves by diffusion (as a result of an electron concentration gradient) to the clear anode on top. Meanwhile, the dye molecule has lost an electron, and the molecule will decompose if another electron is not provided. The dye strips one from iodide in the electrolyte below the TiO$_2$, oxidizing it into a tri-iodide. This reaction occurs quite quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short-circuit the solar cell. The dynamics of electron transport in cell are unknown.

The tri-iodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electrons after flowing through the external circuit.

### 7.2 Power conversion efficiency and quantum efficiency of solar cells

The conversion efficiency ($\eta$) of solar cells is calculated as the ratio of the generated maximum power ($P_m$) obtained from a solar cell to the incident optical power ($P_{in}$) on it. The incident power is found to be equal to the irradiance of AM1.5 spectrum, normalized to 1000 W/m$^2$ [76]. The power conversion efficiency of a solar cell is determined from the current versus applied voltage (I-V) characteristics under illumination.
Fig. 7.2: I-V curve of a typical solar cell under illumination (bottom curve) and dark (upper curve).

Power conversion efficiency can be written from [76-77];

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{I_{\text{sc}}V_{\text{oc}}FF}{P_{\text{in}}}, \quad (7.2a)
\]

\[
FF = \frac{I_{\text{mp}}V_{\text{mp}}}{I_{\text{sc}}V_{\text{oc}}}, \quad (7.2b)
\]

\(V_{\text{oc}}\) is open circuit voltage and \(I_{\text{sc}}\) is short circuit current. \(P_{\text{in}}\) is the power per unit area that irradiated the surface area of solar cells. The quantum efficiency (QE) of a solar cell is defined as [78-79], the ratio of the number of carriers collected by the solar cell to the number of photons of a given energy incident on the solar cell. The quantum efficiency may be given either as a function of wavelength or as energy. If all photons of a certain wavelength are absorbed and the resulting minority carriers are collected, then the quantum efficiency at that particular wavelength is unity.

\[
\text{IQE} = \frac{1240(w.nm / A)}{\lambda(nm)} \times R(A / w), \quad (7.2c)
\]

\[
R = \frac{PC(A)}{P_{\text{in}}(w)}, \quad (7.2d)
\]
where, \( R \) is called the Responsivity of a solar cell. The Responsivity of a cell is defined in which an optical signal is converted into an electrical current. PC is photocurrent of that solar cell.

### 7.3 External quantum efficiency of solar cells

The "external" quantum efficiency of a silicon solar cell includes the effect of optical losses such as transmission and reflection. However, it is often useful to look at the quantum efficiency of the light left after the reflected and transmitted light has been lost. "Internal" quantum efficiency refers to the efficiency with which photons that are not reflected or transmitted out of the cell can generate collectable carriers. By measuring the reflection and transmission of a device, the external quantum efficiency curve can be corrected to obtain the internal quantum efficiency curve [79] per photon incident on the solar cell and is dependent upon the fraction of light absorbed by the sensitizing dye (\( \eta_{\text{ABS}} \)) and the internal quantum efficiency (IQE) of the system as shown in equation [80, 81]:

\[
EQE = \eta_{\text{ABS}}(\lambda) \times \text{IQE}
\]

where, \( \eta_{\text{ABS}} \) is coupling efficiency representing the number photon coming out of the device per number of photons generated from the device. However, DSCs have high internal quantum efficiencies (>90%) and in portions of the visible spectrum can absorb >90% of the light [80].

### 7.4 Open circuit voltage and short circuit current

The I-V characteristics of a solar cell are well described by an equivalent electrical circuit (shown in figure 7.4) [82]. Under illumination, a constant photocurrent (\( I_{\text{ph}} \)) is generated. If a forward voltage bias is applied, a dark diode current (\( I_{\text{dark}} \)) flows in the opposite direction. A shunt resistance (\( R_{\text{shunt}} \)) may arise from charge recombination in the photoactive layer and induce
a shunting current \( (I_{\text{shunt}}) \). The series resistance \( (R_{\text{series}}) \) includes the contact resistance at interfaces, the bulk resistance, and the sheet resistance of the transparent electrodes. The total measured current is;

\[
I = I_{\text{ph}} - I_{\text{dark}} - I_{\text{shunts}} = I_{\text{ph}} - I_s \left( \frac{qV}{e^{\frac{qV}{mkT}} - 1} \right) - \frac{V + IR_{\text{series}}}{R_{\text{shunt}}}
\]

Where, \( I_s \) is the diode saturation current, \( V \) is the applied bias voltage, \( m \) is an ideal factor \( (m = 1 \) for an ideal cell), \( k \) is the Boltzmann constant, and \( T \) is the device temperature. If we neglect the shunt and series resistance \( (R_{\text{shunt}} \rightarrow \infty, R_{\text{series}} \rightarrow 0) \), we find simple expressions for the short-circuit current \( (I_{\text{sc}}) \) and the open-circuit voltage \( (V_{\text{oc}}) \) of the device:

\[
I_{\text{sc}} = I_{\text{ph}} \quad \text{for} \quad V = 0 \quad \text{and} \\
V_{\text{oc}} = \frac{mkT}{q} \ln \left( \frac{I_{\text{ph}}}{I_s} + 1 \right) \quad \text{for} \quad I = 0
\]

The short circuit current increase in light intensity, as higher intensity means more photons, which in turn means more electrons. Since the short circuit current is roughly proportional to the area of the solar cell, the short circuit current density, \( J_{\text{sc}} = \frac{I_{\text{sc}}}{A} \), is often used to compare solar cells.

When a load is connected to the solar cell, the current decreases and a voltage develops as the charge builds up at the terminals. The resulting current can be viewed as a superposition of the short circuit current, caused by the absorption of photons, and a dark current, which is caused by the potential built up over the load and flows in the opposite direction. As a solar cell contains a PN-junction, just as a diode, it may be treated as a diode. For an ideal diode, the dark current density is given by
Here $J_0$ is a constant, q is the electron charge and $V$ is the voltage between the terminals. The resulting current can be approximated as a superposition of the short circuit current and the dark current:

$$J = J_{sc} - J_0 \left( e^{qV/kT} - 1 \right)$$

**Fig.7.4:** Equivalent circuit of solar cell.

### 7.5 Operation of generation of Gratzel (DSSC)/QDSC Cells

The common feature of QD-based solar cell is the quantum confinement of the exciton in the absorber material leading to a size-dependent absorption spectrum. QDSCs are based on a nanostructure of a wide-band gap material that is sensitized with a QD mono-layer. Conceptual similarities and differences to dye-sensitized solar cells (DSCs)[83-84], and extremely thin absorber (ETA) cells [83-84] are discussed. In layered QD solar cells, as compare to DSC, the absorber film consists of a QD multilayer, which is located in between electron- and hole-conducting phases.
Nano-structured wide-band gap semiconductor films provide a microscopic surface area, orders of magnitude larger than their geometric area, which can be sensitized with a thin absorbent layer of low absorbance. The lowest optical density of a QD monolayer is compensated by a light path that passes through tens to hundreds of QD mono-layers. Dye-sensitized solar cells and ETA cells make use of the same concept, and light to electric power conversion efficiencies above 10% have been reached with DSCs [85]. Wide-band gap semiconductor mesoporous films, nanorods, nanowires, nanotubes, nanosheets, and more have been used as nanostructures. The large microscopic surface area is sensitized with a monolayer of QDs, while a redox electrolyte fills the free space around the nanostructures (figure 7.1 & 7.5 (a-b)). The QDs absorb light and inject electrons from their excited levels into the conduction band (CB) of the wide-band gap semiconductor, while oxidized QDs are recharged by the redox electrolyte. Charge transport to the front electrode (usually a transparent conducting oxide, SnO2:F), as well as transport of oxidized redox species to the back contact, is diffusion-driven. The absorber thickness in QDSCs, DSCs and also in ETA cells are too small for extended space-charge regions that provide a built-in electrostatic field for charge separation, in contrast to p-n junction solar cells [83].

![Energy Band Diagram](image)

**Fig.7.5 (a):** Schematic diagram of energy band diagram of QD shows electron flowing direction and recombination path.
For dye sensitized based cells (DSCs) on TiO2 films in conjunction with an organic electrolyte containing the I2/I3- redox couple, it was shown that band-edge movement of the TiO2 upon illumination is negligible [83-84] and that the electrostatic potential changes only in the vicinity of the TCO/TiO2 interface. Light-induced injection increases the electron concentration in the mesoporous TiO2 film and leads to an upward shift of the electron quasi-Fermi level E_Fn towards the CB edge, while the redox potential E_redox remains nearly unperturbed due to the high concentration of redox species typically used in DSCs (Figure 7.5(b)).

Under open circuit conditions, electron injection is balanced by recombination and the energy difference E_Fn - E_redox determines the open-circuit voltage Voc. For un-concentrated sunlight, it was argued that a shift of E_Fn into the wbSC CB is unlikely, such that the upper limit of the Voc is determined by the energy difference of the CB edge ECB and E_redox of the electrolyte [86]. Since DSCs are same as QDSCs. However, the much wider variety of materials used for QDSCs including aqueous electrolytes, structural differences such as QD coverage of less than a monolayer and the lack of ideal counter electrodes/back contact for certain electrolytes must be considered to understand the working principle of a specific QDSC configuration.
Fig. 7.5(b): Energy-band diagram showing the conduction- (CB) and valence-band (VB) edges of the wide-band gap semiconductor (wbSC), the ground and excited level of the QD and the redox potential $E_{\text{Redox}}$. Upon illumination electrons are injected from the excited QD state into the wide-band gap semiconductor, while the oxidized QD is recharged by the redox electrolyte. The relaxation time $\tau$ will be measured.

In summary, the main working principle of QDSCs is very similar to DSCs, but further effects such as photo-induced band edge movement can occur in QDSCs, depending on the composition of the cell material.
Chapter 8

Quantum Dots Sensitized Solar cell

Quantum dot solar cells are an emerging field in solar cell research that uses quantum dots as the absorbing photovoltaic material, as opposed to better-known bulk materials such as silicon, copper indium gallium selenide (CIGS) or CdTe. Quantum dots have band gaps that are tunable across a wide range of energy levels by changing the quantum dot size.

Quantum dots are particles of semiconductor material with the size so small that, due to quantum mechanics considerations, the electron energies that can exist within them are limited. These energy levels, defined by the size of quantum dots, in turn define the band gaps. The dots can be grown to any needed size, allowing them to be tuned across a wide variety of band gaps without changing the underlying material or construction techniques. In typical preparations, the tuning is accomplished by varying the duration or temperature of synthesis.

Russian physicist Alex I. Ekimov discovered QDs at the beginning of the 1980. The idea of QDs as a path to high efficiency was first noted by Burham and Duggan in 1990 and later NREL discovered QD solar cells (Duggan at el TT Journal of Applied Physics 67: 3490)TT.

There are various types of quantum dots (QDs) such as CdS, CdSe, CdTe, CuInS2, Cu2S, PbS, PbSe, InP, InAs, Ag2S, Bi2S3 and Sb2S3 used for QDs sensitized solar cells. These QDs are deposited onto wide-band gap nano-structures as a sensitizer. Depending on their size, these materials can absorb photons over a broad spectral range or within a confined window of the solar spectrum. Especially CdS, CdSe and PbS have been used to investigate the operating principles of QDSCs [83].
In this chapter, we will discuss QD sensitized TiO$_2$ solar cell, Zn(OH)$_2$/ZnGO solar cell, solar cells, band diagram of ZnGO/TiO$_2$ solar cells, and two photon fluorescence image of solar cells.

8.1 QD Sensitized ZnGO solar cells

Dye-sensitized solar cells (DSCs) are based on light harvesting by a sensitizing dye attached to a wide band gap semiconductor [68]. Silicon based cells have achieved 24% efficiency. Low-cost and high-efficiency dye-sensitized solar cells are regarded as an excellent candidate for exploiting solar energy, which is one of the most important alternative energies [69]. To enhance the operation of Gratzel-like solar cells for energy conversion one needs to expand the active photon spectral zone from UV to NIR develop a more solid state version, and to reduce the nonradiative processes in active solar media. The aim is to obtain higher solar energy conversion in the range of above 44%. Semiconductor Quantum Dots (QDs) offers a broad spectral capture band to serve as a sensitizer for light harvesting assemblies in solar cells [70]. The size quantization of QDs leads to the capability of tuning UV–visible-NIR spectrum response and varying band offsets to modulate the vectorial charge transfer across QDs with different sizes [71]. By anchoring different-sized QDs and material types on mesoporous electrodes, the researchers hope to prepare rainbow solar cells which take advantages of both the faster electron injection of small QDs and the greater absorption range of large QDs [72]. Among other benefits of the use of QDs in solar cells, hot electrons can generate carrier multiplication in QDs [73] for UV and NIR spectral regions.

Thin films of wide direct band gap semiconductor materials, TiO$_2$, ZnO, Zn(OH)$_2$, have attracted considerable attention due to their potential applications in many fields, such as, gas sensors, and solar cells [70]. A large band gap of TiO$_2$ (3.0-3.23 eV) [78] and ZnGO-2 (~2.90 eV) [78] are suitable for use in a dye or quantum dot (QD) -sensitized solar cells, because the
band gap influences on the conversion of efficiency of a solar cell [50]. The energy conversion efficiency ($\eta$) and quantum efficiency (QE) are the two significant parameters for characterizing a solar cell. This thesis focuses on efficiency of Hybrid Solar cells with quantum dot-sensitized of micro/meso porous Zinc(hydr)oxide and its composites with 2% and 5% graphite oxide (Zn(OH)2, ZnGO-2 and ZnGO-5) with two kinds of electrolytes (KI and Perovskite).

8.1.1 Experimental Method of ZnGO Solar cells

Thin films of Zn(OH)2, ZnGO-2, ZnGO-5 were deposited onto the SnO2:F conducting glass by a spray pyrolysis method [84, 87]. A 10% solution of Zn(OH)2, ZnGO-2, and znGO-5 in ethanol (4 ml) was sprayed onto the conducting glass (1cm x 1 cm) followed by heating it up to 450°C for 30 minutes to activate and dehydrate these materials. The long edges were covered to avoid the spray and to make electric contacts later on. Thickness of each and every film was measured with “Thicknes Tester (i.e., a product of US-based Company named Accupro USA)” which could be regarded as a “thin film thickness measurement gauge” and the average thickness of the films was found to be around 35 microns and the resolution of this device was found to be ~ 1 micron. The sample was heated up to 140°C for ~2 minutes. After that the sample was soaked with 6 drops of (12 vol%) CdSe QDs (absorption peak at 500nm) for ~ 3 hours. Two types of electrolyte are used: standard iodine (Potassium iodide) and new perovskite liquid state. The CdSe QDs were commercially obtained from Nanomaterials and Nanofabrication Labs (NN-Labs, Inc). The absorption peak and emission peak of these QDs were recorded at 500±10 nm and 540±10 nm, respectively. Potassium Iodide (KI) and perovskite were used as electrolytes. After that same amount of electrolyte (KI) or perovskite was applied on the top of QDs. The synthesis of organo metal halide perovskite was undertaken following procedures reported
elsewhere [88]. Briefly, 33 wt% methylamine (CH₃NH₂) solution in absolute ethanol (24 mL) was inserted in a round bottom flask and allowed to react with 57 wt% water solution hydroiodic acid (HI) (15mL) under nitrogen atmosphere in ethanol (150 mL) at room temperature. Crystallization of methylammonium iodide (CH₃NH₃I) was achieved using a rotary evaporator; a white colored crystalline powder was formed. Methylammonium iodide (CH₃NH₃I) and lead (II) chloride (PbCl₂) was dissolved in anhydrous N,N-Dimethylformamide at a 3:1 molar ratio of CH₃NH₃I to PbCl₂, to produce a mixed halide precursor solution. The solution was diluted and used for further spectroscopic measurements. Potassium iodide electrolyte was about 0.127 grams of I₂ adding with 10 mL of ethylene glycol and 0.83 g KI (potassium iodide) adding with the same amount of ethylene glycol (10 mL). Mixing together with a clean glass rod or mixing instrument. This electrolyte solution is 100% water free. The bottom conductive glass was covered with carbon and catalyst for making the counter electrode shown figure 7.1

The morphology of Zinc (hydr) oxide and its composite electrodes were characterized by means of the two photon fluorescence imaging described in ref 8. Photocurrent (PC) was recorded using a lock- in- amplifier SR 830 at the range of 300 nm to 800 nm. The current-voltage (I-V) characteristics measurements were performed using Keithley 236 tools. The current-voltage (I-V) characteristics of solar cells measured under the illumination of a Tungsten lamp (intensity of 12.1mW/cm² by silicon power meter). The size of the light beam is 1mm.

**8.1.2 Electrical characteristics of ZnGO cell**

The current–voltage characteristics of the Zn(OH)₂ and its composites ZnGO-2 and ZnGO-5 solar cells with CdSe QDs and liquid electrolyte (KI) or liquid Perovskite under illumination are shown in shown in fig. 8.1.2(a) and fig.8.1.2 (b) respectively.
Fig. 8.1.2: (a) Current–voltage (I–V) curves of a Zn(OH)2 and ZnGO plus QDs with liquid electrolyte solar cell under illumination; (b) Current–voltage (I–V) curves of a Zn(OH)2 and ZnGO plus QDs with liquid solar cell under illumination.

Both of curves in fig. 8.1.2 (a and b) were taken using forward bias under illumination. Since applying forward show in fig. 7.1, electrolyte or perovskite indicates these layers are p type semiconductor and can serve as a hole transport layer. Zn(OH)2/ZnGO layer works as n-type semiconductor. Under light illumination, (X-axis) at short-circuit current condition the maximum generated photocurrent flows and (-Y axis) at flat band condition the photogenerated current is balanced to zero. In the fourth quadrant (between X and –Y axis) the device generates power.

The power conversion efficiency of a solar cell is calculated by using equations 7.2 (a) & 7.2 (b) [previous chapter];

$$\eta = \frac{I_{sc} V_{oc} FF}{P_{in}}, \text{ where,}$$

$$FF = \frac{I_{mp} V_{mp}}{I_{sc} V_{oc}},$$
where, $V_{oc}$ (Volt) is the open circuit voltage, $I_{sc}$ (A) is the short-circuit current, FF is the fill factor and $P_{in}$ (=12.1mW/cm$^2\times10^{-2}$cm$^2$=121$\mu$W) is the incident light power density. The standardized (STC) at 100mW/cm$^2$ (AM 1.5) for solar cell testing with calibrating under the illumination of a Tungsten lamp (intensity of 12.1mW/cm$^2$ by silicon power meter). With a 1m x 1m excitation area, under the illumination, the open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$) and power conversion efficiency have measured using Equations 7.2 (a and b) that are shown in following Table 8.1.2. Sample calculation is given in Appendix C.

**Table 8.1.2:** Open circuit voltage, short circuit current and efficiency calculated for Zn(OH)$_2$ and its composites of ZnGO-2/ZnGO-5 solar cells.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$V_{oc}$(Volt)</th>
<th>$I_{sc}$(μA)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(OH)$_2$/QD/E</td>
<td>0.41</td>
<td>43</td>
<td>0.72</td>
<td>10.49</td>
</tr>
<tr>
<td>ZnGO-2/QD/E</td>
<td>0.36</td>
<td>70</td>
<td>0.51</td>
<td>10.62</td>
</tr>
<tr>
<td>ZnGO-5/QD/E</td>
<td>0.65</td>
<td>40</td>
<td>0.35</td>
<td>7.52</td>
</tr>
<tr>
<td>Zn(OH)$_2$/QD/P</td>
<td>0.39</td>
<td>29</td>
<td>0.212</td>
<td>2</td>
</tr>
<tr>
<td>ZnGO-2/QD/P</td>
<td>0.35</td>
<td>56</td>
<td>0.321</td>
<td>5.2</td>
</tr>
<tr>
<td>ZnGO-5/QD/P</td>
<td>0.25</td>
<td>55</td>
<td>0.288</td>
<td>3.27</td>
</tr>
</tbody>
</table>

Under illumination, photovoltaic effect can be observed despite the open voltage ($V_{oc}$) using perovskite is shorter than open circuit voltage ($V_{oc}$) using electrolyte solar cell. It seems only ultraviolet light can be absorbed by the higher band gap materials of composites of Zn (OH)$_2$ and . There is much series resistance may another reason for lower $V_{oc}$ or $I_{sc}$. On the other hand, CdSe QDs between electrolyte (KI) and Zn(OH)$_2$/ZnGO electrodes improve light absorption and consequently lead to more light induced carriers and higher current as shown in I-V curve in fig. 8.1.2(a).
Fig. 8.1.3: Photocurrent spectra as a function of wavelength (nm) of samples (a) Zn(OH)$_2$ and its composites (ZnGO-2 and ZnGO-5) with CdSe QDs and electrolyte (KI), (b) Zn(OH)$_2$ and its composites (ZnGO-2 and ZnGO-5) with CdSe QDs and perovskite.

The photoconductivity experiments were carried out using a Triax 320 monochromator to select the wavelength of light from a Quartz Tungsten Lamp in a wide spectrum ranging from 300 nm to 800 nm. Photocurrent spectra were recorded by a SR 830-DSP Locking Amplifier. The light beam coming from monochromator was focused onto an illuminating area in between electrodes over the samples. Lamp spectrum emerging from monochromator was measured by a UV enhanced silicon detector. The photocurrent spectra of the six samples were measured under zero bias and are shown in fig. 8.1.3 (a and b). The absolute values of photocurrent are not comparable between the samples since the potential difference between electrodes could not be controlled. All photocurrent spectra cover a wide wavelength range from 300 nm to 800 nm. Large current of both curves are shown between 400 nm to 550 nm, its mean surface layer of Zn(OH)$_2$/ZnGO and CdSe QD (absorption peak at ~500±10 nm) absorb more light in this reason, the result gets more current. Quantum efficiency was determined using a monochromator as previously described [84, 89, 90]. Quantum efficiency was calculated from spectral responds [78];
Fig. 8.1.4: Quantum efficiency as a function of wavelength (nm) of samples (a) Zn (OH)\textsubscript{2} and its composites (ZnGO-2 and ZnGO-5) with CdSe QDs and electrolyte (KI), (b) Zn (OH)\textsubscript{2} and its composites (ZnGO-2 and ZnGO-5) with CdSe QDs and perovskite.

\[
\text{IQE(\%)} = \frac{1240 (\text{w.nm} / \text{A})}{\lambda (\text{nm})} \times R (\text{A} / \text{w}) \times 100, \\
R = \frac{\text{PC(A)}}{P_{\text{in}} (\text{w})},
\]

where, R is called the responsivity of a solar cell. The responsivity of a cell is defined in which an optical signal is converted into an electrical current. PC is photocurrent of that solar cell. Quantum efficiency was calculated according to the measured lamp spectrum. The results are plotted as functions of wavelength and are shown in Fig. 8.1.4 (a) and (b). The quantum efficiency of these samples was performed at room temperature and the maximum internal quantum efficiency (30-40\%) of the samples was found in the wavelength range from 400 nm to 550 nm. Internal quantum efficiency of both figures 8.1.4 (a and b) are very similar. The QE of sample ZnGO-2 in figure 8.1.4 (a) looks maximum peak at 450 nm. Its mean, quantum dots (QDs), whereby absorption of a photon bearing at least twice the band gap energy produces two or more electron-hole pairs.
The I-V characteristic measurements, under the illumination of a Tungsten lamp (intensity of 12.1 mW/cm², monitored by a silicon power meter), were performed using Keithley 236 tools. The power density of 1000 W/m² commonly used for solar cell testing with a spectral intensity distribution matching that of the sun on the earth's surface at an angle 48.2°, which is termed as the 1.5 AM spectrum. A power density of 12.1 mW/cm² obtained from a Tungsten Lamp (calibrated by a silicon power meter). The area of excitation was estimated to be 1 mm² (1 mm x 1 mm). It is important to note that using 12.1 mW/cm² as the incident power density, $P_{in}$ (W/cm²) the output power density, $P_{out}$ (W/cm²) would proportionately increase likewise. It is instructive that with increasing optical power density (mW/cm²), higher output current (mA) is expected. The output current ($\mu$A) as a function of input intensity of light (mW/cm²) is found to be superlinear in Ref.90A [S. Prezioso et al., Appl. Phys. Lett. 94, 062108 (2009)]. On a log–log plot of current versus intensity for ZnGO2 QDs CdSe shows a superlinearity in $J_{sc}$ vs $P$ provides on log–log plot a value of the slope as 2.8 (i.e., $n = 2.8$), meaning $I = P^{2.8}$. Hence, the efficiency of solar cell would remain the same.

Fig.8.1.5: Superlinearity curve shows current vs. $P^{n=2.8}$ of ZnGO-2+CdSe+KI solar cells.
From fig. 8.1.5 show the parameter, n is the dependence of power. In this result, n=2. 8 obtained from the fitting curve. The value of n is higher than 2 means the sample has some defects from pores and QDs. This may provide a higher energy conversion at higher light powers.

8.1.3 Summary

Two types of electrolytes: KI and perovskite are used for new hybrid Zn(OH)₂ and ZnGO solar cells with efficiencies from 2% to 10% performed similar to iodide based liquid electrolyte. The efficiency of the perovskite solar cell was lower in comparison with electrolyte(KI) solar cells. This result demonstrates possible higher light harvesting efficiency of Zn(OH)₂/ZnGO CdSe QD plus electrolyte solar cell in the UV to visible light due to add of different QDs media and the multi exciton generation from UV and NIR can be used for all solid state solar cells with supplements of quantum dots such as from CdS and PbS/PbSe to increase the efficiency of photovoltaic cells.

8.2 QD Sensitized TiO₂ solar cells

Section 8.1 we discuss QD sensitized ZnGO meso/microporous solar cells. Another approach to low-cost organic PV devices is based on the sensitization of a high-band gap material, such as nanocrystalline TiO₂ with CdSe quantum dots as well as using liquid potassium iodide or perovskite.

Titanium dioxide (TiO₂) is a versatile material with a broad range of applications, for example, as a pigment in paints, a photocatalyst film for surface decontamination, and a photovoltaic material for solar energy conversion [91]. Among numerous semiconductor photocatalysts developed so far, TiO₂ is regarded to be the most efficient and environmentally benign, which has been most widely used for photo-degradation of various pollutants.[92] However, its large band gap (~3.0 eV) along with a fast recombination rate of photogenerated
electron-hole pairs in TiO2 hinders its photocatalytic activity, limiting further commercialization and industrial applications. For instance, CdS/TiO2 heterojunction has been widely studied for effective decomposition of organic compounds [93-95] and for photocatalytic water splitting.[96-98] In CdS/TiO2 heterojunction, CdS with narrow band gap acts as a visible-light sensitizer; combined with TiO2, CdS is also responsible for effective charge separation that enables suppression of the recombination process.[99]

In this research, we have reported two types of solar cells (i) TiO2/QD (CdSe) /Electrolyte and (ii) TiO2/QD (CdSe) / pervskite (ABC samples, A= CH₃NH₂, B= CH₃NH₃I, and C= PbCl₂).

### 8.2.1 Photovoltaic properties of TiO2 solar cells

The current–voltage characteristics of the TiO2 solar cells with CdSe QDs and liquid electrolyte or liquid perovskite in under illumination are shown in shown in fig. 8.2.1

![Current–voltage (I–V) curves of TiO2 plus QDs solar cells with liquid electrolyte and perovskite solar cells under illumination.](image)

**Fig. 8.2.1:** Current–voltage (I–V) curves of TiO2 plus QDs solar cells with liquid electrolyte and perovskite solar cells under illumination.
Both of them curves in fig. 8.2.1, were taken using forward bias under illumination. Since applying forward is shown in fig.7.1, electrolyte or perovskite indicates these layers are p type semiconductor and can serve as a hole transport layer. Fig.8.2.1 shows the I-V curve of the device fabricated in this work. The result shows a great enhancement in terms of photocurrent from TiO2/CdSe/ perovskite film to the TiO2/CdSe/Electrolyte composite semiconductor system. The key parameters of each elaborated structure, such as short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and efficiency ($\eta$) were extracted from the I–V curves and shown in table 8.2.1 under 12.1 mW/cm$^2$.

Table 8.2.1: Open circuit voltage, short circuit current,and efficiency calculation of composites of TiO2 solar cells.

<table>
<thead>
<tr>
<th>Name</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (µA)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2/QD/E</td>
<td>0.64</td>
<td>32</td>
<td>0.52</td>
<td>10.38</td>
</tr>
<tr>
<td>TiO2/QD/P</td>
<td>0.56</td>
<td>42</td>
<td>0.65</td>
<td>12.61</td>
</tr>
</tbody>
</table>

Figure 8.2.1 shows the short circuit current of TiO2/QD/P cells is 42 µA or 4.2 mA/cm$^2$ (illuminating on 1 mm$^2$ on areas of the cell) where as TiO2/QD/E cell is 32 µA or 3.2 mA/cm$^2$ which is 23% higher than using liquid electrolyte. On the other hand, open circuit voltage is 0.56 volts of TiO2/QD/P and 0.64 volts of TiO2/QD/E which is 14% lower than using electrolyte.

Under illumination, photovoltaic effect can be observed despite the open voltage ($V_{oc}$) using perovskite is shorter than open circuit voltage ($V_{oc}$) using electrolyte solar cell. It seems only ultraviolet light can be absorbed by higher band gap materials of TiO2 and perovskite. On the other hand, CdSe QDs between electrolyte (KI) and TiO2 electrodes improve light absorption and consequently lead to more light induced carriers and higher current are shown in I-V curve in fig. 8.2.1 (a).
Figure 8.2.2 shows the quantum efficiency of TiO2/CdSe/perovskite and TiO2/CdSe/Electrolyte solar cells. This quantum efficiency is called internal quantum efficiency (Internal photon converted to electron-IPCE). Internal Quantum Efficiency (IQE) is the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given energy that shine on the solar cell from outside and are absorbed by the cell. Quantum efficiency can be determined from current density (I-V curve) or spectral responds. G.P. Smestad et al defined [ref. 84] the quantum efficiency from IV characteristics, Quantum efficiency was determined using a monochromator as previously described [90,100]. The short circuit photocurrent, it was measured, as was the input optical power, \(P_{in}\); at the given wavelength. Operationally, the incident photon to electron current quantum efficiency (IPCE) is given by,

\[
\text{IPCE(\%)} = \frac{1239 \times J_{sc} (\mu A/cm^2)}{\lambda (nm) \times P_{in} (mW/cm^2)}
\]

The units corresponding to the use of the constant in this equation are given in parentheses.

**Fig. 8.2.2:** Quantum efficiency as a function of wavelength (nm) of samples TiO2 with CdSe QDs and electrolyte (KI) and Perovskite.
In this paper, quantum efficiency was determined from spectral responds and photocurrent that was following:

\[
\text{IQE(\%)} = \frac{1240 (\text{w.nm/A})}{\lambda (\text{nm})} \times R (\text{A/w}) \times 100,
\]

\[
R = \frac{\text{PC(A)}}{P_{in}(\text{w})},
\]

where, R is called the responsivity of a solar cell. Responsivity of a cell is defined in which an optical signal is converted into an electrical current. PC is photocurrent of that solar cell. Quantum efficiency was calculated according to the measured lamp spectrum that was described in section 8.1.2.

The maximum internal quantum efficiency (called quantum efficiency-QE) between 30-40\% of the samples was found in the wavelength range from 400 nm to 550 nm. The quantum efficiency of TiO2/QD/P at around 450nm is more than 40\% whereas TiO2/QD/E is 32\%. It is 20\% less than Perovskite cell. This increase in the IQE can be explained as, the improvement of carrier collection at the cell emitter, probably due to the saturation of dangling bonds mainly caused by the coordination of back contact/cathode (SnO2) atoms to the TiO2 atoms, which improve the contact between the active TiO2 layer and the front electrical contact and increase of the collection probability of the minority carrier in the bulk of the solar cell, likely caused by the enhanced optical path.

8.2.2 Summary

Two types of electrolytes: KI and Perovskite are used for TiO2 solar cells with efficiencies of 10 to 12\% performs similar to iodide based liquid electrolyte. The efficiency of the cell was higher in comparison with electrolyte solar cells. This result seems perovskite is better work with TiO2 films. Probably be electron –holes recombine doing faster and generate more current. Our results
also demonstrate that a single TiO2–CdSe-electrolyte or TiO2-CdSe-perovskite interface can function efficiently in charge transfer. Our studies demonstrated that the use of flat, dense TiO2 can be used for a technique and the tool to establish the effectiveness of hole transfer as compared to liquid junction devices. Both electrolyte (KI) or Perovskite works similar based as iodide based liquid electrolyte.

8.3 2P Image of ZnGO/electrolyte/ perovskite solar cells

Figure 8.3 is the two photon imaging of four samples. It shows the internal structures of quantum dots sensitized micro/mesoporous of Zn(OH)2 and its composites solar cells. Two photon photoluminescence images of these three materials previously reported in ref. [46, 64] without QDs. Two-photon excitation microscopy is a fluorescence imaging technique that allows imaging up to a depth of approximately one millimeter. The application of two-photon excitation fluorescence microscopy has become a powerful tool for studying biological functions in live tissues and offers many advantages over conventional imaging techniques. TPF is a technique in which a fluorophor QD and composite is excited by the simultaneous absorption of two photons. Two photon fluorescence (TPF) imaging was performed with the Ultima Multi-Photon-Microscope (Olympus BX-51 of Prairie Tech.Inc.,WI,USA). An excitation energy between 2.7 eV (460 nm) and 1.15 eV (1080 nm) was used to conduct TPF imaging. In particular, The samples were excited with 100-fs laser pulses with an energy of 1.569 eV (i.e., 790 nm) using
Fig. 8.3: Two photon fluorescence images show the internal structure of quantum dots sensitized solar cell of (a) ZnGO-2 micro porous with electrolyte (b) ZnGO-2 micro porous with perovskite (c) ZnGO-5 micro porous with electrolyte (d) ZnGO-5 with perovskite, film growth on conductive glass with QDs. Where the white region refers as quantum dots attached to ZnOH/ZnGO porous materials.

The Ti-Sapphire (Chameleon Ultra II laser, Coherent Inc.) laser, and the fluorescence emitted from the specimen was collected by the photomultiplier tubes (PMTs) after passing barrier filters (460–560 nm). The image stacks were analyzed using Image J software (National Institutes of Health). After importing images into image J, image properties of pixel width (0.234 µm) and height (0.234 µm) in the X and Y directions, and voxel depth (1 µm) in the Z-direction were provided [64]. Figure 8.3(a-d) shows the surface morphology of composites Zn(OH)$_2$.
micro/meso porous films and CdSe quantum dots plus electrolyte or grown on fluoine doped SnO$_2$ conducting glass. Surface morphology such as light emitting zone and pores were discussed [46,64]. Samples of figures 8.3(a-b) are made of ZnGO-2 and quantum dots with electrolyte and perovskite samples of figure 8.3(c-d) were made of ZnGO-5 and quantum dots with electrolyte and Perovskite respectively. White regions refer to more lights emitting from the materials. The pores were reported in [46] but the figure 8.3 shows there are no pores inside the structure. The pores may be filled up due to quantum dots and electrolyte or and makes the enhancement of the structure. We assume monolayer absorption of CdSe QDs on the surface of Zn(OH)$_2$/ZnGO, as reported in [46]. The monolayer absorption facilitates the penetration of CdSe QDs to the porous network of ZnOH/ZnGO, whereas some pores may be too cabined for the QDs to transport [101].

8.4 The fabrication temperature effect on IV and QE of ZnGO solar cell

Dye and quantum dots sensitized organic/inorganic solar cells are expected to have an influence on solar energy conversion over the next ten years. Though these technologies have lower module efficiencies, their cost per Watt is estimated to be three to four times lower than for conventional c-Si systems [102]. The thrust is to make these Gratzel-like solar cells more efficient. The Quantum dots sensitized solar cell is recognized as a highly promising technology for inexpensive solar electricity production using most of the solar spectrum from uv , visible into the near infrared.

Thin films of wide direct band gap semiconductor materials, TiO$_2$, ZnO, Zn(OH)$_2$ have attracted considerable attention due to their potential applications in many fields such as gas sensors, and solar cells [70]. A large band gap of TiO$_2$ (3.0-3.23 eV) [78] and ZnGO-2 (~2.90
eV) [46] are suitable for use in a dye or quantum dot (QD)-sensitized solar cells, because the band gap influences on the conversion of efficiency of a solar cell [78]. The energy conversion efficiency ($\eta$) and quantum efficiency (QE) are the two most significant parameters for characterizing a solar cell.

The quantum dots-sensitized solar cell (QDSC) is a micro/nano-structured photo-electrochemical device. Light is absorbed by a dye attached to the surface of a mesoporous large band gap semiconductor. Solar energy is transformed into electricity via the photoinduced injection of an electron from the excited dye into the conduction band of the semiconductor. The electrons move through the semiconductor to a current collector and the external circuit. A redox mediator in the pores ensures that oxidized dye species are continuously regenerated and that the process is cyclic [103].

In this letter, the composite materials of zinc (hydr) oxide with 2 wt % graphite oxide (referred as ZnGO) hybrid solar cells have been investigated in the experimental method using different temperatures such as $80^0\text{C}$, $120^0\text{C}$, $200^0\text{C}$, and $450^0\text{C}$. The temperature effect on the current - voltage curve and quantum efficiency curve describes of quantum dots sensitized ZnGO solar cell. The quantum efficiency was determined from photocurrent as well as spectral responds to call responsivity.

**8.4.1: I-V and QE characteristics of ZnGO solar cell**

The current-voltage (I-V) characteristics measurements were performed using Keithley 236 tools. The current-voltage ($I$-$V$) characteristic of solar cells measured under the illumination of a Tungsten lamp (intensity of $12.1 \text{mW/cm}^2$ by silicon power meter). The size of the light beam is $1\text{mm}$. 
The effect of temperature on the electrical efficiency of a photovoltaic cell can be traced to the influence upon the current, \( I \), and the voltage, \( V \), as the maximum power is given by [104];

\[
P_m = V_m I_m = (FF) V_{OC} I_{SC} \quad 8.4.1a
\]

In this fundamental expression, which also serves as a definition of the fill factor, FF, subscript \( m \) refers to the maximum power point in the module’s I–V curve, while subscripts \( V_{OC} \) and \( I_{SC} \) denote open circuit and short circuit values, respectively. It turns out that both the open circuit voltage and the fill factor decrease substantially with temperature (as the thermally excited electrons begin to dominate the electrical properties of the semiconductor), while the short circuit current increases only slightly [104].

**Fig.8.4.1.1:** Current–voltage curves of ZnGO samples plus QDs with liquid electrolyte solar cell under dark and illumination.

The current–voltage characteristics of a ZnGO solar cell in the dark and under illumination are shown in fig.8.4.1. In the dark, there is almost no current flowing until the contacts start to inject heavily at forward bias for voltages larger than the open circuit voltage. Under light illumination,
(X-axis) at short-circuit current condition the maximum generated photocurrent flows and (-Y axis) at flat band condition the photo-generated current is balanced to zero. In the fourth quadrant (between X and -Y axis) the device generates power. Under the illumination, the open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$) and power conversion efficiency have measured using Equations 1 that are shown in following Table 8.4.

**Table 8.4:*** Open circuit voltage, short circuit current and efficiency of ZnGO solar cells obtained with 1 mm$^2$ area under the illumination of a Tungsten lamp (intensity of 12.1mW/cm$^2$ measured by silicon power meter)

<table>
<thead>
<tr>
<th>Temp($^0$C)</th>
<th>$V_{OC}$(V)</th>
<th>$I_{SC}$(µA)</th>
<th>FF</th>
<th>$\eta$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.35</td>
<td>43</td>
<td>0.216</td>
<td>2.69</td>
</tr>
<tr>
<td>120</td>
<td>0.30</td>
<td>45</td>
<td>0.322</td>
<td>3.59</td>
</tr>
<tr>
<td>200</td>
<td>0.42</td>
<td>50</td>
<td>0.236</td>
<td>4.10</td>
</tr>
<tr>
<td>450</td>
<td>0.36</td>
<td>70</td>
<td>0.51</td>
<td>10.62</td>
</tr>
</tbody>
</table>

Quantum efficiency (QE) measurements, as previously reported [89], were done as well can calculated from spectral response [78];

The Responsivity of a cell is defined in which an optical signal is converted into an electrical current. PC is photocurrent of that solar cell. The results are plotted as functions of wavelength and are shown in figure 8.4.1.2. QE of these samples was performed at room temperature and the maximum internal quantum efficiency (30-40%) of the samples was found in the wavelength range from 400 nm to 550 nm.
Internal quantum efficiency of all samples using different temperature in figure 8.4.1.2 is very similar. QE of the sample using 450°C in fig 8.4.1.2 shows a maximum peak at 450 nm% with efficiency =10.62%.

Fig. 8.4.1.2: Quantum efficiency as a function of wavelength (nm) of samples ZnGO solar cell with CdSe QDs and electrolyte (KI) fabricated at different temperatures of 80°C, 120°C, 200°C, and 450°C respectively.

The dark current in figure 8.4.1.1 is 2.0 µA, its mean there is some leakage current flowing through the junction like a reverse bias. The quantum dots sensitized solar cell is sensitive on temperature too. Increase in temperature reduce in the band gap energy of cells resulting increase short circuit current and decrease open circuit voltage. Figures 8.4.1.1 and 8.4.1.2 shows the effect of consecutive temperatures of 80°C, 120°C, 200°C, and 450°C applied for fabricating the solar cells. The short circuit current increases with respect to increasing temperatures are shown in figure 8.4.1.3.
Fig. 8.4.1.3: The effect of fabrication temperature on the short circuit current of ZnGO solar cells.

At the temperature increases, the diffusion lengths in ZnGO will increase, because the diffusion constant stays in the same or increases with temperature, and the minority lifetime increases with temperature [82]. The increase in minority carrier diffusion length causes an increase in $J_L$. However, $V_{OC}$ will rapidly decrease because of the exponential dependence of the saturation current on temperature[82] shown in figure 8.4.1.1. At the temperature $80^0C$ and $120^0C$, short circuit current are $43\mu A$ and $45\mu A$ whereas open circuit voltage $0.35V$ and $0.30V$ respectively. The Similar effect shows in temperature, $200^0C$ and $450^0C$ short circuit current increases whereas open circuit voltage decreases ,respectively.
8.4.2: Temperature effect on internal structure of ZnGO solar cell

Two photon fluorescence image shows the internal structure difference in figure 8.4.2 of ZnGO solar cells. There are big pores in ZnGO materials that uses in room temperature. Pores in ZnGO structure are reported in earlier published paper [46]. Using the $450^\circ$C temperature, the pores are combined by melting and filled up the big pores shown in figure 8.4.2 (b).

![Two photon fluorescence image showing internal structure difference](image)

**Fig.8.4.2.1:** Temperature dependent internal structures of ZnGO solar cells fabricated at (a) room temperature, (b) $450^\circ$C temperature.

The structures of the ZnGO solar cell become more uniform for carrier transport due to use high temperature $450^\circ$C resulting higher current than other three low temperatures shown in figure 8.4.1.1.

![Comparison of ZnO and ZnO/RGO](image)

**Fig.8.4.2.2.** Changes in the color of zinc oxide with the addition of the graphene phase.
Heating the samples at 450 °C in air changes the nature of materials. Even though the graphene phase is may partially burn and more reduced graphite oxide (RGO) results in an increase in the intensity of the dark color (figure 8.4.2.2) a significant dehydroxylation took place as discussed in Ref. [57] this process occurs between 400 and 600°C. XRD diffraction indicates the well define crystallographic hexagonal phase of zinc oxide structure at 2 theta 31.75, 34.40, 36.23, 47.52, 56.58, 62.85 and 67.93° [105] present in all samples as a result of the treatment applied. Since GO epoxy groups decompose at about 200 °C [106] the resulting film can be considered as reduced graphite oxide/zinc oxide composites. We refer to the composites as ZnO/RGO-2 and ZnO/RGO-5 following the original content of GO in the samples [106]. Zn(OH)₂ is converted into ZnO.

8.4.3: Summary

The efficiency of ZnGO solar cell has calculated from IV curves. Four ZnGO samples photocurrent near 450 nm representing each of the most distinctive QE of >10 %behaviors versus wavelength were analyzed in terms of their spectral power and electrical characteristics. The I-V behavior shows high temperature at 450 C gives good photocurrent as well as good open circuit voltage produced high efficiency.

8.5 Open circuit voltage condition of QD sensitized solar cell

Under open-circuit voltage conditions the photogenerated electron and holes must completely recombine inside of the QDSC (i.e. photocurrent is zero), which means that the internal quantum efficiency of the QDSC must also be zero. The charge transfer and recombination rates play a critical role in determining the internal quantum efficiency and short circuit current density as well as open circuit voltage.
There are six charges transfer process shown in figure 8.5. The two important processes from LUMO (lowest unoccupied molecular orbital) to TiO2/ZnGO electrode and the holes regeneration ($K_{\text{reg}}$) of the oxidized QD by the iodide in the electrolyte. Once LUMO is excited both radiative ($K_{\text{rad}}$) and non-radiative ($K_{\text{nr}}$) can occur quenching the exciton and preventing charge separation. Electron of the TiO2/ZnGO may recombine with holes in the QD ($K_{\text{rec}}$) or triiodide in the electrolyte ($K_{\text{br}}$). It should be noted that the charge kinetic rates are for QDSCs under short-. As a load (or an applied voltage) is placed across the device there is an increase in the electron carrier concentration inside the TiO2 the directly increases the $k_{\text{rec}}$ and $k_{\text{br}}$ rates.

![Diagram of charge transfer rate in QDSC](image)

**Fig. 8.5:** Charge transfer rate in QDSC

The change in applied voltage is not likely to have a large influence on the electron separation probability so the greatest reduction in the IQE will come from a decrease in the hole separation probability and decrease in the charge collection efficiency. For sensitizing dyes that are capable of fast regeneration, the back reaction ($k_{\text{br}}$) rate will be the primary recombination mechanism that determines the open-circuit voltage in state-of-the-art QDSCs.
Chapter 9

Black silicon with ZnGO solar cells

Black silicon is a cone-shaped surface structure where cones are made of single-crystalline silicon and have a height above 10 microns and diameter <1 micron. Its main feature is an increased absorption of the incident light – the high reflectivity of the silicon, which is usually 20–30% for quasi-normal incidence, is reduced to about 5%. This is due to the formation of a so-called effective medium by the cones. Within this medium, there is no sharp interface, but a continuous change in the refractive index that reduces Fresnel reflection.

Black silicon forms on the n-type mono-crystalline silicon. Irradiation of a silicon surface with intense, short laser pulses in an atmosphere of sulfur hexafluoride leads to a dramatic change in the surface morphology and optical properties. Following irradiation, the silicon surface is covered with a quasi-ordered array of micrometer-sized, conical structures. In addition, the microstructured surface has near-unity absorption from the near-ultraviolet (250 nm) to the near-infrared (2500 nm). This spectral range includes below-band gap wavelengths that normally pass through silicon un-absorbed [107].

Black silicon is a semiconductor material, a surface modification of silicon with very low reflectivity and correspondingly high absorption of visible (and infrared) light. The modification was discovered in the 1980s as an unwanted side effect of reactive ion etching (RIE). Another method for forming a similar structure was developed in the Eric Mazur's laboratory at Harvard University (1998).
9.1 Black Silicon fabrication

There are several groups people fabricate black silicon different ways, D Kong et al [108] describe reactive-ion etching method, Ye-Hua Tang et al [109] describes wet etching method in their paper.

In 1999, a group led by Eric Mazur and James Carey at the Harvard University developed a process in which black silicon was produced by irradiating silicon with several hundreds femtosecond laser pulses [110] with fluence 10 kJ/m². After irradiation in the presence of a gas containing in at atmosphere of sulfur hexafluoride (SF₆) and other dopants, the surface of silicon develops a self-organized microscopic structure of micrometer-sized cones. The resulting material has many remarkable properties, such as an enhanced absorption that extends to the infrared below the band gap of silicon, including the wavelengths for which unmodified silicon is transparent. This property is caused by sulfur atoms being forced to the silicon surface, creating a structure with a lower band gap and therefore the ability to absorb longer wavelengths.

![Scanning electron microscopy (SEM) image of typical surface morphologies for femtosecond laser microstructured silicon (p-type) at 2 (μm) magnifications. These micrographs are taken at a 45° angle.](image)

Fig. 9.1: Scanning electron microscopy (SEM) image of typical surface morphologies for femtosecond laser microstructured silicon (p-type) at 2 (μm) magnifications. These micrographs are taken at a 45° angle.
The morphology of the microstructures exhibited spontaneous ordering and sharpness unmatched by other laser structuring methods at the time (figure 9.1). Black silicon made without special gas ambient - laboratory LP3-CNRS Similar surface modification can be achieved in a vacuum using the same type of laser and laser processing conditions. In this case, the individual silicon micro-cones lack sharp tips (see image). The reflectivity of such a micro-structured surface is very low, 3-14% in the spectral range 300–1250 nm [111] Such reduction in reflectivity is considered to be contributed by the geometry of these micro-cones, which increases the light internal reflections between them.

Hence, the possibility of light absorption by the silicon is increased. The gain in absorption achieved by femtosecond (fs) laser texturization is found to be superior to that achieved by using an alkaline chemical etch method [112] which is a standard industrial approach for surface texturing of mono-crystalline silicon wafers in solar cell manufacturing. It is also found that such surface modification is independent of local crystalline orientation. A uniform Texturing effect can be achieved across the whole surface of a multi-crystalline silicon wafer. The very steep angles lower the reflection to near zero and also increase the probability of recombination, which is why it thus far has not been used in solar cell manufacturing.

The quasi-ordered array of microstructures shown in figure 9.1 are made with the following experimental conditions: irradiation of an p-doped silicon wafer (p-Si (100), 260 μm thick, resistivity $\rho = 8 – 12 \, \Omega \cdot m$) with an average of 500 laser pulses (80 fs, central wavelength 800 nm, fluence 4 kJ/m2) with 100 torr pressure of SF6. For historical reasons we choose these as our standard conditions. We vary the aforementioned parameters and employ microscopy and chemical measurements to monitor changes in the surface morphology and composition.
9.2 Optical properties of black silicon

In order to measure optical properties, a Hitachi U-4001 spectrophotometer equipped with an integrating sphere was used. With the spectrophotometer, measuring the total hemispherical (specular and diffuse) reflectance ($R$) and transmittance ($T$) of a sample. The integrating sphere ensures that both specular and diffuse reflectance, as well as both direct and scattered transmittance, are measured accurately. Light from two lamp sources, one for the UV and one for the visible and near-IR, is sent into a monochromator that selects a single wavelength and directs it onto a sample; the amount of light, transmitted or reflected, is then measured relative to a baseline reading taken using a highly reflective titanium oxide blank. The operational wavelength range for this device is 250 nm to 2500 nm.

For reflectance measurements, samples are carefully taped on an optical quality, calcium fluoride window for support; the window is used because samples are smaller than the access ports of the integrating sphere. The calcium fluoride window is then placed on the back part of the integrating sphere in order to reflect light back into the integrating sphere detector. The reflectance of the calcium fluoride window is low ($< 6\%$) in the operational wavelength range [113]. For transmittance, samples are suspended at the front port of the integrating sphere; all transmitted light (scattered or direct) enters the integrating sphere detector. The spectrophotometer setup is described in more detail by Younkin [113].

By measuring both the reflectance ($R$) and transmittance ($T$) from 250 nm to 2500 nm, we calculate the absorptance of each sample with

$$A(\lambda) = 1 - T(\lambda) - R(\lambda) \quad (9.2)$$
Fig. 9.2: (a) Reflectance, (b) transmittance, and (c) the calculated absorptance of microstructured silicon for standard conditions. For reference, the same measurements are shown for unstructured, crystalline silicon. Absorptance of femtosecond-laser microstructured silicon as a function of wavelength. The absorptance of unstructured silicon is shown for reference. The large drop in absorptance of unstructured silicon at 1100 nm corresponds to the band gap energy of crystalline silicon [These experiments were performed by Eric Muzur group at Harvard University].
Figure 9.2 shows the measured reflectance, transmittance, and calculated absorptance for an unstructured silicon wafer and microstructured silicon. The drop in the absorptance for crystalline silicon near 1100 nm corresponds to the band-gap energy of crystalline silicon (1.07 eV). Light at longer wavelengths does not contain enough energy to promote an electron from the valence band to the conduction band and absorption becomes negligible for crystalline silicon. Microstructured silicon has a drastically decreased reflectance and transmittance over the entire measured spectrum. The lowered transmittance and reflectance results in near-unity absorptance in the entire wavelength region 250 nm <λ< 2500 nm. The increased absorption in the visible is consistent with the black appearance and, indeed, across this large range of wavelengths the surface is quite ”black.” By varying experimental parameters that we examine what is responsible for the high, featureless absorption. In the following sections, we present only absorptance, which is calculated from a measured reflectance and transmittance (Equation 9.2) [107].

**9.3 New design hybrid black silicon solar cells**

Black silicon is a fairly young field with the earliest work being done in 1999 by the Harvard professor Eric Mazur and his group. It has become much attractive in research field due to very low band gap (<1.0 eV). The band gap of Si limit operation to wavelengths 1.11µm, which makes it unsuitable for many near infrared applications [114]. Since black silicon has a band gap lower than 1.0 EV, it can be absorbed NIR solar spectrum which has more potential of the solar cell application. 18.2% efficiency of nano-structured black silicon solar cells were recorded by Jihun oh el al [ref. 115]. This efficiency developed on the high surface area solar cell with nano- and microstructured semiconductor absorbers.
The City College of New York ultra-fast spectroscopy and laser lab, Prof. Alfano and his group have been developed a new designed Multi-Exciton UV to NIR Black Silicon-ZnGO Quantum dot Hybrid Solar Cells. This new designed solar cell is based on micro-structured black silicon (BSi) and zinc(hydr)oxide with 2 wt % graphite oxide (referred as ZnGO). A high efficient hybrid solar cell was developed and tested using part of the solar cell spectrum from UV to NIR for solar energy conversion to electricity. The theoretical efficiency limit for QD solar cell is 64% whereas the limit for BSi solar cell is 30% - 40% were at 15% of experimental efficiency were recorded in our results.

9.3.1 Fabrications of BSi-ZnGO solar cells

This new design hybrid solar cell is fabricated following:

![Fabrication flow chart of new designed black silicon-ZnGO solar cells](image)

**Fig. 9.3.1:** Fabrication flow chart of new designed black silicon-ZnGO solar cells
Fabrication of black silicon reported in section 9.1 details. Fabricate BSi aided by femtosecond (fs) laser pulses induced on silicon surfaces at different annealing temperatures and doping levels in the presence of halogen-containing gases, forming spiked BSi; Deposit NIR PbS (emission peak 700nm-1000nm) QDs (nanomaterials) on BSi substrates; PbS nanoparticles suitable for the use as a light absorber or NIR or IR emitter. The range of black silicon particles exhibiting a band gap in the NIR range. While macroscopic lead sulfide (PbS) has a band gap of 0.37 eV (analog to a wavelength of 3300 nm) it can be increased in nanoparticles with decreasing size up to 1.3 eV (analog to an absorption maximum at 950 nm). This effect is called size quantization effect.

**Fig. 9.3.2:** schematic diagram of black silicon-ZnGO hybrid solar cell. The 3-dimensional structure Cross-section view of the multi-exciton UV to NIR black silicon quantum dot hybrid micro-meso scale solar cells.

Deposition of ZnGO on the conducting glass described in section 8.1.1 in the previous chapter. Once the micro/meso porous ZnGO paste deposit on the glass. Two parts black silicon and
ZnGO electrode glass added together make a sandwich shaped solar cells that shown in figure 9.3.2.

**9.3.2 Working procedure of new cells**

Working procedure of Gratzel like new hybrid solar cell is very similar that discussed in section 7.1 and 7.5 in the previous chapter. A schematic presentation of the operating principles of the QDSC is given in above fig.9.3.2. At the heart of the system is QDs with black Silicon films. Electrolyte /hole converter can be redox (I-/ I₃⁻) works a p-type semiconductor. Zn(OH)₂/ZnGO layers work as n-type semiconductor. In this system, QDs and BSi are absorbing light and then inject electrons from their excited levels into the conduction band (CB) of the wide- band gap semiconductors (ZnGO ~2.9 eV), while oxidized QDs are recharged by the redox electrolyte (fig. 9.3.2)

![Diagram of exciton generation process](image)

**Fig 9.3.3:** (Left) the exciton generation process is presented in a band diagram. NIR QD multi-exciton generation scheme (C-conduction band, V-valence band, EF-Fermi level, NR-non-radiative process, NIR-near infrared, UV-ultraviolet, QD-quantum dots, e-electron, i-current). (Right) summarizes the dominate exciton process in the hybrid solar cells shown roles of different wavelength-dependent exciton generation processes with respect to the solar spectrum.
The QDs molecule is regenerated by the redox system, which itself is regenerated at the counter electrode / back contact by electrons passed through the load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall, the device generates electric power from light without suffering any permanent chemical transformation [116].

From figure 9.3.3 shows the entire solar spectrum uses to generate the maximum energy conversation. The visible and NIR uses single excitons generation. The UV part of spectrum uses in QDs and BSi to produce multi excitons (2 to 4) for creating carriers; the visible light photons use in BSi for photo carrier generation, and the NIR part of the spectrum will be converted into carriers in QDs.

For the UV spectrum of the solar radiation, there are two exciton generation processes: multiple exciton generation (MEG) and single exciton generation. MEG is enabled by the QDs attached on the Perovskite. This is an important process that could potentially boost the external quantum efficiency above 100%. Un-captured UV photons that passed through the Perovskite layer will be absorbed by the BSi to create single exciton. In the visible spectrum, single excitons are created from QDs as well as from BSi.

Both materials (QDs and BSi) have exhibited extraordinary absorption characteristics in the NIR. Sub-band gap absorption arises due to the extremely high doping levels; the dopants, rather than forming distinct states, form an impurity band within the band gap of silicon. The dopant atoms are not just optically active; they also act as electron donors. The junction between the laser doped region and the crystalline substrate forms a diode. Finally, the heavily doped layer possesses states in the band gap that absorb sub-band gap radiation (i.e., with photon energies
less energy gap = 1.1 eV) via the creation of free electron-hole pairs. Thus, by exploiting the absorption of sub-band gap radiation can create optoelectronic devices that operate in the near-infrared, a spectral region to which silicon is generally transparent (λ_{gap}=1.1\mu m).

**9.3.3. Results and discussion**

Current –voltage characteristics of black silicon –ZnGO-2 hybrid solar cell in the dark and under light illumination shown in figure 9.3.3 (a).

![Graph showing current-voltage characteristics](image)

**Fig. 9.3.3 (a):** current –voltage characteristics of black silicon, black silicon with PbS QD and black silicon-ZnGO hybrid solar cells under the dark and illumination.

Figure 9.3.3 (a) shows, open circuit voltage (V_{oc}), short circuit current (I_{sc}) and efficiency of black silicon and black silicon with quantum dots are very low (table 9.3.3), the reason of this cell is only one type (p-type) semiconductor. It is not solar cell. On the other hand, black silicon-ZnGO hybrid solar cell is very high open circuit voltage, rescission of meso/micro porous ZnGO works as n-type semiconductor and thickness is between 45-50nm.
**Fig. 9.3.3 (b):** Photocurrents of black silicon, black silicon with PbS QD, and black silicon-ZnGO-2 hybrid solar cells as a function of wavelength (nm).

Figure 9.3.3 (b) shows the photocurrent of black silicon, black silicon with PbS QD, and black silicon-ZnGO hybrid solar cell measured between 300nm to 1400nm. Only black silicon absorbed between 600 nm to 1300 nm solar spectrum, one drop PbS QD has been applied in this cell resulting current increased shown in red color curves. On the other hand, black silicon-ZnGO hybrid solar cell absorbed more broadening solar spectrum that started from 460 nm to 1300 nm.

**Fig.9.3.3 (c):** Quantum efficiency of black silicon, black silicon with PbS QD, and black silicon-ZnGO-2 solar cells as a function of wavelength (nm)
Figure 9.3.3 (c) shows the quantum efficiency of black silicon, black silicon with PbS, and black silicon-ZnGO hybrid solar cell. The quantum efficiency of black silicon and black silicone with PbS Qd reaches almost 90% at the wavelength of 1000 nm whereas black silicon-ZnGO solar cell reaches 85% at 550nm.

Table 9.3.3: Open circuit voltage, short circuit current, and power conversion efficiency of black silicon, black silicon with PbS QD, and black silicon-ZnGO hybrid solar cells under 1 mm² illuminations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voc (V)</th>
<th>-Isc (µA)</th>
<th>FF</th>
<th>η(%)</th>
<th>Max QE</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSi</td>
<td>0.1</td>
<td>30</td>
<td>0.48</td>
<td>0.60</td>
<td>80% @ 1000nm</td>
</tr>
<tr>
<td>BSi+QDs(PbS)</td>
<td>0.2</td>
<td>32</td>
<td>0.28</td>
<td>0.75</td>
<td>90% @ 1050nm</td>
</tr>
<tr>
<td>BSi/ZnGO-2/PbS/E/P</td>
<td>0.9</td>
<td>59</td>
<td>0.512</td>
<td>11.32</td>
<td>90% @ 550nm</td>
</tr>
</tbody>
</table>

9.3.4 Summary

Black Silicon-ZnGO hybrid solar cell is shown in figure 9.3.3 (b), light absorbed from 460 nm to 1300 nm. It has really improved by the black silicon solar cell but not enough for increasing efficiency. There is no UV absorption resulting no multiple photon exciton. One drop (6%) PbS quantum dot added to the black silicon solar cell. The black silicon solar cell is very small area (0.5 mm x 0.5 mm). There is no enough room to add more PbS QD. We believe, if we can add more quantum dots (e.g. 3 or more) then the cell will absorb more UV absorption as as well more quantum efficiency.
Chapter 10

Multi-Exciton Generation (MEG) of UV, visible, and NIR Converter

10.1 Introduction

By shown in the figure, the solar spectrum contains photons with energies ranging from 350nm to 2480nm (0.5eV to 3.5eV). Photons below the semiconductor band gap are not absorbed, while those with energies above the band gap are absorbed and create charge carriers (electron and holes) with a total excess kinetic energy equal to the difference between the photon energy and the band gap (see the figure 1.1).

The possibility of achieving higher conversion efficiency in single band gap cells by utilizing electrons (termed hot electrons and holes created by the absorption of solar photons larger than the band gap) before these hot electrons and holes relax and convert their excess kinetic energy to heat through phonon emission [117]. The bulk nonradioactive creates lots of optical phonon emission. This is very difficult in the case of bulk semiconductor because hot electron relaxes very rapidly. However, in semiconductor quantized QD, quantum well nano-crystal (also termed quantum dots), discrete quantized energy levels are formed that dramatically affect the relaxation dynamics of hot electron and holes into multiexcitons and allow other relaxation channels to compete with phonon emission.

Due to optical phonon emission, the excess kinetic energy of hot carriers is lost into heat result decrease in energy efficiency. The higher energy photons are absorbed in the higher band gap
semiconductors and lower energy photons in the lower band gap semiconductors, thus reducing
the overall heat loss due to carrier relaxation via phonon emission. In this limit of an infinite
stack of band gap perfectly matched to the solar spectrum ultimately increase conversion
efficiency to 80%.

10.2 Multiple excition generation of carriers in QD

One of the potential approaches to overcome nonradiative loss in bulk is carrier multiplication
(CM), or multiple excition generation (MEG). The MEG phenomenon has been known in bulk
semiconductors since the 1950s. Due to the restrictions imposed by energy and momentum
conservation, the power conversion efficiency improvement due to MEG was less than 1\%. The
MEG for solar cells was then not affected. [120] Recently, Schaller et al discovered that while
being low efficiency in bulk semiconductors, MEG can become extremely efficient in ultrasmall
semiconductor nanocrystals such as QDs. MEG of carrier described in chapter 9 section 9.3.2
details.

10.3 Electron-holes pair multiplication in QDs

The formation of multiple electron-hole pairs per absorbed photon in photo-excited bulk
semiconductors is a process typically explained by I.I. In this process, an electron or holes with
kinetic energy greater than that of semiconductor band gap produce one or more additional
electron-hole pairs. The kinetic energy can be created either by applying an electric field or by
absorbing a photon with energy above the semiconductor band gap energy.

In quantum dots, the rate of electron-phonon interactions can be significantly reduced because
the discrete character of the electron-hole spectra, and the rate of Auger process [121], including
the inverse Auger process of exciton multiplication is greatly enhanced because of carrier confinement and the concomitantly increased electron-hole Coulomb interaction (figure 10.4)

Fig. 10.3: Multiple electron–hole pair (exciton) generation (MEG) in quantum dots [121]

Furthermore, crystal momentum need not be conserved because momentum is not a good quantum number of three-dimensionally confined carriers (from the Heisenberg Uncertainty Principle the well-defined location of the electrons and holes in the nanocrystal makes the momentum uncertain). The concept of enhanced MEG in QDs is indicated in figure 10.3. Indeed, the result of PbS and PbS/CdSe quantum dots have been reported below.

10.4 Mutiexciton absorption ZnGO-PbS I-V and QE characteristics

Current-Voltage characteristics of mutiphoton excitation PbS/Cdse quantum dots sensitized ZnGO solar cells. This I-V curves are measured under illumination that shown in figure 10.4. Open circuit voltage, short circuit current, and efficiency shown in table 10.4.
In our setup an AM 1.5 solar lamp used to test the devices. A silicon power meter was used for calibration before measuring power on sample per area. For 1 mm$^2$ area under the illumination of intensity of Tungsten lump 12.1 mW/ cm$^2$.

**Fig. 10.5:** (a) Photocurrent of multiphoton exciton ZnGO solar cells, (b) Quantum efficiency of multiphoton ZnGO solar cells. Figure 10.5(a) shows the difference in conversion in uv and NIR from QD PbS between ZnGO+CdSe and ZnGO+PbS+CdSe solar cells in shaded parts.

Figure 10.5 (a) shows the photocurrent spectrum as a function of wavelength (nm).
Fig. 10.5.1: Superlinearity curve shows current vs. $P^{n=2.8}$ of (a) ZnGO-2+CdSe+KI solar cells, (b) ZnGO-2+PbS+CdSe+KI solar cells.

From the figure 10.5.1 (a) and (b) show superlinearity of current vs. power$^n$ which is discussed in previous chapter 8 in section 8.1.2 (page 98). The difference between figure 10.5.1 (a) and 1.5.1 (b) is $n=2.8$ and $n=1.8$ respectively. The figure we got above 2 that means this sample (ZnGO-2+CdSe+KI) has some defective due to pores while figure 10.5.1 (b) has not any defective resulting get more efficiency that sample (ZnGO-2+PbS+CdSe+KI).

This photocurrent absorption spectrum starts at 350 nm (UV) which has created 4 multiphoton excitation carrier showing in shaded parts in us and near infrared zones in figure 10.5 (a) results to get more conversion efficiency from QDs PbS.

**Table 10.4:** Open circuit voltage, short circuit current, and efficiency of ZnGO-PbS solar cells taking under illumination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voc(V)</th>
<th>-Isc(µA)</th>
<th>FF</th>
<th>η(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnGO-2+PbS</td>
<td>0.34</td>
<td>90</td>
<td>0.474</td>
<td>11.99</td>
</tr>
<tr>
<td>ZnGO-2+PbS/CdSe</td>
<td>0.44</td>
<td>80</td>
<td>0.51</td>
<td>13.83</td>
</tr>
</tbody>
</table>
Figure 10.6 (b) shows the quantum efficiency of multiform excitation ZnGO solar cell. This quantum efficiency covers a broad spectrum of light absorbed from 350nm to 900nm. Maximum quantum efficiency of ZnGO+PbS reaches ~40% at 600nm whereas ZnGO+PbS/CdSe is 35% at 550 nm.

10.5 Summary

Above diagram of multieexciton diagram is the key of our solar cell as well as research. The entire solar spectrum used to generate the maximum energy conversion. The visible and NIR uses single excitons generation. The UV part of spectrum used in PbS QDs and ZnGO to produce multi excitons (4) for creating carriers at 400nm (3.1eV); the visible light photons will be used in ZnGO for photo carrier generation, and the NIR part of the spectrum has converted into carriers in PbS QDs.
Chapter 11

Conclusion

The objective of this thesis was to propose structural development of a new ZnGO hybrid material and alternative designs for the fabrication of quantum dots sensitized ZnGO hybrid solar cells using a *multiexcitons generation process* that can enhance the efficiencies as well as reduce the cost by making it more amenable to large scale production.

In this research several experiments were accomplished in ultrafast spectroscopy lab. In earlier works, we have determined the optical properties of Zinc (hydr) oxide and its composites with 2% and 5% graphite oxide. Among this optical properties, we determined band gap, absorption, fluorescence and photoconductivity of materials. We have developed some structural properties of composite materials. In this composite material there are some pores/ big holes inside the structures results reduce the current. Electron traps or stuck with pores while travel through this device, we develop these pores using quantum dots as well as annealing in temperature 450°C. Due to large temperature apply to the sample melts and fill out the gap, hence electron can easily travel though the structure.

We have developed a new model for fitting curve for finding rise and fall time of electron carriers. After all these new materials have been used as a solar cell device. We have built a new hybrid solar cell using two quantum dots (CdSe and PbS) and two electrolyte (potassium iodide) and Perovskite. For new designed PbS quantum dots solar cell absorption spectrum of starts 350nm which has generated *multiphoton excitation (n=4 excitons)* results getting more
efficient. A more than 13% power conversion efficiency were reported. In the chapter 10 in section 10.4 described the difference between ZnGO+CdSe and ZnGO+PbS+CeSe solar cells showing in shaded zones which means more multiexciton and single exciton generation in uv and near infrared zones. Results of this difference from QDs from CdSe and mainly from QD PbS we would says more energy to convert in the range from 900nm to 2500nm. So NIR zone is also important for solar energy conversions.

In chapter 8 on page 98 described about superlinearity variations of short circuit photocurrent arises from QDs with increasing input optical power. In brief, it is possible to get more current at higher power to give energy conversion efficiency if we increase more input optical power.

A fabricated temperature depended solar cell were reported in our research. 450°C temperature is suitable for fabrication but it may burn the graphite oxide. For ZnGO solar cell a 200°C may use instead of 450°C. Thickness of ZnGO micro/messo porous films should be between 30 μm to 40 μm but in our system we cannot control the thickness that causes the lower current.

**Future Works**

**Pump-Probe absorption spectroscopy**

The bottom figure 11.1 shows the experiment to be done for measuring relaxation between two interfaces such as QDs and ZnGO, ZnGO and Si, and QDs and electrolyte interface, etc. by time-resolved infrared (IR) absorption spectroscopy.
The details of the femtosecond (fs) IR pump and visible probe absorption need to be set up. In this measurement, we have decided to set pump the QD at 800nm and probe the ZnGO at 400 nm.

**Fig. 11.1:** Schematic diagram shows relaxation of delaying electron flows.

The details of the femtosecond (fs) IR pump and visible probe absorption need to be set up. In this measurement, we have decided to set pump the QD at 800nm and probe the ZnGO at 400 nm. In this system, we can pump our quantum dot PbS at 800nm. PbS is the direct band gap semiconductor. That's why electrons are jumping from the valence band to the gamma valley of the conduction band. The lowest conduction band of PbS is located in the gamma valley (0.35eV measured from the top of the gamma valence band). Due to pump of QD, conduction band of PbS is excited and goes up than the conduction band of ZnGO. So electrons easily slide to the wide-range band gap (2.90 EV) of ZnGO. Due to pump in PbS at 800nm, there are other electrons occupied in the lowest conduction band of black silicon. The band gap of Si is 1.1 2eV and Fermi level of Si lower than ZnGO. Due to setting pump at 800 nm, PbS has absorption at
800 nm and 400 nm (2\(^{nd}\) pulse). Two absorptions make complexity between QDs/ZnGO interfaces (fig 11.2)

There are ways to solve these problems. If we can relax (\(\tau_2\)) the electron from an upper conduction band to a lower conduction band (see in picture 11.1), in this way electron can inject QDs from ZnGO. There is another way we can solve the problem. In this way there will no more absorption at 400 nm.

![Fig.11.2](image)

**Fig.11.2:** (a) Schematic diagram of electron transfer between QDs and ZnGO. (b) Graph showing absorption is a function of a delay time.

a) QDs / BSi interface (pump=800nm, probe=1200nm)
b) BSi/ZnGO interface (pump=800nm, probe=1000nm)
c) QDs/ZnGO/BSi (pump=800nm, probe=1200nm)

If we are able to set above probes for supper continuum in three systems, there will be no more absorption at 400nm into our system.

In this way we can measure, various relaxation time showing in figure in 11.1. The graph will be absorbed at IR as a function of delay time of probe setting (\(\lambda_{probe}\)) in semiconductors.
Appendix: A

Simulation of fitting curves for band gap energy

Algorithm of fitting curves

The least-squares fit technique has been applied for curve fitting. This algorithm has divided by both polyfit and polyval methods. Specifically, the polyfit method is used to generate the \( n + 1 \) coefficients \( a_j \) of the \( n \)-th degree polynomial,

\[
P_n(x) = a_n x^n + a_{n-1} x^{n-1} + \cdots + a_1 x + a_0 \quad (1)
\]

used for fitting the data. This simulation used for zinc (hydr) oxide sample’s fitting curve that described in chapter 2 in sections 2.3 and 2.4. This fitting curve has been performed by MATLAB 10.10 software.

```matlab
% Non-linear curve fit
% SM Z. Islam
% Experiment data
x=xlsread('matlab_105.xls');
% Constants
h = 6.626e-34   ; % Units: Js
% c = 3e8         ; % Units: m/s
lambda=x(:,1)   ; % Units: nm ( 1nm= 10^-9 m)
% Determine Energy (eV)
E=1240.7./lambda; % E=hc/lambda, Units: 1J=6.242e18 eV
Abs=x(:,2);
a=Abs/150e-4    ; % absorption coefficient, a= Abs/l, l=165 micron ( 1micron=1e-4cm)
% Determine Direct band gap
% Parameters
```
a_{OD} = 330 \text{ ; % Units: cm}^{-1} \\
E_g = 3.01 \text{ ; % Units: eV} \\
\% Formula \\
a_1 = a_{OD}\sqrt{E - E_g}; \% Direct band gap \\

\% Determine Urbach tail \\
\% parameters \\
E_{op} = 3.05 \text{ ; % Units: eV} \\
E_u = 0.36 \text{ ; % Units: eV} \\
a_{Ou} = 58 \text{ ; % Units: cm}^{-1} \\
\% Formula \\
a_2 = a_{Ou}\exp{(E - E_{op})/E_u}; \% Urbach Tail \\
A = a_1 + a_2; \\
a_3 = a_2; \\
\% curve fitting \\
a_2(343:end) = 0; \\
a_1(1:342) = 0; \\
x = a_1 + a_2; \\

LA = \log(\text{Abs}); \% take log of Abs \\
plot(lambda, LA, 'r.') \% plot to see what kind of relationship between them \\
coe = polyfit(lambda, LA, 3); \% log of Abs is assumed to be third order polynomial of lambda \\
LA_fit = polyval(coe, lambda); \\
plot(lambda, LA_fit, 'k') \% this show how good the fit is \\
Alpha = coe; \\

Fitted_Absorption = \exp(polyval(Alpha, lambda)); \% Abs has the exponent of the 3rd polynomial of lambda \\
figure \\
plot(lambda, Abs, 'r.'); hold on \\
plot(lambda, Fitted_Absorption, 'k'), xlabel('Lambda'), ylabel('Absorption coefficient(cm^{-1})'), title('Fitted curve')
figure
clc
disp(Alpha) % display fitting coefficients
subplot(221),
plot(E,a,E,a1),xlabel('Energy(eV)'), ylabel('Absorption coefficient(cm^-1)'),title('Direct band gap'),
subplot(222),
plot(E,a,E,a3),xlabel('Energy(eV)'), ylabel('Absorption coefficient(cm^-1)'),title('Urbach tail'),
subplot(212),
plot(E,a,'b.',E,x,'r'),xlabel('Energy(eV)'), ylabel('Absorption coefficient(cm^-1)')
title('Co-efficient Vs. Energy curve (Theoretical and Experimental'),figure

LA1=log(a); % take log of a
plot(E,LA1,'r.') % plot to see what kind of relationship between them
coe1=polyfit(E,LA1,10);hold on % log of a is assumed to be third order polynomial of Energy
LA_fit1=polyval(coe1,E);
plot(E,LA_fit1,'k'); % this show how good the fit is

Alpha1=coe1;
Fitted_Absorption1=exp(polyval(Alpha1,E)); % Abs has the exponent of the 3rd polynomial of Energy
figure,
plot(E,a,'b. ');hold on
plot(E,Fitted_Absorption1,'k',E,x,'r'),
xlabel('Energy(eV)'), ylabel('Absorption coefficient(cm^-1)'),title('Fitted curve'),
legend('Data','Fitted curve','Theoretical')
clc
Appendix: B

Photoluminescence formula calculation

The photoluminescence formula for peak for direct transitions, \( E_p = E_g + kT/2 \) is described in section 4.2 (chapter 4).

The photoluminescence intensity \( I(E) \) depends on density of states times the Boltzmann factor. The peak of the PL can be extracted from the derivative of the product of the density of the states and Boltzmann factor is equal to zero.

Hence we have:

\[
I(E) = A(E - E_g)^{1/2} \left( e^{-E/kT} \right) \\
\frac{\partial I(E)}{\partial E} = A \left[ \frac{1}{2}(E - E_g)^{-1/2} \left( e^{-E/kT} \right)(1) + (E - E_g)^{1/2} \left( e^{-E/kT} \right)(-1/kT) \right] = 0 \\
\text{or, } (E - E_g)^{1/2} \left( e^{-E/kT} \right) = 1/2(E - E_g)^{-1/2} \left( e^{-E/kT} \right) \\
\text{or, } (E - E_g) = \frac{kT}{e^{E/kT}} \\
\therefore E_p = E_g + kT/2
\]

This formula has been used for determining the optical band gap for any semiconductor materials using photoluminescence method.
Appendix: C

Simulation of fitting curves for new lake model

Algorithm of fitting curves of new lake model for rise and fall time

Fit "exponential decay functions" performs a nonlinear fitting of the given signal to an exponential function of the form,

\[ I(t) = A_1 \left[ e^{-kt/\tau_0} - e^{-t/\tau_1} \right] + A_2 \left[ e^{-t/\tau_0} - e^{-t/\tau_1} \right], \]

taking, \( A_1 = A_2 = A \)

\[ I(t) = A \left[ e^{-kt/\tau_0} + e^{-t/\tau_0} - 2e^{-t/\tau_1} \right], \]

Where, \( t \) is the time period (ps), \( \tau_0 \) is the carrier life time (ps), \( \tau_1 \) is the rise time(ps), \( k \) is fluorescent decay rate constant, and \( A \) is the parameter of the equation. The signal returned from this function corresponds to the fitting function with parameters that give the best fit for the input signal. This function takes either one signal as input. This signal is used as a weighting function consisting of the individual standard deviations of the input signal samples. This fitting curve used Origin 8.5 software that described in Chapter 6 in section 6.4.

1. First import the data→highlight and click plot→click Analysis→Go to Fitting→Non-linear curve fitting→Open dialog box
2. When the dialog window appears on the screen, click category and change to exponential then click function to exponential decay 2, then click new fitting function.

3. Build your own “C” code and saved. Click parameter and change parameter to get appropriately fits.
Appendix: D

Tools setup: for ZnGO hybrid solar cell

The following set up figure used for measuring photocurrent as well as quantum efficiency. A monochromator is used to shine light of different wavelengths on the sample. Shorter wavelengths have a higher absorption coefficient and get absorbed within the first 300 nm, while the longer wavelengths penetrate deeper and generates carriers at the other end of the intrinsic layer.

**Fig Appendix C:** Tools set up for ZnGO hybrid solar cell.

On sample devices the measurement is done at zero bias and at a negative bias of -0.5 V or -1 V. Placing the sample under a negative bias increases the collection of the carriers. The light from the monochromatic source passes through a chopper rotating at a frequency of 13.5 Hz. This AC beam is focused on the sample using a couple of lenses and then reflected off a mirror onto the sample. The current generated from the sample is converted into a voltage signal, and then detected by a phase lock amplifier (PLA). The amplifier is programmed to lock in on a frequency
of 13.5 Hz. Thus the usage of a PLA removes the noise from other electronic instruments in the vicinity. The wavelength emitted by the monochromator is varied and the signal is recorded. The photocurrent and spectral response of a sample is then measured.
Appendix: E

Power conversion efficiency calculation

In our setup an AM 1.5 solar lamp used to test the devices. A silicon power meter was used for calibration before measuring power on sample per area. For 1 mm$^2$ area under the illumination of intensity of Tungsten lump 12.1 mW/ cm$^2$.

\[ P = \text{(intensity)}(\text{Area}) = (12.1 \text{mW/cm}^2)(1 \text{mm}^2) = 12.1 \times 1000 \mu\text{W/cm}^2 * 10^{-2} \text{cm}^2 = 121 \mu\text{W} \]

Sample : ZnGO – 2/QD/E
\[ V_{oc} = 0.36 \text{ V} \]
\[ I_{sc} = 70 \mu\text{A} \]
\[ V_{mp} = 0.22 \text{ V} \]
\[ I_{mp} = 58 \mu\text{A} \]

\[ \text{FF} = \frac{(I_{mp})(V_{mp})}{(I_{sc})(V_{oc})} = \frac{(0.22 \text{V})(58 \mu\text{A})}{(0.36 \text{V})(70 \mu\text{A})} = 12.76/25.2 = 0.51 \]

\[ \text{Efficiency (\%)} = \frac{(I_{sc})(V_{oc})(\text{FF})}{P_{in}} \times 100 = \frac{(70 \mu\text{A})(0.36\text{V})(0.51)}{121 \mu\text{W}} \times 100 = \frac{12.852}{121} \times 100 = 10.62\% \]
Publications

Journals


5 SM Z. Islam, Naing Tint, Taposh Gayen, Lingyan Shi, Mykola Seredych, Teresa J. Bandosz, Robert Alfano, “Hybrid Solar Cells of Quantum Dots Sensitized micro/mesoporous of Zn(OH)2 and its composites” Journal of Photonic for energy (Accepted, Dec 2013)

Conference and proceeding


2 S M Z. Islam, Taposh Gayen, Mykola Seredych, Teresa J. Bandosz, Robert Alfano “Optical properties of porous nano-composites of zinc (hydr)oxide with graphite oxide,” for the conference Optical Components and Materials X._ SPIE, California, USA, 2-7 Feb 2013 (Presented and Published)

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