Photo – Physical Investigation of Organic Donor – Inorganic Acceptor Interface & Preparation of ZnO Thin -Film by Sol – Gel Method.

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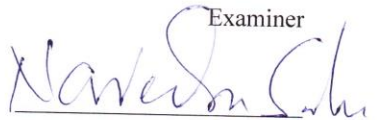
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Acknowledgements

Dedicated to

My work is dedicated to my loving Parents and my B.Sc. classmates.

Abstract

In the present work zinc oxide nanoparticles (ZnO) were successfully synthesized by a sol-gel method and zinc acetate dehydrate and ethanol, HCl and DI water were used as the precursor materials. The wet films dried in hot oven at 100°C for 4 min and further annealing at 250°C for 10 min. The samples were characterized by Scanning Electron Microscopy (SEM), UV- visible spectroscopy and optical profilometer. Results shows that the calcinations temperature significantly affected the crystalline nature, particle size, and optical properties of the processed ZnO nanoparticles. The optical properties of the samples are investigated by measuring the UV-VIS absorption at room temperature. The optical profiler shows that the variation in uniformity of ZnO thin film.

We report the photo – physical study of a novel anthracene based organic dye G1 interacting with Titania nanoparticle of 25nm mono-dispersity. We used photoluminescence and absorption spectroscopy to measure the electron transfer process taking place in G1 – Titania complexes in toluene solution. We observed that the electron injection from dye G1 to Titania occurs. The absorption spectra shows the two peak at wavelength 372 nm and 424 nm with a shoulder at 510 nm. Photoluminescence spectra of dye G1 – Titania particle show that peak will reduce i.e. electron transfer will take place from dye G1 to Titania nanoparticle

Contents

Chapter - 1

1.1 Introduction and Motivation

At the end of last century, the possibility to use devices based on molecular components for the construction of a robust large-scale solar electricity production facility seemed to be originate. But the seminal paper by O'Regan and Gratzel in 1991 spurred researchers to take on the challenge. With the development of dye-sensitized solar cells (DSCs), conventional solid-state photovoltaic technologies are now challenged by devices functioning at a molecular and nano level. The prospect of low-cost investments and fabrication are key features.DSCs perform also relatively better compared with other solar cell technologies under diffuse light conditions and at higher temperatures. DSCs offer the possibilities to design solar cells with a large flexibility in shape, color, and transparency. Here for DSCs applications we are using organic dye G1 and inorganic semiconducting material TiO2 interface. Then we will took absorption and emission spectra of dye and TiO2 interface. The absorption spectra are determined by the intrinsic absorption of the dye molecules and the dye – TiO2 interaction. Dye-dye (solute-solute) interaction is negligible because of the large average distance between the dye molecules. The absorption spectra obey the Beer-Lambert law, i.e. the absorption cross sections are independent of concentration.

Semiconductor compounds have drawn much attention during the last few years because of their novel optical and transport properties which have great potential for many optoelectronic applications. ZnO is a wide band gap semiconductor that displays high optical transparency and luminescent properties in the near ultra violet and the visible regions. Due to these properties ZnO is a promising material for electronic and optoelectronic applications such as solar cells (anti-reflecting coating and transparent conducting materials), gas sensors, liquid crystal displays,heat mirrors, surface acoustic wave devices etc. The high exciton binding energy of ZnO (~ 60 meV) would allow for excitonic transitions even at room temperature, which could mean high radiative recombination efficiency for spontaneous emission as well as a lower threshold voltage for laser emission. Studies have been carried out to fine-tune the properties of ZnO to adopt it for different applications; for example, the band gap of ZnO is modified to use as UV detectors and emitters. ZnO nanoparticles are widely employed in fundamental research and potential applications, such as hydrogen-storage, field emitters, ultraviolet lasers and diodes, piezoelectric devices and photo catalysts fluorescence labels in medicine and biology, controlling units as UV photo detectors and as high-flame detectors in cosmetic industry and as a component of sun screens.

Chapter - 2

2.1 Introduction and Motivation

ZnO is a special characterized semiconductor with many potential applications. The tetrahedral coordination indicate the covalent bonding of Zn-O bond with very strong ionic character. ZnO is used as many conducting compound in many opto electronic device like solar cells, gas sensors and light emitting diode etc. Thin films made of ZnO has a high transmittance and conductivity which are used in solar cells and energy efficient window display. ZnO films are thermally and chemically stable with a wide band gap 3.37 eV at room temperature.

ZnO thin films can be prepared by different methods, like chemical vapor deposition, sol-gel, molecular beam epitaxy pulsed laser deposition and magnetron sputtering. The sol-gel process is a simple and less expansive with which coating can be obtained at room temperature. There are some factor that effect microstructure and properties of thin film, such as concentration, precursor, solvent the aging time of solution, temperature and heat treatment etc.

In present work we used sol-gel method to obtain ZnO thin films and studies have reported ZnO thin films using ethanol as complexing agent. The optical and structural properties of thin films formed are analyzed by UV- visible. Optical profilometer and scanning electron microscopy.

2.2 Experimental Setup:

2.2.1 Spin Coater:

Spin coater is used for application of thin films. A typical process involves depositing a small puddle of a fluid resin onto the center of substrate a then spinning sunstrate at high speed. Centripetal acceleration will cause the resin to spread to, and eventually off, the edge of the substrate leaving a thin film of resin on the surface. Final film thickness depand on nature of the resin and the parameters chosen for spin process. Factors such as final rotational speed, accelration, and fume exhaust contribute to how the properties of coated films are defined.

Image of Spin Coater

Spin Coating Process Description:

A typical spin process consists of a dispense step in which the resin fluid is deposited onto substrate surface, a high – speed spin step to thin the fluid, and a drying step to eliminate excess solvents from the resulting films.

Static Dispense: It is simply depositing a small puddle of fluid on or near the center of the substrate. This can be range from 1 to 10 cc depending on the viscosity of fluid and size of the substrate to be coated. Higher viscosity and or larger substrates typically re-quire a larger puddle to ensure full coverage of the substrate during the high-speed spin step.

Dynamic Dispense: It is the process of dispensing while he substrate is turning at low speed. A speed of about 500 RPM is commonly used during this step of the process. This serves to spread the fluid over the substrate and can result in less waste of resin material since it is usually not necessary to deposit as much to wet the entire surface of the substrate.

After the dispense step it is common to accelerate to a relatively high speed to thin the fluid to near its final desired thickness. Typical spin speeds for this step range from 1500-6000 RPM, again depending on the properties of the fluid as well as the substrate. This step can take from 10 seconds to several minutes. The combination of spin speed and time selected for this step will generally define the film thickness. In general higher spin speeds and longer spin times create thinner films.

2.2.2 Optical Profilometer:

it is device used to measure the roughness of surface and gives the difference between the high and low point of a surface in nanometer. There are two types of profilometer:

Non – Contact Profilometer

Contact Profilometer

In our experiment we are using Non – contact profilometer by Optical methods which is

Vertical Scanning interferometry

Phase – Shifting Interferometry

Differential Ineterference Contrast Microscopy

Working Principle of Optical Profilometer:

 In non – contact profilometer we use beam of light project towards the sample   and measure the time it takes to return. The light beam is split, refeleting from reference (known/flat) and sample. When there two beam interect with each other, depending on the path difference between them constructive and destructive interference occurs and it forms the light and dark bands depending on the interference. The optical path difference between two beam is due to the height variances between the two surfaces.
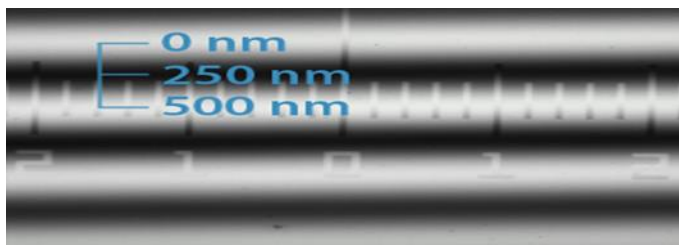
Interference Image

In this image constructive interefernce area as lighter and destructive interference area as darker. Light and dark fringes above represents one – half a wavelength of difference between the reference path and test sample path. From the image; lower portion is out of focus means less interference and greatest contrast means best focus.

Image of Optical Profilometer

2.2.3 Scanning Electron Microscope:

The scanning electron microscope scan a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition.

An electron microscope uses an electron beam to produce the image of the object and magnification is obtaines by electromagnetic fields. But in case of optical microscopes uses light wave to obained the image and magnification obtained by optical lenses, smaller the wavelength of light, the greater is its resolving power.

In scanning electron microscope, the sample is exposed to the narrow electron beam from an electron gun, which rapidly moves over the surface of the sample. This cause the release of a secondery electrons and other types of radiations from the sample.

Image of Scanning Electron Microscope

The intensity of these secondery electrons depends upon the shape and the chemical composition of the irradiated object. These electrons are collected by a detector, which generates electronic signals. These signals are scanned in the manner of a television system to produce an image on a cathode ray tube.

2.2.4 UV – Vis Spectroscopy:

UV – Vis spectroscopy is refer to absorption spectroscopy or reflectance spectroscopy in which light of ultra-violet and visible region (200-700 nm.) is absorbed by the molecule. The absorption or reflectance directly affects the color of chemicals involved.
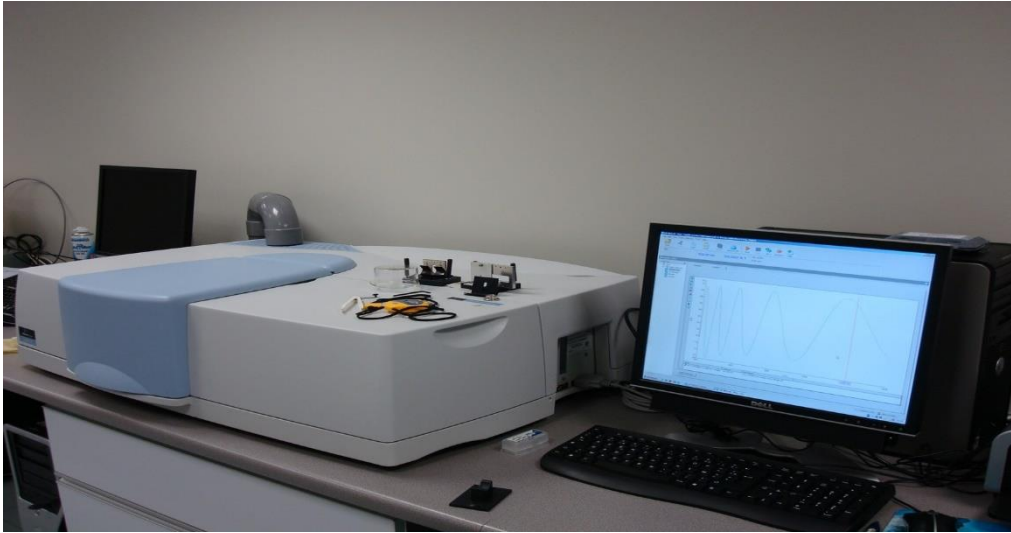
Image of UV – Vis Spectrometer

Working Principle of UV – Vis:

The functioning of the instrument is straight forward. A beam of light from the UV/Visible light source is separated into its component wavelengths by a diffraction grating.
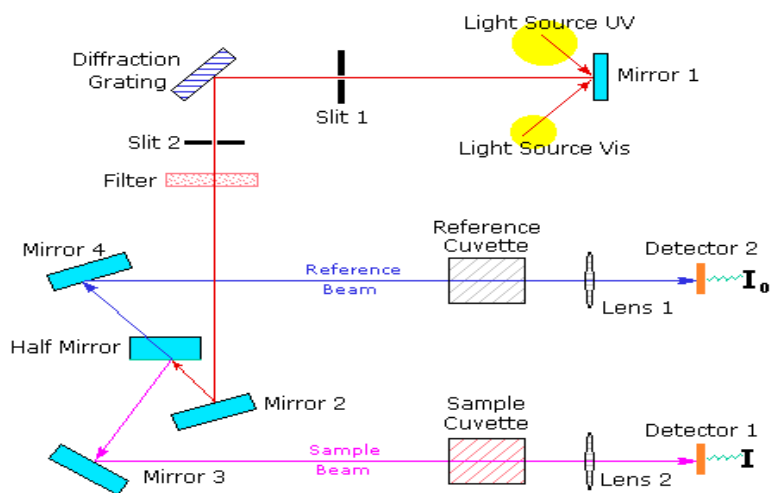
Each monochromatic beam in turn split into two equal intensity beam by a half silvered mirror or by beam splitter. One beam, sample beam, passes through a sample thin film being studied on a transparent glass substrate. The other beam, the reference beam, passes through an

identical glass substrate. The intensity of these beam are measured by electronic detector and compared.

The absorbance or optical density of a molecule absorbing in ultraviolet or visible region depends on molecular structure and its concentration is given by Beer – Lamberts relationship

$$A = \log \frac{I_o}{I} = Ebc$$

Where I_0 and I are intensity of reference beam and sample beam after passing through the glass substrate and the sample thin film respectively.

E is known as molar absorptivity, b is the thickness of thin film and c is the concentration.

2.3 Experimental Procedure:

The preparation of ZnO thin film by sol-gel technique and the characterization method are introduced. The preparation of ZnO films consist of three steps:

Preparation of solution

Film coating

Heat treatment

The solution was prepared by using zinc acetate dehydrate dissolved in ethanol (99.5% Hychem laboratory, CH_3CH_2OH) and De-ionized water and hydrochloric acid stirred at 0°C temperature for 12 hours.

Here we are preparing 0.01792 moles of final solution of volume 30 ml.

To prepare this solution we need:

Zinc Acetate Dehydrate:

The molecular weight of zinc acetate dehydrate (M_w) = *219.49 g/moles*

0.01792×219.49 = 3.9332 g.

De-Ionized water:

$$\frac{\eta_{H_2O}}{\eta_{Zno}} = 2$$

$$\eta_{H_2O} = 2 \times 0.01792 moles = 0.03584 moles$$

$$\left(M_W \right) \text{ of } H_2O \ = \ 18 \frac{g}{mol} = 18 \times 0.03584 = 0.64512$$

0.64512 g of H_2O = 0.64512 ml.

Hydrochloric Acid:

$$\frac{\eta_{Hcl}}{\eta_{Zno}} = 0.01$$

$$\eta_{Hcl} = 0.01 \times 0.01792 moles = 0.0001792 moles$$

$$\left(M_W \right) \text{ of Hcl} \ = \ 36.5 \frac{g}{mol} = 36.5 \times 0.0001792 = 0.006540 g$$

0.00654 $g \ of \ HCl$ = 0.00654/1.18 = 5.542 μl.

d_{HCl} = 1.18 g/ml.

Here we use 70% HCl the volume we need to use = 5.542/0.70 = 7.9171.

Ethanol:

Finally we need 30 ml solution.

So, ethanol volume 30 – (0.007917 + 0.64512) = 29.3469 ml.

After mixing both solution and zinc acetate dehydrate, the mixture is stirred at 0°C for approximately 12 hours until the transparent solution was formed. Before coating the films by spin coating we have to filter the solution by syringe filters of 0.2μm. The substrate of glass were cleaned with distilled water and Acetone respectively. The substrate were cleaned ultrasonically with duration of 10 min at room temperature. For films preparation, the glass substrate was spin coated by spin coater while spinning rate was kept at 1000, 1500, 2000 and 2500 rpm. The wet films dried in hot oven at 100°C for 4 min and further annealing at 250°C (in case of films on normal glass substrate) for 10 min.

The sample were characterized by scanning electron microscopy, Morphology of the sample were examined by optical profilometer. Optical absorption was studied by UV – Visible absorption spectrometer.

2.4 Result and Discussion:

2.4.1 UV – Vis measurement:

The direct band gap energy (E_g) for the ZnO nanoparticles is determined by fitting the reabsorption data to the direct transition equation $\alpha h\upsilon = E_D (h\upsilon - E_g)^2$, where α is the optical absorption coefficient, $h\upsilon$ is the photon energy, E_g is the direct band gap and E_D is a constant. Plotting $(\alpha h)^2$ as a function of photon energy and extrapolating the linear portion of the curve to absorption equal to zero gives the value of the direct band gap to be 3.2142 eV .This value is less than that of 3.3 eV reported in the literature (Berger et al. 1997). Band gap energy increases with decreasing particle size due to quantum size effects

Energy band gap of thin film prepared at 2000 rpm for 60 seconds in single stage mode will be 3.217 eV.
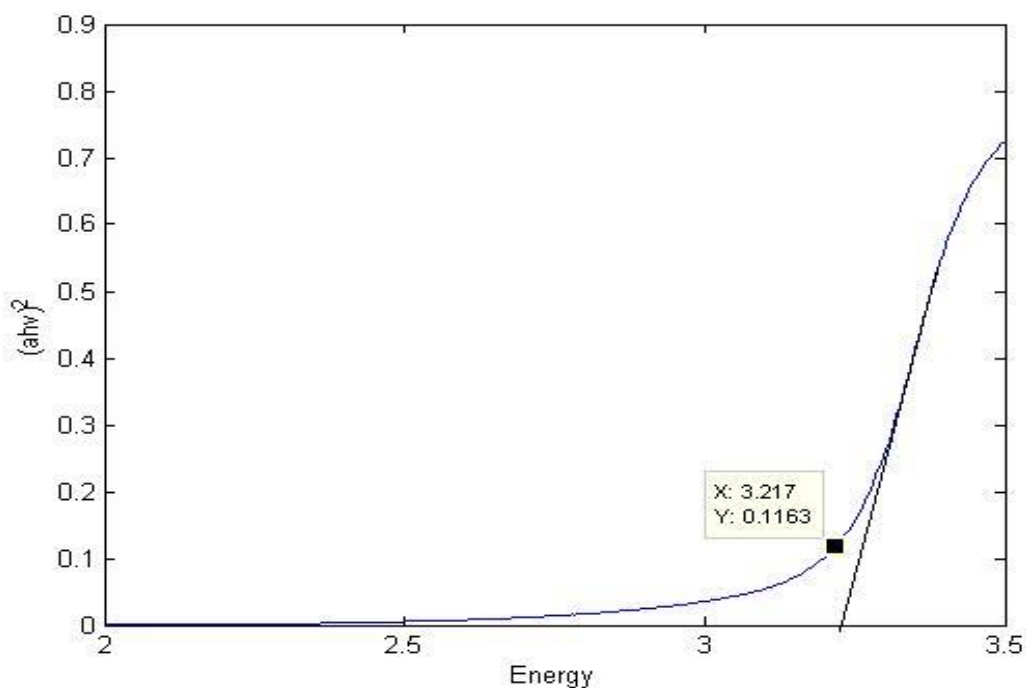
Energy band gap for ZnO thin film at 2000 rpm in single stage is 3.217 eV

Energy band gap of thin film prepared at 1000 rpm for 60 seconds in single stage mode will be 3.221 eV.
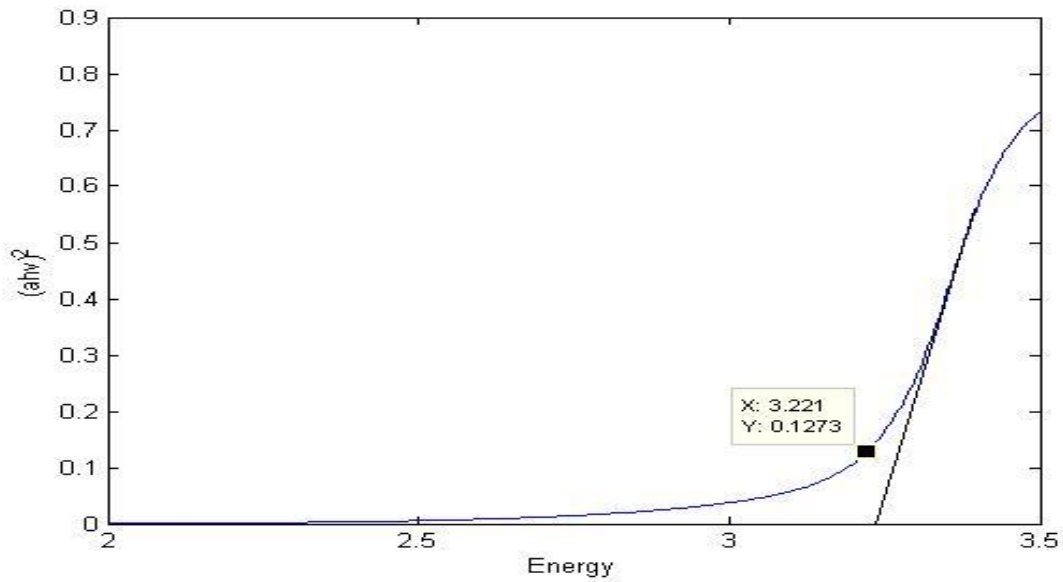
Energy band gap for ZnO thin film at 1000 rpm in single stage is 3.221 eV

Energy band gap of thin film prepared at 1500 rpm for 60 seconds in single stage mode will be 3.208 eV.

Energy band gap for ZnO thin film at 1500 rpm in single stage is 3.208 eV

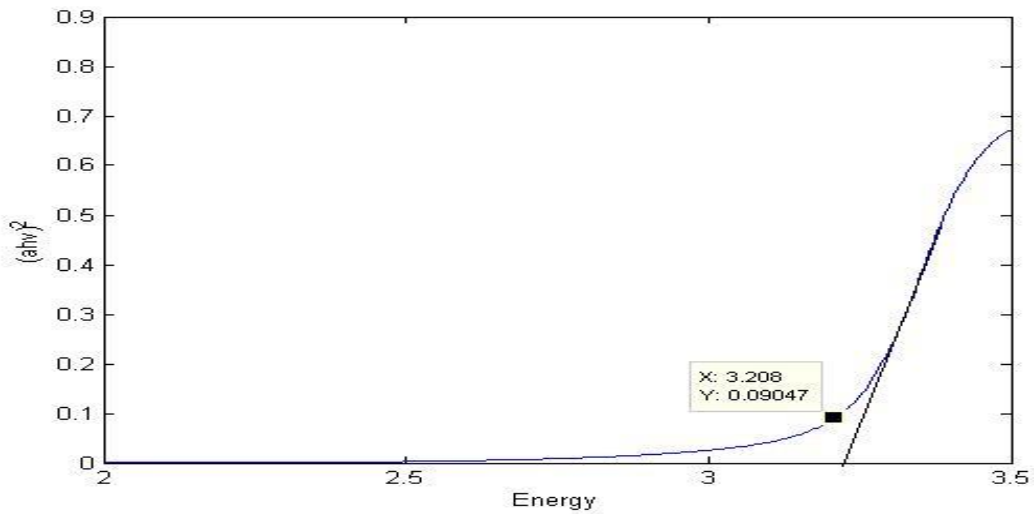Energy band gap of thin film prepared at 2500 rpm for 60 seconds in single stage mode will be 3.233 eV.

Energy band gap for ZnO thin film at 2500 rpm in single stage is 3.233 eV

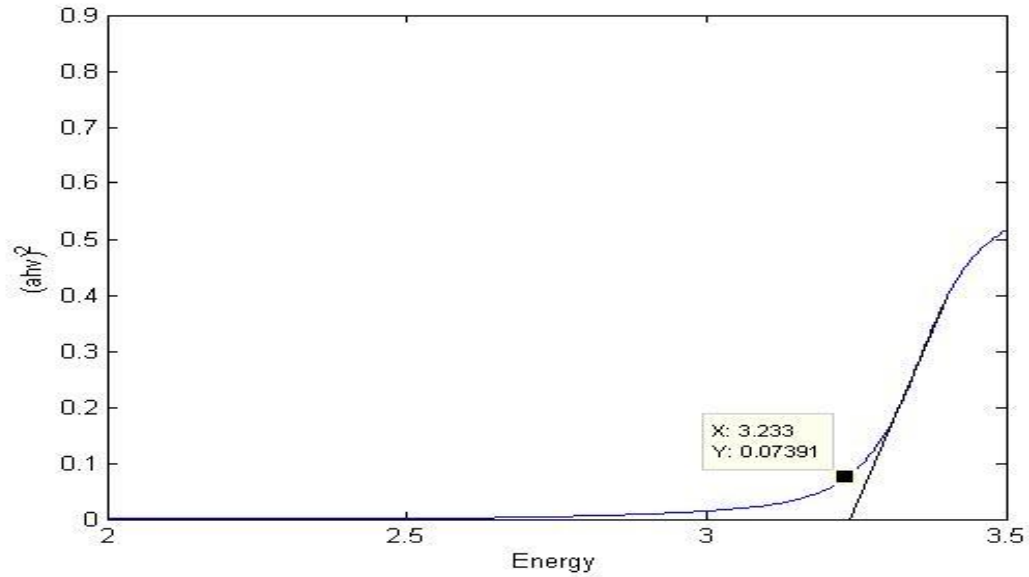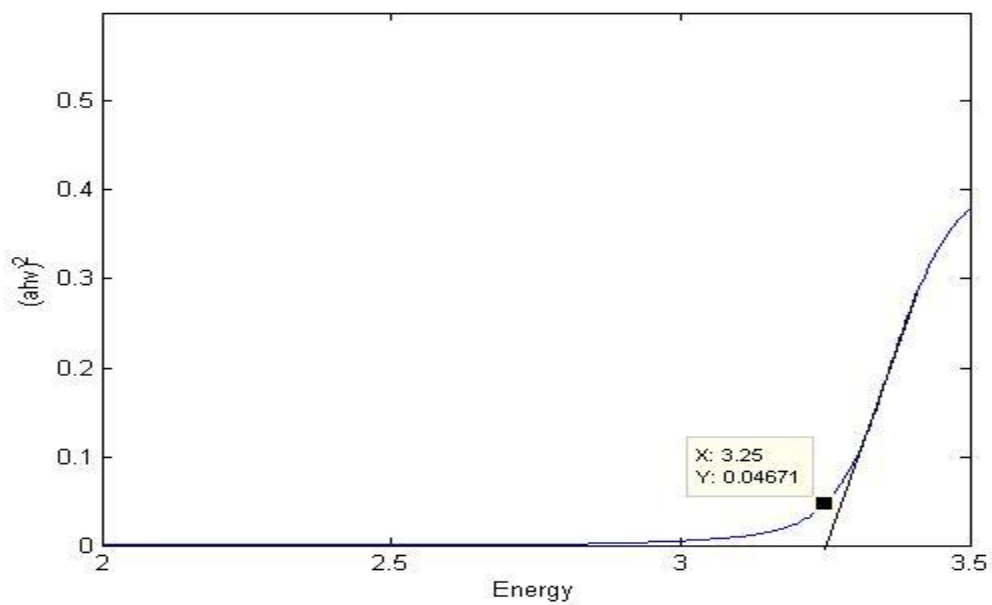Energy band gap of thin film prepared at 3000 rpm for 60 seconds in single stage mode will be 3.25 eV.

Energy band gap for ZnO thin film at 3000 rpm in single stage is 3.25 eV

Energy band gap of thin film prepared at 700 rpm for 60 seconds in single stage mode will be 3.196 eV.
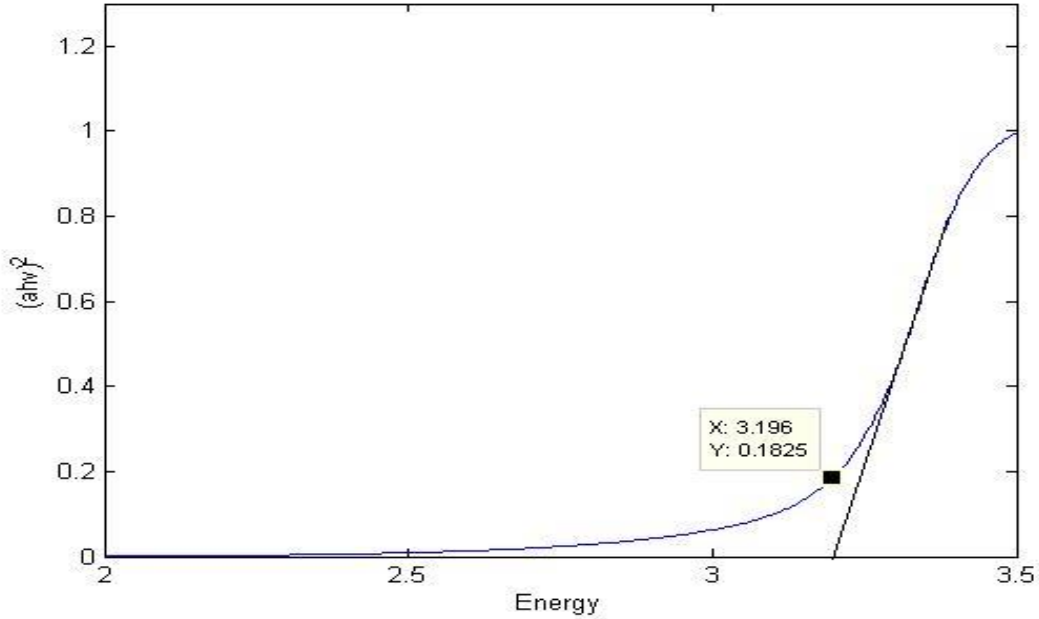
Energy band gap for ZnO thin film at 700 rpm in single stage is 3.196 eV

RPM	Mode	Time(Sec)	Energy Band Gap(eV)
700	Single	60	3.196
1000	Single	60	3.221
1500	Single	60	3.217
2000	Single	60	3.208
2500	Single	60	3.233
3000	Single	60	3.250

Table2.4.1 showing that variation in band gap energy with rpm.

2.4.2 Optical Profilometer Measurement:

Optical Profiler: are interference microscopes, and are used to measure height variations – such as surface roughness – on surfaces with great precision using the wavelength of light as the ruler. Looking at the figures, you might notice that the light and dark bands are not same all over the image. This is because the lower portion of the interferogram is going out of focus; out of focus means less interference. By carefully calculating the area of greatest contrast, optical profilometers determine the point that has best focus. It is going out focus because the thin film prepared by sol-gel method are not same in thickness, or thin films are not uniform.

In practice, an optical profiler scans the material vertically. As the material in the field of view passes through the focal plane, it creates interference. Each level of height in the test material reaches optimal focus (and therefore greatest interference and contrast) at a different time. With well-calibrated optical profilers, accuracy well below a nanometer is possible. A nanometer is ten Angstroms.
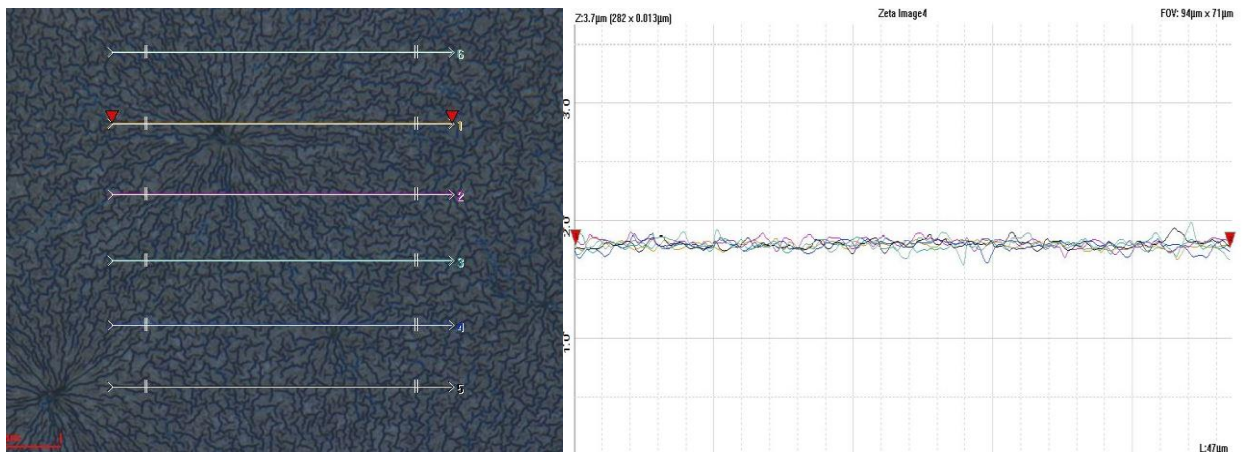
This images shows the roughness of the ZnO thin film at 2000 rpm.

From the image it shows that ZnO thin film prepared by sol – gel method at 2000 rpm, roughness varies from minimum 0.0289µm to maximum 0.0470µm. So the mean of roughness for ZnO thin film prepared by sol-gel method is 0.0365µm, standard deviation is 0.0057µm and Variance 15.7%.
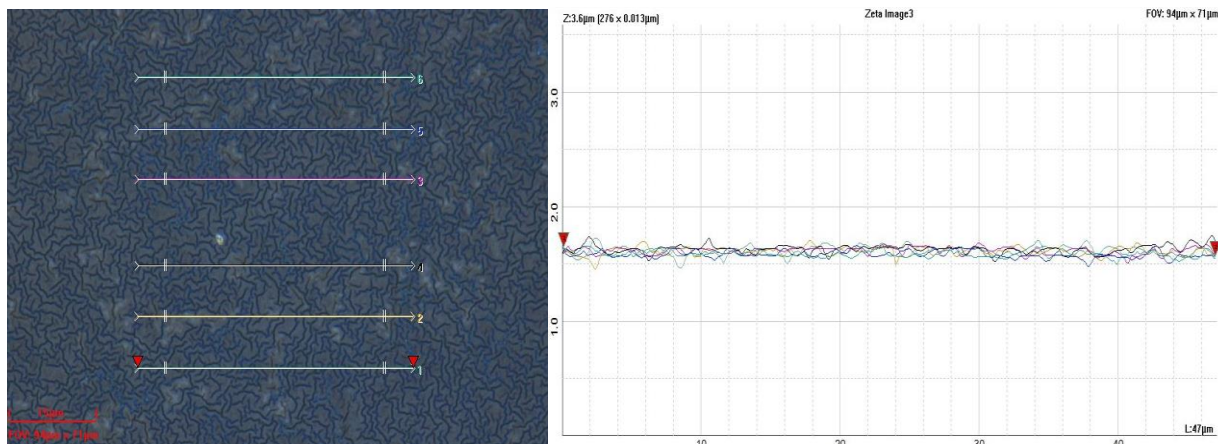
This images shows the roughness of the ZnO thin film at 1500 rpm.

From the image it shows that ZnO thin film prepared by sol – gel method at 1500 rpm, roughness varies from minimum 0.0295μm to maximum 0.0404μm. So the mean of roughness for ZnO thin film prepared by sol-gel method is 0.0337μm, standard deviation is 0.0039μm and Variance 11.7%.

RPM	Stage	Time	Roughness(μm)	Standered Deviation	Variance
700	Single	60	0.0694	0.0096	13.8%
1000	Single	60	0.0466	0.0037	7.96%
1500	Single	60	0.0337	0.0039	11.7%
2000	Single	60	0.0365	0.0057	15.7%
2500	Single	60	0.0762	0.0038	4.99%
3000	Single	60	0.0365	0.0044	12.1%

Table 2.4.2 showing that variation in roughness, SD, and variance with rpm.

2.4.3 Scanning Electron Microscopy:

A scanning electron microscope is a type of electron microscope that is used for observation of specimen surface. When the specimen is irradiated by the fine electron beam from the electron gun. These electron interacts with the atom of the sample and because of this interaction secondary electron are emitted from the specimen surface. These secondary electrons can be detected in the detector and topography image of the surface can be observed by two dimensional scanning of the electron probe over the surface. Scanning electron microscopy is used to measure the surface topography and morphology. The image shows that, the ZnO thin film prepared by sol – gel method at 2000 rpm contains uniform nanowires of dimension approximately 5µm.
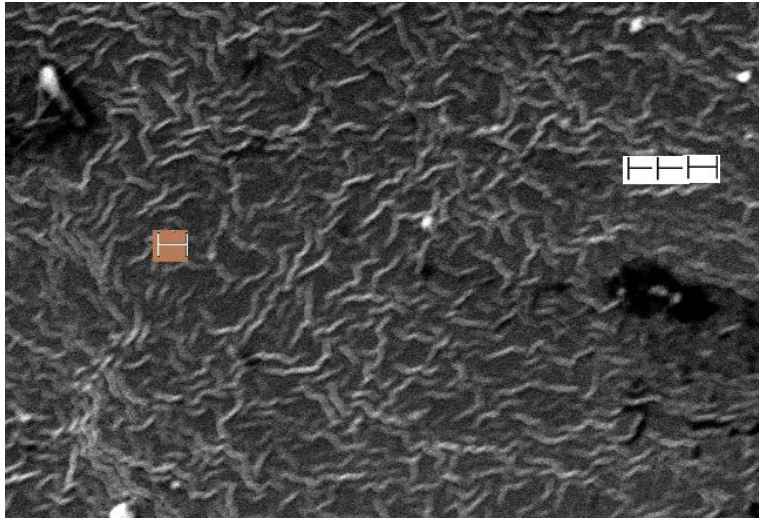
SEM Image of ZnO thin film prepared at 2000 rpm

Chapter - 3

3.1 Introduction and Motivation:

With constant progress in technology, the power requirement of mankind rises. Currently, fossil fuels are the main source of man-made energy on the earth. Heat is gained by burning these fossil fuels (coal, oil, natural gas), which not only produces atmosphere contamination but also contributes to global warming. This is an environmentally unfriendly energy source that will eventually be depleted. Energy can also be produced by nuclear power plants, which represent the most efficient kind of power production today. This production however generates radioactive by-products, which remain active for a significant period of time. The principle of gaining energy is often the same: heat is produced and converted afterwards into electricity by turbines and water steam.

An alternative to these approches is to use sun as an energy source. Solar energy is clean, nearly unlimited and the suns energy can be convertd directly into electricity without mechanical parts or noise pollution. The idea to producing electricity from solar energy is not new. For some years there have been stable and efficient solar cells on the market. Unfortunately the manufacturing costs of thin film solar cell components with high purity are too high, so that they still cannot complete with other energy sources on the present market.

Dye sensitized solar cell (DSSC) is a source solar power and intensely investigated at present. This solar cell, which was introduced by Grätzel and co-workers has a nanostructured TiO 2 /dye interface as its core. This system, which can be cheaply fabricated, has a big potential to become a low priced and non – toxic source of electric energy. The system is indeed very complex combining of organic and inorganic chemistry with surface science. Some of the important processes take place on microscopic level, where molecular and electonic characteristic of great importance. In DSSC, the dye molecule is responsible for absorption of light and should be senstive part of large visible solar spectrum. As semiconductor are used anatase TiO2 nanoparticle; as dye are used G1(anthracene derivative). We use photoluminiscence and absorption spectroscopy to determine the electron transfer from dye to TiO2. The highest occupied molecular orbital (HOMO) of the G1 dye is located near the middle of the semiconductor band gap and that the lowest unoccupied molecular orbital (LUMO) level overlap with TiO2 conduction band. The decrease in the peak of photoluminiscence of dye, indicate that the some of the electron transfer take place from dye to TiO2 molecule.

3.2 Dye G1 and Dye TiO₂ interface:

3.2.1 Dye: G1

In DSSC, the dye molecule is responsible for optical feature of the system – it facilitates absorption of light in solar spectrum. A good overlap of energy levels between the lowest unoccupied molecular orbital (LUMO) of the dye and conduction band of the semiconductor, as well as mixing of these energy leves, are important factors to initiate a fast electron transfer into the conduction band of the semiconductor. Electron transfer from the excited dye to the semiconductor should process as fast as possible to decrease the recombination rate with the corresponding hole.

Anthrance derivative of organic dye G1 which is provided by Dr. Giribabu from IICT. The optical properties of organic dye G1 is given by the highest occupied molecular orbit lies at energy 4.95 eV and lowest unoccupied molecular orbit lies at energy of 2.95 eV. And the band gap for the Dye: G1 molecule is 2.21 eV. Its structure shown in figure. The carboxyl group (COOH) is the anchor group, with which the molecule bind to a semiconductor surface.
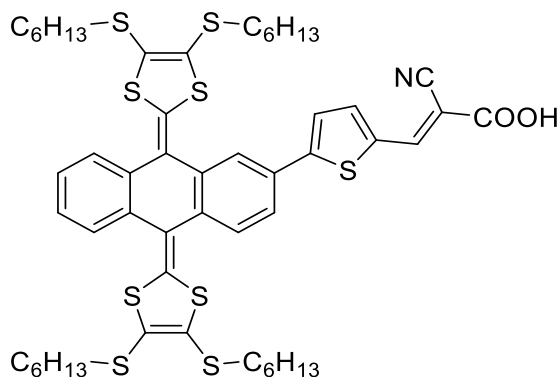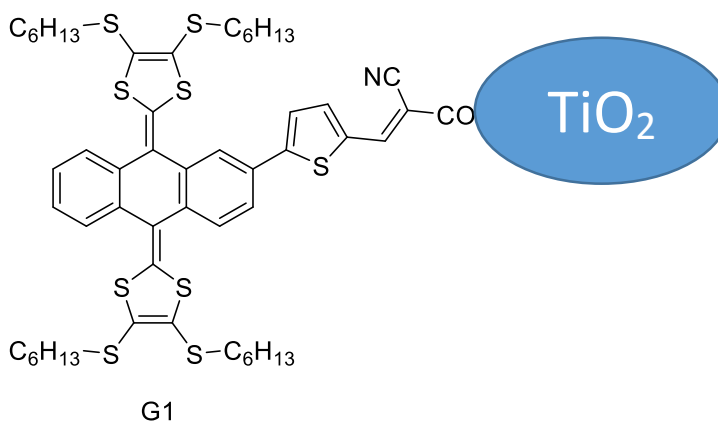

Structure of the G1 molecule

3.2.2 Preparation of TiO₂ and Dye G1 interface:

G1 and TiO₂ interface is prepared by mixing dye G1 and TiO2 paste in Toluene solution, the resulting solution is stirred at 580 rpm at 30°C for 3 hours.

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Bonding Configration:

G1 has carboxyl group that would be bind with TiO_2 either by moleular or dissociative adsorption. This lead the possible configuration by which G1 molecule might bind bond to TiO_2 surface. Several binding studies agrees that the mpst probable binding configuration is through one COOH group where the OH group is replaced by TiO_2 molecule as shown in figure.

Structure of the G1 and TiO₂ interface

The dye molecule is responsible for absortption of light. Antase TiO_2 nanoparticle hav ean optical band gap of 3.2 eV and can only absorbed light with wavelengths less than 340 nm. Since the optical band gap of G1 on TiO_2 is 2.21 eV , the G1 dye moleculeis able to absorb light in visible and near infrared spectrum and covers therefore emission peak of solar spectrum (561 nm, 2.21 eV).

As dye molecule absorbs a photon with an appropriate energy, an electron is excited from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). Since both of these possess a certain energy width,a continuously spectrum of photon energy can absorbed.

The absorption of photon leads to the existance of an electron - hole pair, which must be separated in order to produce current. The electron is transferred into the semiconductor and hole in the dye molecule is filled by donation of an electron from a negative ion of electrolyte solution. The alignment of the involved electric levels is here of great importance. The LUMO level muxt be located above the conduction band minimum for electron transfer into the

semiconductor to occur. The hybridization of molecular levels (in particular the LUMO) with the substrate can play an important role in electronic transfer. A LUMO that is highly delocailized over the substrate will allow a fast electron transfer from the dye to the substrate. The ioniztion potential of the electrolyte – redox pair has been located above the HOMO level of dye molecule, in order to refill the hole in the dye molecule by an electron of the electrolyte. The process electron – hole separation occurs for TiO_2 in a time scale on order of 50 fs and for ZnO in a typical time scale of 100 ps. The stronger binding and the faster electron from the G1 dye to TiO_2 in comparision to ZnO are possible reasons for better efficiency of TiO_2 – based over the ZnO – based solar cell. Efficient electron transfer to conduction band avoid recombination of electron with the hole, as well as an energy and voltage loss by relaxation to the bottom of the semiconductor conduction band.

Once electron leaves the dye molecule, the electron is not trapped on the surface and enters the bulk of TiO_2. While the electron diffuses through the bulk to the electrode, it relaxes to the bottom of conduction band which is thought to occur by vibration coupling. If electron return or remains trapped at the surface, it combine with the positive charge residing on the electrolyte mediator.

3.2.3 Limitations in The Arrangement of Energy Levels:

As maintioned earlier, the peak of emission of the sun light is at a wavelength of 561 nm (2.21 eV). The sun possesses a continuous spectrum of light from infrared to ultraviolet. The power output of an electrical device is defined in general as the product of current and voltage. The closed circuit current and open circuit voltage both are dependent on energy alignment of the HOMO and LUMO levels of dye.

The closed circuit current of solar cell is dependent on the intensity of the incoming light and the absorption spectrum of wavelengths is limited in a DSSC in higher wavelengths. In order to increase the current of a DSSC, the dye molecule should adsorb light with wavelengths up to 900 nm, which can be managed by a decreased by HOMO – LUMO gap. The HOMO – LUMO gap cannot be decreased arbitrarily since this energy gap is directly related to open circuit voltage of DSSC.

3.3 Experimental Setup:

3.3.1 Photoluminiscence Fluorimeter system:

The specrofuorimtere contains a 450 W xenon CW lamp as a steady state excitation source and a pulsed xenon lamp for phosphorimetry. The light path is directed to a double – grating monochromator where the slit size and wavelength are calibrated all the times. The sample

compartment is bifurcated to accommodate two monochromator/detector sets: one consists of a single grating monochromator attached to a fully automated iHR spectrometer with dual detection mode (250-1050 nm) and a single monochromator attached to a thermoelectrically cooled InGaAs NIR PMT module (950- 1400 nm). All detectors are operated in the single photon counting mode; the signals from the detector are then amplified and sent to a data acquisition system and a computer.
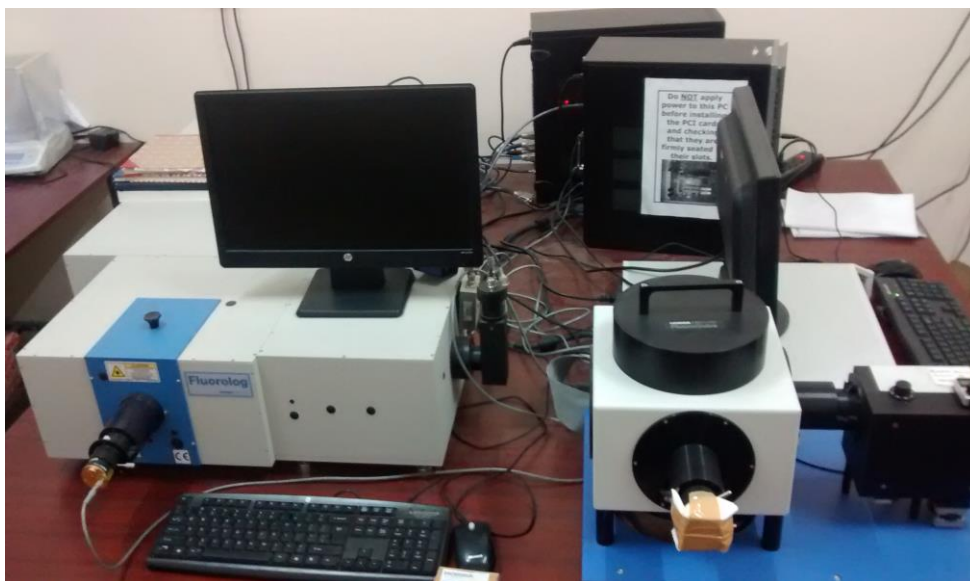

Image of experimental setup for emission spectrum

Sample Preparation:

The shape and intensity of fluorescence spectrum is highly dependent on the nature of the sample, its concentration, and solvent choice. Given that small particles within the solution induce light scattering, the scattered photon may find their way to detector introducing measurement errors. The fluorescence intensity is linearly dependent on the sample concentration over a limited range optical densities. The threshold concentration above which deviation from the linear behavior are observed depends on the chromophore. Finally, it is strongly recommended once an excitation wavelength has been chosen, a plot of optical density versus fluorescence intensity is generated in order to determine if the measurement is done in linear regime and that there is no reabsorption.

3.4 Result and Discussion

   In general dyes dissolve in monomers, dimers, trimers, etc. At low concentrations monomers dominate. With increasing concentration dimers and higher aggregates may gain importance. Each component (monomer, dimer, etc.) may have a different absorption behavior. At high concentration the constituting components (monomers, dimers, trimers, etc.) of the solution come near together (statistical random walk distribution of constitutes) and if two neighboring components are within an interaction volume the mutual solute-solute interaction changes the absorption behavior.

3.4.1 Absorption Spectrum:

The absorption spectra of G1 dye and dye G1 + TiO2 are recorded in the wavelength ranging from 300 – 800 nm. The absorption spectra of the G1 dye is shown in figure. The G1 dye show a broad absorption peak in visible region wavelength at 424 nm and in near UV region at 372 nm and it shows a very small bump in the absorption at wavelength 514nm. The absorbance of Dye + TiO2 solution increase and as shown in the figure, the peak near UV region at 372 nm is red shifted and absorption is more than the dye solution but absorption in visible region at wavelength 424 nm is same as that of the dye. The absorption of Dye + TiO2 is more in visible region at wavelength 514 nm. The figure shows that the absorbance of dye will increase as it mixed with TiO2 paste.
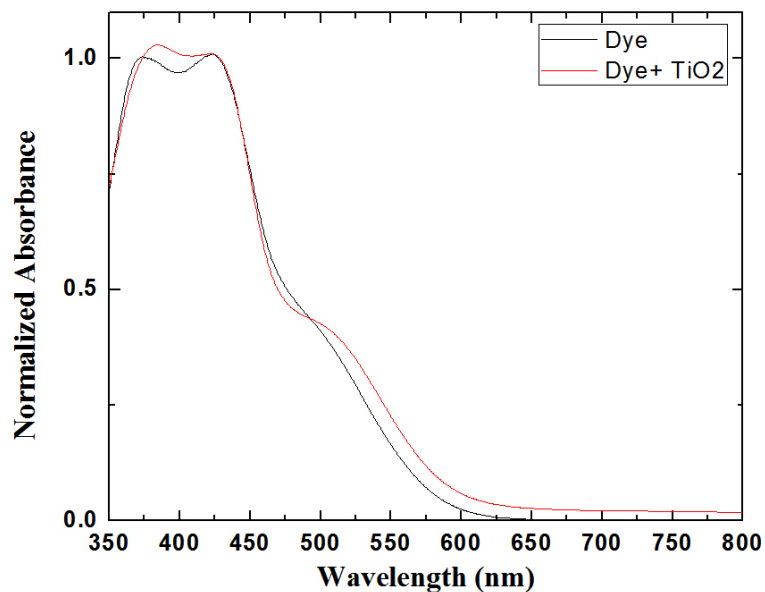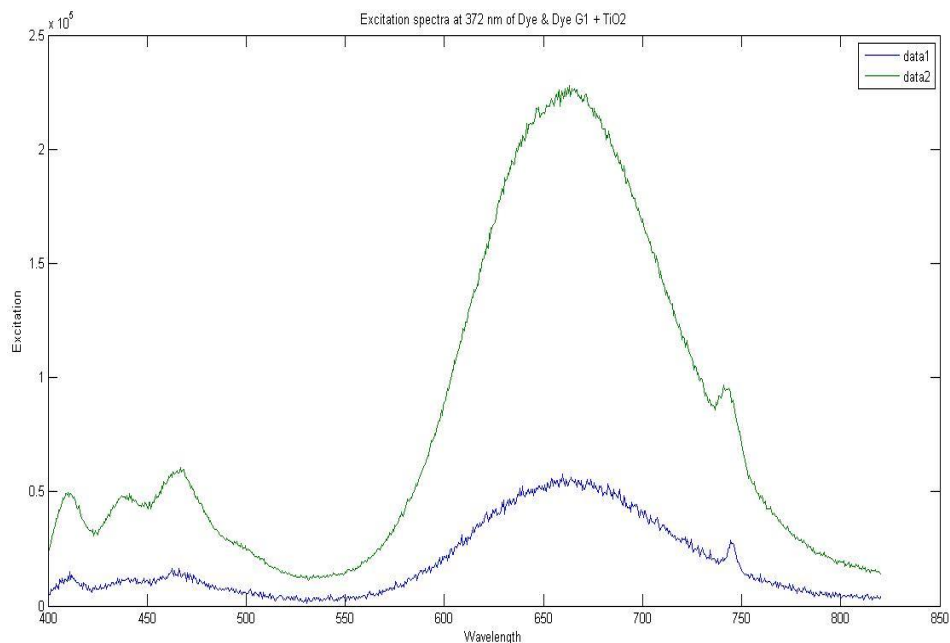
The figure show Absorption Spectrum of dye and dye + TiO$_2$ solution

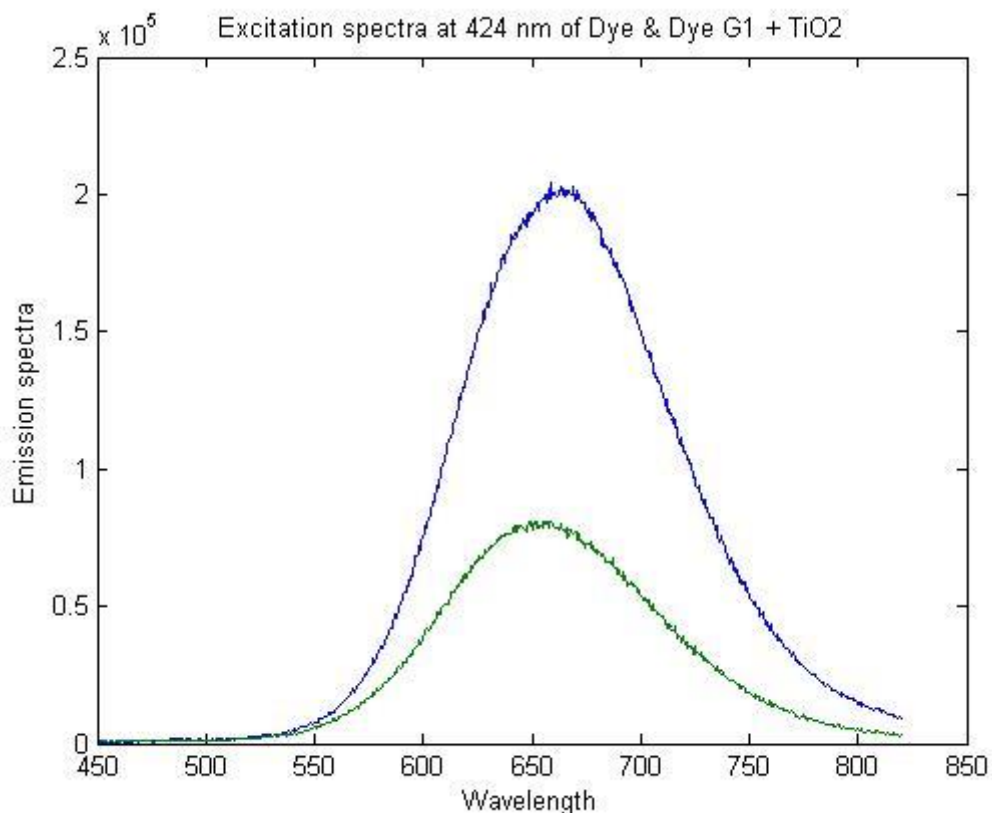## 3.4.2 Photoluminescence Spectra:

Excitation at 372nm:

The photoluminescence spectra of Dye G1 and Dye G1 + TiO$_2$ is shown in figure, obtain at an excitation wavelength of 372 nm. It shows that the peak will be at 664nm which is the characteristic peak of the Dye G1 molecule and one more peak will occur at wavelength of 745nm which is second order spectra of G1. When dye G1 + TiO$_2$ emission spectrum was taken, the peak at 664 nm will reduce from its maximum value as shown in figure (blue). It is mainly due to the electron transfer takes place from G1 to TiO$_2$ molecule.

The figure show emission spectrum of dye and dye + TiO$_2$ solution by excitation at 372 nm

Excitation at 424nm:

The photoluminescence spectra of Dye G1 and Dye G1 + TiO$_2$ is shown in figure, obtain at an excitation wavelength of 424 nm. It shows that the peak will be at 662nm which is the characteristic peak of the Dye G1 molecule. When dye G1 + TiO$_2$ emission spectrum was taken, the peak at 664 nm will reduce from its maximum value as shown in figure (blue). It is mainly due to the electron transfer takes place from G1 to TiO$_2$ molecule.
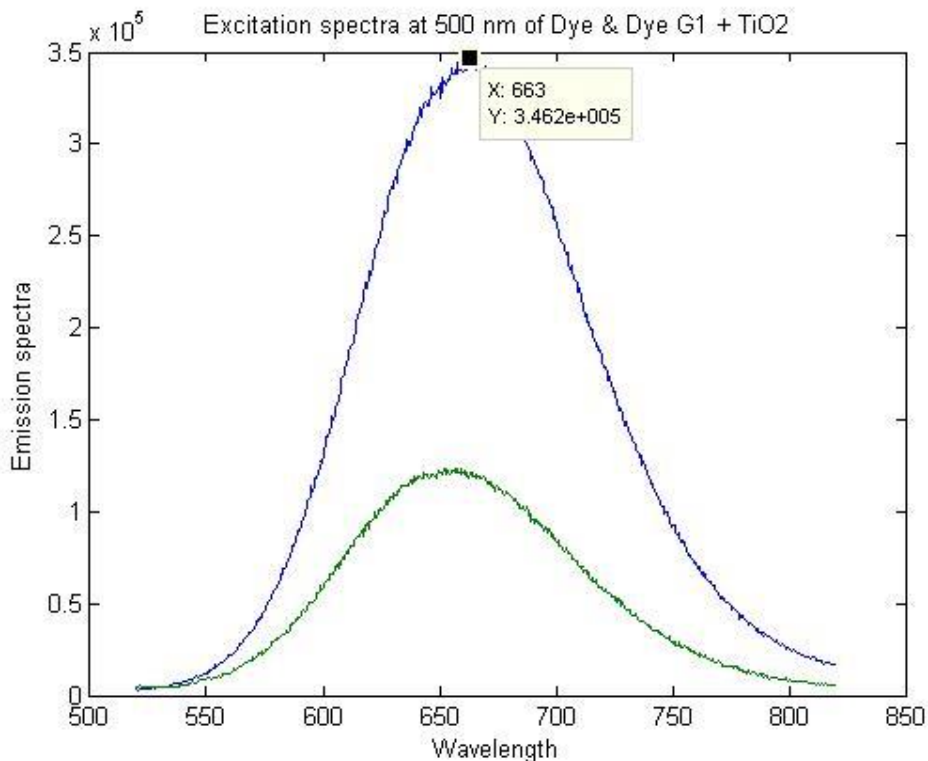
The figure show emission spectrum of dye and dye + TiO$_2$ solution by excitation at 424 nm

Excitation spectra at 500 nm:

The photoluminescence spectra of Dye G1 and Dye G1 + TiO$_2$ is shown in figure, obtain at an excitation wavelength of 500 nm. It shows that the peak will be at 664nm which is the characteristic peak of the Dye G1 molecule. When dye G1 + TiO$_2$ emission spectrum was taken, the peak at 663 nm will reduce from its maximum value and the peak will be shifted towards the

lower wavelength which is at 656 nm as shown in figure (blue). It is mainly due to the electron transfer takes place from G1 to TiO_2 molecule.

The figure show emission spectrum of dye and dye + TiO2 solution by excitation at 500 nm

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