Chapter 2: Synthesis, experimental and characterization

In this work, Zinc Oxide and Bismuth Vanadate has been synthesized via chemical route using hydrothermal method to form composites and photo anodes. After synthesizing the material, it is necessary to confirm its formation, which requires a combination of several characterization techniques. This chapter describes in detail the method used in the present study for the preaparation of Zinc Oxide and Bismuth Vanadate and subsequent formation of ZnO-$BiVO_4$ nanocomposite photocatalyst and photoanodes for PEC experimentation. First the experimental procedures of cleaning, growth and annealing process are discussed. This is followed by a discussion on the effect of synthesis parameters and conditions on the quality of prepared samples and with the characterization techniques used for analysis of samples.

2.1 Introduction

It is well known that ZnO and $BiVO_4$ exist in various forms of crystal structure. However, for the utilization of a material as an efficient photocatalyst or photoanode, it is important to have suitable crystal structure, as all are not efficient for this field of application [53,192]. ZnO exists in two main forms, hexagonal wurtzite and cubic zinc blende while $BiVO_4$ commonly appears in monoclinic or tetragonal phase. It is well studied and reported that hexagonal wurtzite-ZnO and monoclinic-$BiVO_4$ is best suited as photoactive materials as opposed to other existing crystal phases. Achieving monoclinic phase of $BiVO_4$ requires conversion from its initial amorphous phase to crystalline form through chemical route. Various methods have been reported in literature for the synthesis of these materials. Among these, hydrothermal synthesis using glass substrate and sol-gel method are the two main techniques suitable for synthesizing high quality, eco friendly and cost effective materials. However, growth of materials using sol gel method is unsuitable for crystalline form of ZnO and $BiVO_4$. On the other hand, hydrothermal synthesis is apt technique for crystallization of materials form high temperature. The ability to create crystalline phases of materials is one of the advantages of hydrothermal method [193]. The method is particularly preferable for the growth of large crystals with good quality and controlled composition. German geologist Karl Emil von Schafhäutl was the first to synthesize monoclinic-$BiVO_4$ by hydrothermal route. In hydrothermal synthesis of the material, the precursor solutions are poured into Teflon lined stainless steel autoclave so that they occupy 80% of volume of autoclave. The autoclave is then heated at certain temperature range for a set duration of time. After completion of the reaction, the reaction mixture is cooled to room temperature to obtain the precipitate. Precipitates are centrifuged and washed with DI water several times and dried to get the final product.

The quality and crystallinity of hydrothermally grown materials can be remarkably affected by the synthesis conditions; therefore, optimizations of favourable synthesis conditions are very pivotal [193]. Several attempts have been made to improve the crystal phase and structure of metal-oxides by understanding the correlation between its quality and the synthesis parameters. Therefore, influence of different growth environment conditions, such as, temperature, pressure, time duration, cooling rate, etc are being extensively investigated by researchers.

The main focus of this chapter is to present a comprehensive picture of the experimental procedure of ZnO, $BiVO_4$, ZnO/$BiVO_4$ nanocomposites/photo-anodes and effects of synthesis parameters on the quality of metal-oxide materials grown by hydrothermal method on glass substrate. The synthesis conditions for ZnO and $BiVO_4$ have been controlled and optimized by regulating the synthesis parameters of annealing temperatures of both the materials, synthesis temperature and duration. The physical mixing and milling effect for nanocomposite preparation was also studied and optimised by varying the milling time duration.

2.1.1 Hydrothermal Method

Hydrothermal method is an effective approach for the synthesis of single crystal nano-materials. It is an environment-friendly, low cost and simple method [148]. It involves crystallization of substances in aqueous solutions under high temperature and high vapour pressure condition. Temperature and pressure are important parameters for controlling the output of hydrothermal reaction [149]. Hydrothermal crystal growth is carried out in a Teflon lined steel pressure vessel autoclave. Necessary reagents required for chemical reaction are dissolved in water and transferred to autoclave. Autoclave is then heated at high temperature after tightly sealing it to avoid leakage of water vapours. Accumulated water vapours increase the pressure inside the chamber, thus this high temperature and high pressure condition results in the formation desired compound or material. Additionally, in a supercritical environment of high pressure, material or compound dissolution reduces and starts nucleating to form crystals; this process of nucleation is fast and results in the formation of nano-crystals with uniform shape and size.

2.1.1.1 Uses

1) Hydrothermal is widely used for the synthesis of large number of pure phase nano-crystal compounds like mono metal oxides, bi or complex metal oxides, elemental nano crystals, sulphides, tumgstates, silicates, nitrides etc.

2) Due to low cost involved in hydrothermal method many carbon allotropes or carbon related materials like fullerene [150], water soluble fullerene, multi-walled carbon nanotubes [151], graphitic carbon nitrides [152] etc which were earlier prepared by complex and high cost techniques are now being synthesized using hydrothermal approach.

3) Hydrothermal is also intensively used in the core shell and nano-composite material synthesis [153–155].

4) Also many research groups have used this method to effectively synthesize doped nano-materials [156,157].

2.1.1.2 Equipment for hydrothermal crystal growth

Autoclaves are steel cylinders with thick-walls with heavy metallic seal which must withstand high pressures and temperature for longer time periods. Autoclave's inner lining is usually composed of carbon free silver, copper, gold, titanium, platinum, glass (or quartz), or Teflon, depending on the solution and temperature used for experimentation. Inner lining should be non reactive so as to prevent its reaction with any kind of solvent used for reaction and should also protect outer steel autoclave from corroding. Teflon inner container may have the same shape as of autoclave inner cavity so that it can fit inside autoclave (contact or floating type insert). Due to the involvement of high pressure, design of the autoclave, closure is of utmost importance. Of many seal designs, Bridgman seal is the most preferred one as it can withstand high pressure up to 40,000 Mpa in comparison to other designs which can only withstand pressures up to 400 Mpa [158].

2.1.1.3 Advantages and disadvantages

Hydrothermal method has advantages of crystal growth over other methods which include:

- To create crystalline phases of materials which are not stable at melting points.
- Material having high vapour pressure at melting point can also be synthesized by this method.
- Better composition, phase and size control is obtained to form good quality crystals.
- Hydrothermal setup is economic and cost effective setup with low energy consumption.
- Provides heating path to avoid transition from meso phase to sub-stable phase.

Disadvantages:

- Inability to monitor crystals during the process of growth.
- Pressure and temperature below the critical point of the specific solvent can affect the growth of crystal.

- Hydrothermal cannot be used for all material synthesis as solubility of certain salts in water is very low. In that case instead of water organic solvents is used this process is called solvothermal method.

2.2 Experimental Procedure

2.2.1 Synthesis

2.2.1.1 Cleaning process

1. Cleaning of the autoclave

To clean Teflon container of autoclave, 50% mixture of sulphuric acid and nitric acid is poured to it up to top level. After keeping the container for almost 48 hours with acid solution in it, the solution is discharged and autoclave is washed thoroughly with de-ionized water. Then it is dried in oven at 60ºC for 4 hours.

2. Cleaning of the glass substrate

To clean the substrate, it is put in 50% mixture of propanol and acetone solution. Solution, with substrate in it, is then ultra-sonicated for around 4 hours to shake off or remove any kind of impurities or dirt from it. Then the substrate is taken out and dried with argon or nitrogen air to remove any liquid bubble.

2.2.2 Chemicals used in sample preparation

All the chemicals of analytical grade were purchased from Sigma Aldrich, India and were used in experimentation without any further purification. Table 2.1 gives the list of chemicals used in this study.

Table 2.1 List of specific chemicals used in the present study

Preparation/ Purpose	Chemical used	Molecular Formula	Physical State	Supplier (with purity)
ZnO	Zinc Acetate	$Zn(O_2CCH_3)_2(H_2O)_2$	Solid	Sigma Ald. 99.99 %
	Sodium Hydroxide	NaOH	Solid	CDH 97%
	SDBS	$C_{12}H_{25}C_6H_4SO_3Na$	Solid	Fisher >=99%
	Monoethanolamine	C_2H_7NO	Liquid	Fisher 99%
	Methoxyethanol	$C_3H_8O_2$	Liquid	Fisher 99+%
	Hexamethylenetetramine	$C_6H_{12}N_4$	Solid	CDH 99%
$BiVO_4$	Bismuth(III) nitrate pentahydrate	$Bi(NO_3)_3 \cdot 5H_2O$	Solid	CDH 98%
	Ammonium Metavanadate	NH_4VO_3	Solid	Sigma Ald. 99.9%
	Nitric Acid	HNO_3	Liquid	Fisher 30% Vol.
	Sodium Hydroxide	NaOH	Soild	CDH 97%

2.2.3 Preparation of nanostructured materials/powder for photocatalysis

2.2.3.1 Preparation of bulk ZnO and ZnO nanosheets

To prepare bulk ZnO, 10 mM (2 gms) of $Zn(O_2CCH_3)_2(H_2O)_2$ was dissolved in 50ml of DI water and 20 mM (0.78 gms) of NaOH was dissolved in another 50 ml of DI water to form white ZnO solution. Then, 2 gm of Sodium Dodecyl Benzene Sulphonate (SDBS) was added to obtain ZnO solution followed by rigorous magnetic stirring for 1 h. Then the mixture solution was poured into 100ml Teflon lined stainless steel autoclave to occupy upto 80% of its volume. The autoclave was heated at 200ºC for 6 hours. After completion of the reaction, the reaction mixture was cooled to room temperature to obtain pure white ZnO precipitate. Precipitate was centrifuged and washed with DI water several times and was dried at 60ºC for 24 hours.

2.2.3.2 Preparation of bulk $BiVO_4$ and $BiVO_4$ nanoparticles

Similarly, bulk $BiVO_4$ was prepared by mixing 6 mM of bismuth and ammonium salt in 50 ml of HNO_3 (2.4 molar) and NaOH (1.9 molar) solution separately, respectively, to form amorphous $BiVO_4$ solution of yellow colour. Then 1 g of surfactant (SDBS) was added to obtained solution and kept for stirring for 1h followed by hydrothermal treatment at 200°C for 4 hrs. Final reaction mixture was allowed to cool at room temperature. Final precipitate was centrifuged and washed with De-ionized water up to 5 times which was then dried at 60º C for about 24 hrs to obtain cystalline bright yellow $BiVO_4$ powder.

2.2.3.3 Preparation of ZnO/$BiVO_4$ photocatalyst

For nanocomposite synthesis, both the materials were taken as synthesized and mixed in 1:1, 1:2 and 2:1 weight ratios. The mixtures were mixed in mortar pestle until homogenous composition was obtained. They were then kept for annealing in the programmable furnace at 450°C for one hour and allowed to cool at room temperature.

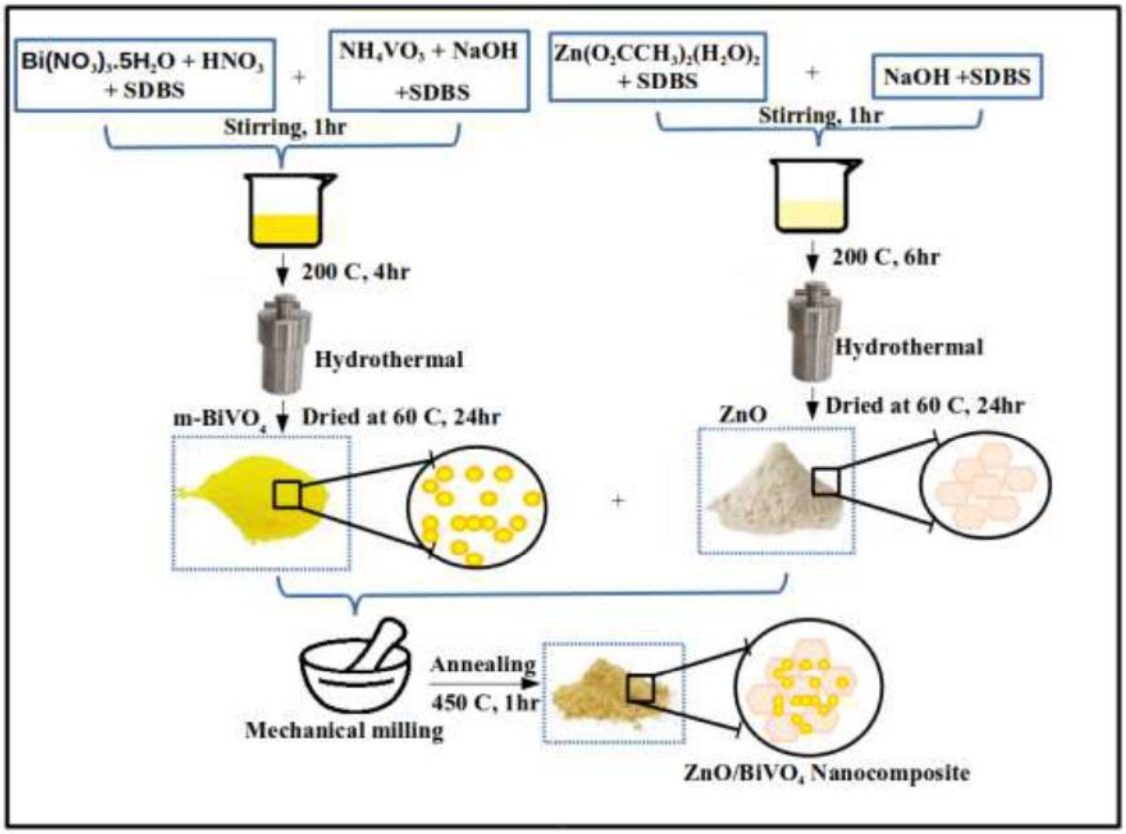

Figure 2.1 Schematic showing preparation of ZnO-$BiVO_4$ nanocomposite

2.2.4 Preparation of photoanodes for PEC

Dual layer $BiVO_4$/ZnO photoanode formation was done in two sequential steps (i) formation of hexagonal ZnO structures on ITO substrates followed by (ii) post deposition of monoclinic scheelite structures of $BiVO_4$ on ZnO. Initially, ZnO seed layer was deposited on ITO glass by dip coating the solution of ZnO nanoparticles obtained by continuous stirring (1h, 60ºC) of 0.22g of Zinc Acetate Dihydrate {$Zn(CH_3COO)_2.2H_2O$}, 0.61 ml of Monoethanolamine (MEA) and 10 ml of Methoxyethanol. The seed layer was dried at 100°C for 3 h. The hexagonal wurtzite structured ZnO was formed on these seed layers using hydrothermal process. The seed layer coated ITO substrates were dipped for 6 h at 90°C in a hydrothermal autoclave that consists a solution made up of 1.1 g Zinc acetatedihydrate {$Zn(CH_3COO)_2.2H_2O$}, 0.7g hexamethylenetetramine (HMTA) and 50 ml of DI water. The prepared samples were washed with DI water to remove the extra ZnO. In order to prepare, $BiVO_4$/ZnO photo anode, the $BiVO_4$ was prepared by co-precipitation {4.85 g of Bismuth

(III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) in 1.17g of Ammonium metavanadate (NH_4VO_3) and 200 ml DI water}technique and then were coated over the hexagonal wurtzite structured ZnO by dip-coating process. The samples were dried overnight in hot air oven at 100°C. Three sets of $BiVO_4$/ZnO photoanode samples were prepared with varying $BiVO_4$ concentration designated as B1 (0.038M $BiVO_4$/ZnO), B2 (0.05M $BiVO_4$/ZnO) and B3 (0.1M $BiVO_4$/ZnO). All measurements were compared with bare ZnO photoanode.

2.3 Variation in the synthesis conditions

In the hydrothermal system, synthesis temperature, synthesis duration, milling process and annealing treatment are the important parameters which can affect the quality of synthesised materials.

2.3.1. Growth temperature

Temperature is one of the important parameter in hydrothermal method that greatly influences the morphology, crystallinity and the crystal phase of the material being synthesised. For ex: it is well reported that pure monoclinic phase of $BiVO_4$ is only obtained at high temperature of 200ºC as also observed in our study. Below 200ºC, phase impurity is observed. Similarly, in the case of zinc oxide it was observed that below 200ºC, with SDBS surfactant hexagonal sheets of ZnO were made. Various morphological changes in ZnO with change in temperature in hydrothermal is well documented.

2.3.2. Effect of mechanical milling

The mechanical milling process not only breaks down the larger particles in smaller size but also introduces the surface defects which greatly affect the chemical and physical properties of the material. In our study of ZnO/$BiVO_4$ composite we documented increased surface defects in ZnO nanosheets leading to the formation of dangling bonds on the surface which resulted in weak bond of interaction with $BiVO_4$ and it resulted in formation of intermediate band in nanocomposite. We also observed smaller $BiVO_4$ size in the milled samples which increased the available surface to volume ratio thus enhancing the surface area available for photoreactions to increase.

2.3.5. Effect of annealing treatment

Just contrary to milling process, high temperature annealing tends to reduce the surface defects in metal oxides by enabling the bonding of metal dangling bonds with environmental oxygen. In case of heterostructures, annealing aids in formation of strong bond of interaction between the two or more materials at the interface. In our case of ZnO/$BiVO_4$ annealing process strengthen the bond between $BiVO_4$ and ZnO thus facilitating the charge exchange at the interface which is beneficial for reducing the recombination rate in the nanocomposites. Weak bonds formed during milling process are strengthened by annealing.

2.4 Characterization

2.4.1 Photocatalyst powder

The crystal structure of pure $BiVO_4$, pure ZnO and ZnO-$BiVO_4$ (1:1) nanocomposite were determined by powder X-ray diffraction (Rigaku, D2-Phaser). The X-ray diffractogram were recorded in the range of $2\theta=10$ to 80° using Cu Kα radiation ($\lambda=0.15406$ nm) with a scan rate of 1°/min. The sample morphologies were studied using transmission electron microscopy (TEM) (FEI Technai G2 200kV). Elemental analysis of nanocomposite was confirmed by Energy Dispersive spectroscopy (EDAX detector in TEM). UV absorption spectra were recorded by Perkin-Elmer lambda 35 UV-Visible spectrometer having wavelength between 200-800 nm. The Photoluminescence emission spectra were obtained using HORIBA LabRAM HR Evolution at the excitation wavelength of 325 nm. The spectrum was recorded from 350-800 nm. Time-correlated single photon counting (TCSPC) using Edinburgh Instruments FLSP920 was used to collect luminescence life-time decays. A 377 nm pulsed laser diode with a 500 kHz pulse repetition rate was used for the lifetime measurements. PL peak maximum for each sample was used to collect their PL emission decay. XPS measurements were performed using electron energy analyser (Specs GmbH, Germany, Model: PHOIBOS 150) and a non-monochromatic Al Kα X-ray source ($h\upsilon=1486.61$ eV) with the base pressure of $<1 \times 10^{-9}$ mbar.

2.4.2 PEC photo anode

The morphologies of the photo anode were examined using Scanning Electron Microscopy (SEM) using a Zeiss microscope at an accelerating voltage of 5-15V. The purity and crystal structure of the samples were examined through powder X-ray diffraction (Philips X'Pert PRO-PW 3040, l = 1.5418 Å, Ni-filtered Cu Ka radiation). Samples have been scanned from range of 20 to 80º glancing angle was used to scan the samples. Shimadzu UV 2600 was used to obtain UV-visible spectrum in the diffuse reflectance mode (R) from which magnitude proportional to the extinction coefficient (K) through the Kubelka–Munk function, F(R∞) was calculated. $BaSO_4$ was used as a standard as it does not absorb UV-visible range of radiation (white standard). Scans range was 250-800 nm with step size of 0.5 nm.

2.5 Computational method for ZnO/$BiVO_4$ nanocomposite

Openmx package was used to perform DFT calculations within local atomic orbital (LCAO) approach. For exchange–correlation function, generalized gradient approximation (GGA) proposed by Perdew–Burke–Ernzerhof (PBE) was used. Soft pseudo potentials were used for Bi, Zn, O and V to describe interaction between valence electron and ionic cores. In heterojunction, vacuum spacing of 15Å was used between the layer of ZnO (101) and $BiVO_4$ lattice to avoid strong bond interaction between them. Therefore, PBE-D2 with van der waals (vdw) correction was used to describe the long range interaction between them. Cut-off energy was set to 520 eV for heterojunction and 400 eV for pristine structures. BFGS algorithm was used for geometrical optimization of 8X8X8 K-grid to reduce the system energy and forces upto 10-6 eV and 0.01 eV/Å respectively. Band dispersion and Density of states were calculated after geometrical optimization.

2.6 Transmission electron microscopy (TEM)

Transmission Electron Microscopy is a vital and powerful tool of characterization for directly imaging nanomaterials to obtain quantitative measures of particle and/or grain size, morphology, quality and size distribution. It operates on the same basic principles of light microscope but uses electrons instead of light. Because of the much smaller wavelength of electrons than that of light, the optimal resolution attainable for TEM images is many orders of magnitude (by a factor of 1000!) better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure such as the crystal structure and features like dislocations and grain boundaries and in some cases as small as individual atoms. In this study, we use a FEI Technai G2 transmission electron microscope operating at an accelerating voltage of 200 kV with bottom mounted GATAN camera. Images from the camera which were in dm3 format were saved as TIFF files of high resolution, and image processing GATAN software packages were used for morphology analysis, image processing like fast Fourier transform (FFT) of image, inverse-FFT of image, particle size analysis etc. Energy Dispersive spectroscopy (EDAX detector from Ametek Inc. in TEM) was used to confirm the Elemental analysis of nanocomposite. Variations in phase and amplitude of the transmitted beam provides a imaging contrast that is a function of the sample thickness and sample material which determines the amount of light to be passed through it. Therefore this becomes a useful technique to distinguish between various mixed samples or nano composites, as in our case. ZnO nanosheets being very thin appeared lighter than $BiVO_4$ particles with higher thickness in $ZnO/BiVO_4$ nanocomposite samples.

2.6.1 Specimen preparation

Specimen preparation is a vital aspect for TEM analysis. To form an image with minimum energy loss, it is required that a TEM specimen must be thin enough to transmit sufficient electrons and thus should be transparent to beam of electrons. Utmost care is necessary while preparing and handling samples as they may be prone to breaking and bending due to being extremely thin. Copper grid coated with thin layer of carbon is used for preparing samples. Different preparation technique follows for different class of materials. Sequence for preparation techniques involves ultrasonic disk cutting, dimpling, and ion-milling. Dimpling is a process that creates a specimen which has a thin central area with sufficiently thick outer rim that allows easy handling of specimen. The last process for the specimen preparation is ion milling, wherein the surface specimen strikes with charged argon ions accelerated by the application of high voltage.

2.7 X-ray diffraction technique (XRD)

X-ray diffraction is a common technique primarily used to investigate crystal structure including atomic arrangement, crystallite size and phase purity or imperfections of the samples. XRD is useful as it is a non-destructive technique, provides quantitative measurement of phase and texture orientation with minimal or no sample preparation requirements at ambient conditions for all analysis. Here, in this study ZnO and $BiVO_4$ samples have been studied using Rigaku, D2-Phaser model of XRD. Most commonly used target material for single-crystal diffraction is copper with CuK_α radiation = 1.5418Å. These X-rays are gathered and focussed on the sample. As the detector and sample are rotated, the intensity of the reflected X-rays is recorded. When the incident X-rays hitting the sample fulfils the Bragg Equation, peak in the intensity occurs due to formation of constructive interference. X-ray diffractometer is placed in the system such that the sample rotates in the path of X-ray beam at an angle θ. The detected X-ray signals are collected by X-ray detector mounted on an arm and rotating at an angle of 2θ. The recorded data is processed to give useful information as output. Commonly, for powder samples 2θ ranges from ~5° to 80° angles.

X-ray study in this study has been primarily carried out to measure-

1. Identification of crystal phase of ZnO and $BiVO_4$ by measuring their respective lattice parameters
2. Determination of change in crystallinity by calculating FWHM values.
3. Measurement of average crystallite size, strain, or micro-strain effects in bulk materials and thin-film
4. Identification of formation of any new planes in nanocomposite material.

The miller indices of the peak were matched from the standard JCPDS database.

2.8 X-ray photoelectron spectroscopy (XPS)

In the field of spectroscopy, the XPS technique is used to analyze the state of the material. A material has electronic & chemical states which can be analyzed with a concentration level of parts per thousand ranges. XPS is utilized widely for surface chemistry analysis. At some certain pressure conditions x-ray beams generate the XPS spectra and along with this any activity in metal surfaced can be observed. After any changes to the state of the material, XPS analysis explains the surface chemistry of the sample. Changes to the sample can be exposure to heat, gases, ultra violet light and ion beam itching etc. However, the best conditions to analyze the sample by X-ray photoelectron spectroscopy is still under the area of research. For the samples in present study, XPS measurements were performed using electron energy analyzer (Specs GmbH, Germany, Model: PHOIBOS 150) and a non-monochromatic Al Kα X-ray source (hv=1486.61 eV) with the base pressure of <1 X 10^{-9} mbar.

Since the material of study is a composite, it's important to understand the kind of interaction between the two constituents of the nanocomposite. Further, XPS was obtained to analyze the surface chemical composition and oxidation state of ZnO-$BiVO_4$ nanocomposite. Generally any XPS spectrum has a plot between electrons detected and their binding energy. XPS analysis starts with a survey scan spectrum of the sample. Based upon this analysis a table can be prepared of all the elements present in sample with their specifications and characteristics observed during analysis. By analyzing the binding energy the existence of each element can be observed. These peaks in plot are according to the configuration of electrons. Presence of element in sample depends upon the number of the electrons in individual peak. So this analysis can be used to find out the atomic percentage excluding hydrogen since H_2 cannot be detected. There are possibilities of errors during the electron counting because there is a specific distance between XPS instrument and material under x-rays. So low pressure conditions are required for electron counting and pressure level can be ultra-high vacuum.

2.9 Photoluminescence spectroscopy

This spectroscopy has an important role to find out the light emission patterns and analysis of semiconductors. When matter absorbs the photons out of the radiations then it emits the light which is known as the photoluminescence. There are many types of light emissions which can be done by exciting the photons. Emission intensity and time period of emission after the absorption can be different based upon the material semiconductor. This light emission can be observed at peak level with particular amount of energy. This can be related with transition energy and excited state which can reveal a number of useful information about the sample. Photoluminescence emission spectra are obtained using HORIBA LabRAM HR Evolution at the excitation wavelength of 325 nm primarily to study the following.

1. Formation of intermediate band

Formation of intermediate band is detected by appearance of new peak or broadening of peak in PL spectra. Intermediate defect bands are quite common in ZnO and they appear as broadening of near band edge emission peak in PL spectrum. In our sample formation of intermediate band in ZnO due to valence band of $BiVO_4$ was confirmed by PL study.

2. Detection of defects and impurity

Defects can be there in semiconductors during detected through radiative transitions. The PL energy with these localized defects can help to find out the defects as well as their concentration. Low concentration of the impurity can also be identified by high sensitive Fourier transform of photoluminescence micro spectroscopy. These low concentration impurities affects the performance of the device.

3. Recombination mechanisms

Recombination includes two processes of radiative and non-radiative and the rate of recombination of these both processes determines the intensity of emitted PL. Recombination process depends upon the non-radiative rates (related with impurities), photon excitation and temperature. So PL determines the quality and recombination mechanism.

4. Analysis of surface chemistry

PL spectroscopy is very sensitive to analyze the surface chemistry of electron-hole surface processes. Traditional methods like Raman spectroscopy cannot be sensitive with low metal oxide concentrations. Although PL can find the optical centers with low concentrations but this is not a quantitative result oriented rather a qualitative approach. Also there are many excited states of optical centers but with low population at low temperature. One more limitation of this spectroscopy is that the luminescence signal disappears gradually.

2.9.1 Time-resolved photo-luminescence (TRPL)

The photoluminescence spectrum of the material is a direct representation of the dynamics of charge carriers. The technique of time-resolved photo-luminescence via time-correlated single photon counting (TCSPC) is highly suitable for fast monitoring of the charge carrier dynamics at the level of the nanoseconds with precise accuracy. Without any special sample preparation, it is possible to examine any kind of thin film, solid powder and liquid in this instrument. Time-correlated single photon counting (TCSPC) using Edinburgh Instruments FLSP920 was used to collect luminescence life-time decays. The spectrum was recorded from 350-800 nm which depicts the intensity of the optical response of the sample as a function of time (vertical axis) and the wavelength (horizontal axis).

The short pulse of light, used to illuminate the sample, creates electron and hole pairs which subsequently recombine and emits light. The emitted light is a measure of transition energies of the sample corresponding to the set of wavelengths. The optical spectrum measurement as a function of time provides a means to measure their lifetimes and the transition energies. Decay times in the order of nanoseconds and picoseconds can be measured. This analysis of charge carriers lifetimes and decay times becomes very useful in cases where availability of charge carriers play a major role. In the field of photocatalysis applications, separation of electron-hole pairs for longer durations is required while recombination is avoidable. The average lifetimes of carriers gives a useful estimation of performance of materials photoactivity.

In our ZnO-BiVO$_4$ nano-composite sample were excited by 325 nm laser with energy larger than the band gap energy of both the samples in composites. Electrons flows from the valence band of BiVO$_4$ to the conduction band some electrons recombine with holes to produce emission. The peak is formed in normal PL with the center at the wavelength of emission. Intensity of PL peak of emission is directly related to number of recombination taking place. So from PL intensity we can have qualitative information about the recombination rate of charge carrier to have quantitative information about recombination rate we did time resolved PL of the samples. TRPL Plot between PL intensity Vs time gives the accurate measure of life time of charge carrier before recombination. This information provided by TRPL helped us understand the mechanism behind improved photocatalytic activity of our samples i.e. reduction of recombination rate of charge carrier through interface formation between ZnO and BiVO$_{4.}$

2.10 Scanning Electron Microscope (SEM)

SEM is a microscope that generates an image in a similar way as an optical microscope. Difference lies in the source of energy that is utilized to create an image. Optical microscope uses visible light, while SEM uses focused beam of high energy electrons to generate an image. As electrons have very small wavelength (0.55 nm at 5 keV), SEM has high resolution capacity with magnification up to 500 times yielding morphological details of less than 5 nm. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes SEM one of the most useful instruments in materials research today. Electron gun generates a beam of electrons and accelerates it towards to the anode which is focussed to a fine spot using scanning coil and magnetic lens. The interaction of the sample surface and incident electrons generates a SEM image with the help of signal produced. The beam of electrons basically scans the surface of the material to gather the information, unlike in the case of transmission electron microscopy wherein the beam of electrons passes through or penetrate through the sample rather just scanning it.

A variety of signals such as secondary electrons, Auger electrons and backscattered electrons may be produced that carries different forms of sample information. Secondary electrons are produced with energies < 50 eV, Auger electrons are produced by the decay of excited atoms, and backscattered electrons possesses energies close to those of the incident electrons. All these signals can be used to generate diffraction patterns or images of the sample and can be analyzed to retrieve spectroscopic information. The characteristic and continuous X-rays as well as visible light can also be produced by de-excitation of sample atoms that are excited by the incident electrons. These signals can be utilized to provide quantitative or qualitative elemental information of the sample. SEM uses secondary electrons to generate an image. The generated signals depend on the incident electrons energy (ranging from 0.2 to 40 KeV). We carried SEM imaging of the ZnO-$BiVO_4$ samples to determine the surface morphology and distribution of $BiVO_4$ particles on the ZnO surface.