

**“Fe-Ni-Co-S BASED NANOCOMPOSITE FOR
PHOTOCATALYTIC APPLICATION”**

**Submitted in partial fulfilment of the requirements for the
award of Master of Science in CHEMISTRY**

By

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DEPARTMENT OF CHEMISTRY

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade “A” by NAAC

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **Mr. MANIKANDAN D (40910014)** who carried out the project entitled "**Fe-Ni-Co-S BASED NANOCOMPOSITE FOR PHOTOCATALYTIC APPLICATION**" under my / our supervision.

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DECLARATION

I **Mr. MANIKANDAN D** student of **SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY** hereby declare that the Project Report entitled **Fe-Ni-Co-S based nanocomposite for photocatalytic application** done by me under the guidance of **Dr. S.SUNITHA, M.Sc., M.Phil., Ph.D.** and **Dr. G.MURUGADOSS, M.Sc., Ph.D. Scientist-E** at **International Research Centre, Sathyabama Institute of Science and Technology, Chennai** is submitted in partial fulfillment of the requirements for the award of **Master of Science degree in CHEMISTRY**.

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MANIKANDAN D

ABSTRACT

Fe-Ni-Co-S nanocomposites were successfully synthesized by hydrothermal method. Structural, morphological, chemical composition, optical, electrochemical and thermal properties were investigated using different analytical techniques like X-ray Diffraction, Fourier transform infrared spectroscopy (FTIR), UV- visible spectroscopy and photoluminescence (PL) spectrophotometry, and Scanning Electron Microscope (SEM). The photocatalytic activities of Fe-Ni-Co-S nanocomposites were investigated by the degradation of methylene blue in aqueous solution under visible light in different condition of pH, initial concentration and different trapping agents for free radicals (Tert-butyl alcohol (TBA), p-benzoquinone (BQ) and disodium ethylenediaminetetraacetic acid (Na₂-EDTA). The results revealed that the photodegradation efficiency of FeS compound with presence of NiS, CoS improved. The optical results show enhancement of nanocomposite absorption under the visible region with a high life time between e⁻/h⁺ at the optimum ratio between (Fe-Ni-Co-S) which can applied to obtain high photocatalytic degradation of methylene blue under visible light. Finally, the catalytic activity has been stabled when such photocatalyst was utilized again for several cycles.

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LIST OF ABBREVIATIONS

ABBREVIATIONS

EXPANSIONS

NP's

Nanoparticles

FeS

Iron sulfide

NiS

Nickel sulfide

CoS

Cobalt sulfide

XRD

X-ray diffraction

SEM

Scanning Electron Microscopy

FTIR

Fourier Transform Infrared Spectroscopy

UV- Vis

Ultra violet visible spectroscopy

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CHAPTER- 1

INTRODUCTION

Sulfide based nanocomposites are widely investigated because of their unique physical and chemical properties. In comparison with their metal oxide analogs, sulfide semiconductors with narrower band gaps hold more promise as photocatalysts for H₂ production. However, the H₂ production performance of metal sulfide-based composite photocatalysts is still limited because of the fast recombination of photoexcited carriers. In addition, photo corrosion is also a major problem for metal sulfide-based photocatalysts. Therefore, many researchers have focused on solving the problems of photo corrosion and carrier recombination, examining the formation of a heterojunction by decorating cocatalysts, introducing noble metal nanoparticles, or using porous conductive substrate. Metal sulfide is a vital species of semiconductor materials, and shows extensive applications in catalysis, photoelectricity, photosensors, etc. However, its low electrical conductivity, as well as its poor film-forming property, remarkably limits its practical applications. The ultimate goal of photocatalyst design is to facilitate reactions between the excited electrons with oxidants to produce reduced products, and reactions between the generated holes with reductants to produce oxidized products. Photocatalysis is a photochemical catalytic reaction that is a highly promising tool for environmental cleanup. It is very effective in the treatment of environmental pollutants due to its unique redox property. It has a wide range of applications for the decontamination of diverse hazardous pollutants in aqueous media. Technological progress in this research field has been achieved toward the improvement of solar sensitivity to enhance the efficiency of pollutant decontamination. As a result, various strategies have been introduced to upgrade the photocatalytic performance with the modification of a prototypical photocatalyst. It has wide applications in the treatment of atmospheric pollutants through oxidative removal and by disinfection. photocatalytic treatment of pollutants in aqueous media are described with respect to the composition of catalysts, experimental conditions, and interfering factors. The major goal for synthesis of nanocomposites is to obtain compounds that are optically clear and thermally stable with good mechanical properties [1]. In this project, Iron-Cobalt-Nickel-Sulfide (Fe-Co-Ni-S) doped nanocomposite was prepared.

1.1 NANOPARTICLES

Nanotechnology is an emerging field of modern science that includes synthesis and development of various nanomaterials. Nanoparticles can be defined as object ranging in size from 1 – 100nm that due to their size may differ from bulk material. Synthesized nanoparticles are in the form of colloids, clusters, powders, tubes, rods, wires and thin films etc. The technique to be used depends upon the material of interest, type of nanomaterial, size and quantity.[2]

1.2 CLASSIFICATION OF NANOPARTICLES.

According to size, synthesis methods, characterizations, applications and properties are the various categories to classify the nanoparticles.

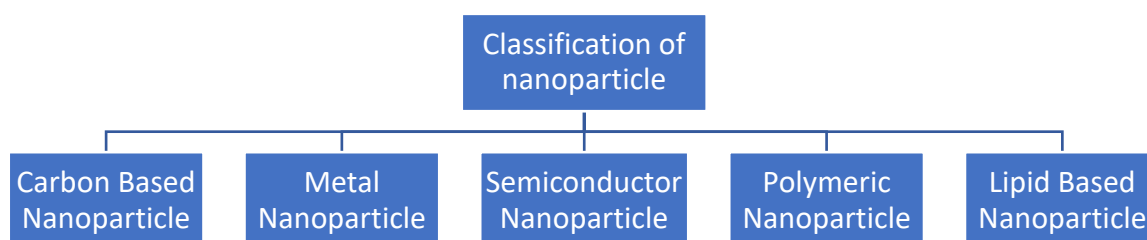


Figure 1.1 classification of nanoparticles

1.2.1 CARBON BASED NANOPARTICLES

Carbon-based nanoparticles consist of two main materials namely carbon nanotubes (CNTs) and fullerenes. CNTs are graphene sheets rolled into a tube. These materials are mainly used for the structural reinforcement as they are 100 times stronger than steel. CNTs can be classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs are unique in a way as they are thermally conductive along the length and non-conductive across the tube.

Fullerenes are the allotropes of carbon having a structure of hollow cage of sixty or more carbon atoms. The structure of C-60 is called Buckminsterfullerene, and looks like a hollow football. The carbon units in these structures have a pentagonal and hexagonal arrangement. These have commercial applications due to their electrical conductivity, structure, high strength, and electron affinity.

1.2.2 METAL NANOPARTICLES

These nanoparticles can be synthesized by chemical, electrochemical, or photochemical methods. Metal nanoparticles are prepared from metal precursors. In chemical methods, the metal nanoparticles are obtained by reducing the metal-ion precursors in solution by chemical reducing agents. These have the ability to adsorb small molecules and have high surface energy. These nanoparticles have applications in research areas, detection and imaging of biomolecules and in environmental and bioanalytical applications.[3]

1.2.3 SEMICONDUCTOR NANOPARTICLES

Semiconductor materials possess properties between metals and nonmetals and therefore they found various applications in literature due to this property. Semiconductor NPs possess wide bandgaps and therefore showed significant alteration in their properties with bandgap tuning. Therefore, they are very important materials in photocatalysis, photo optics and electronic devices. As an example, variety of semiconductor NPs are found exceptionally efficient in water splitting applications, due to their suitable band gap and band edge positions [4].

1.2.4 POLYMERIC NANOPARTICLE

Polymeric nanoparticle is organic based nanoparticle. Depending upon the method of preparation, these have structures shaped like nanocapsular or nanospheres. A nanosphere particle has a matrix-like structure whereas the nanocapsular particle has core-shell morphology. In the former, the active compounds and the polymer are uniformly dispersed whereas in the latter the active compounds are confined and surrounded by a polymer shell.

1.2.5 LIPID- BASED NANOPARTICLE

Lipid nanoparticles are generally spherical in shape with a diameter ranging from 10 to 100nm. It consists of a solid core made of lipid and a matrix containing soluble lipophilic molecules. The external core of these nanoparticles is stabilized by surfactants and emulsifiers. These nanoparticles have application in the biomedical field as a drug carrier and delivery and RNA release in cancer therapy.

1.3 TYPES OF NANOPARTICLES

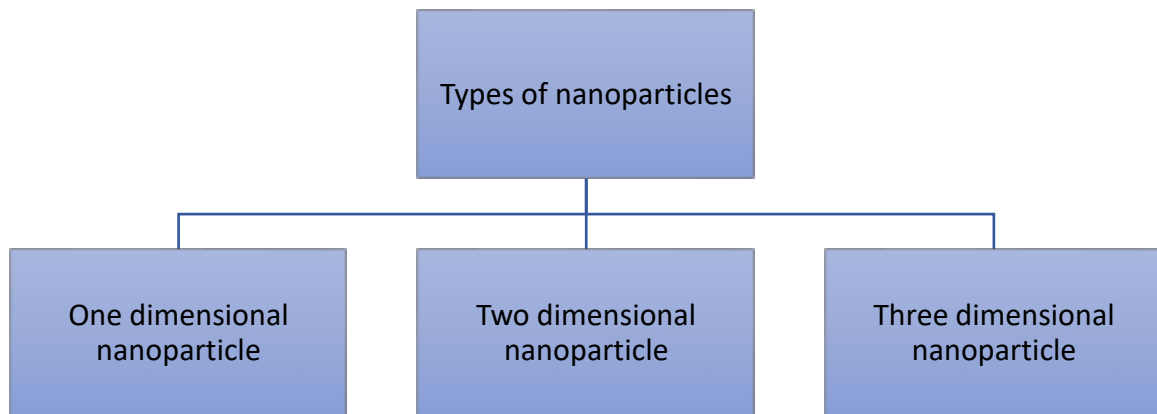


Figure1.2 Types of nanoparticles

1.3.1 ONE DIMENSIONAL NANOPARTICLE:

Atoms are arranged in one-dimensional nano scale range. one dimension is outside the nanoscale. This class includes nanotubes, nanorods, and nanowires. coatings and thin films.

1.3.2 TWO-DIMENSIONAL NANOPARTICLE:

Atoms are arranged in two-dimensional nano scale range. . Examples are nanotubes, biopolymers, nanowires.

1.3.3 THREE-DIMENSIONAL NANOPARTICLE:

Atoms are arranged in three-dimensional nano scale range. . Examples are fullerenes.

1.4 SYNTHESIS OF NANOPARTICLES

Synthesis can be classified into two main categories namely top- down approach and bottom- up approach.

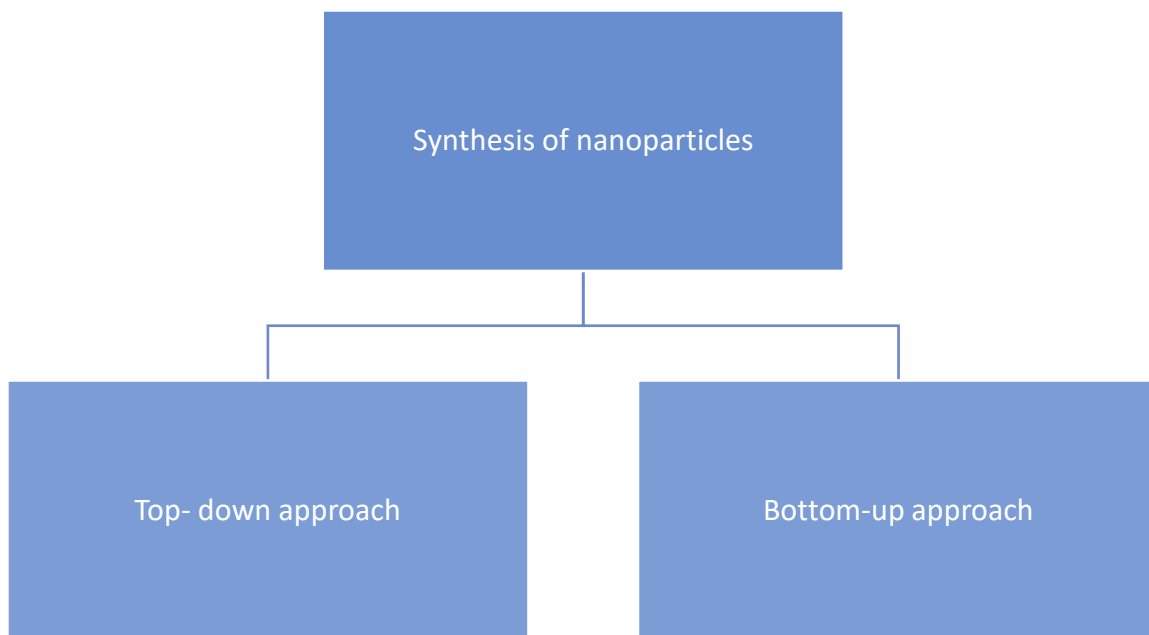


Figure 1.3 Synthesis of nanoparticles

1.4.1 TOP- DOWN APPROACH

Top- down approach involves the breaking down of the bulk material into nanosized structure or particles. Top- down synthesis techniques are the extension of those that have been used for producing micron sized particle. Top- down approach fundamentally simpler and depended either on removal or diversion of bulk material

or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties. [2]

1.4.2 BOTTOM- UP APPROACH

Bottom- up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. Many of these techniques are still under development or are just beginning to be used for commercial production of nano powders. Organometallic chemical route, reverse- micelle, sol-gel synthesis, colloidal precipitation, hydrothermal synthesis, template assisted sol-gel, electrodeposition etc, are some of well-known bottom- up techniques reported for the preparation of luminescent nanoparticles. Bottom- up approach is more economical which has potential of creating less waste.[2]

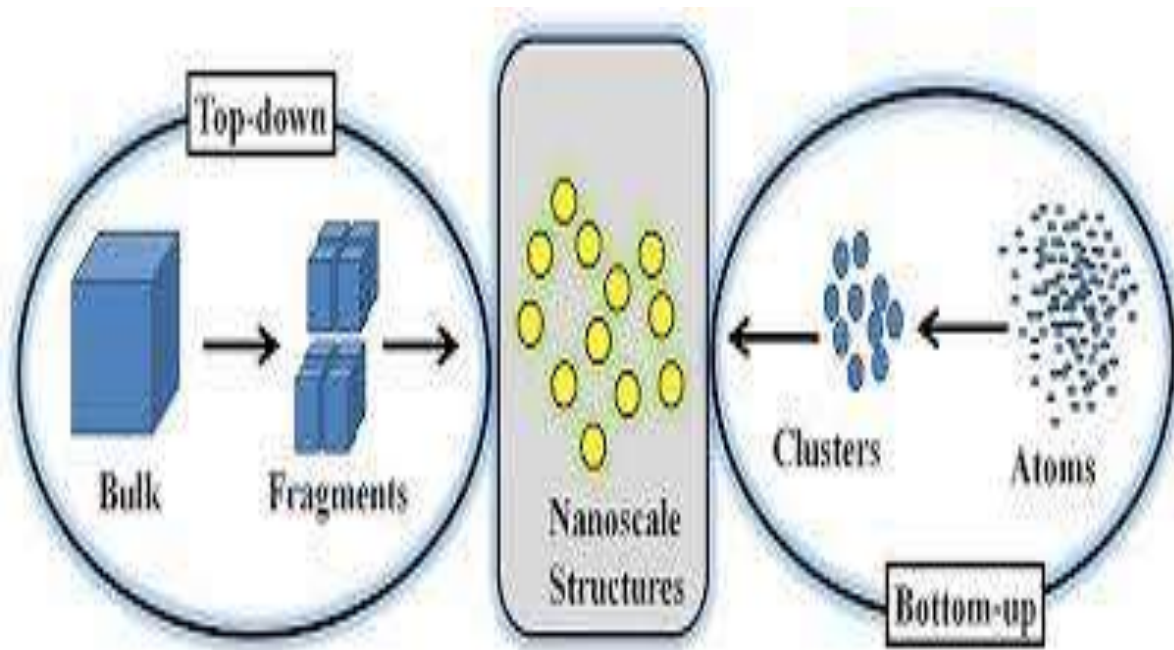


Figure 1.4 Top- down and Bottom- up approaches

1.5 APPLICATION OF NANOPARTICLES

Nanomaterials can occur naturally, be created as the by- products of combustion reactions or produced.

Controlling the size, shapes and material of the nanoparticle to design the photovoltaics and solar thermal products.

1.6 HYDROTHERMAL PROCESS

Hydrothermal synthesis is one of the most commonly used methods for preparation of nanomaterials. In hydrothermal synthesis, the formation of nanomaterials can happen in a wide temperature range from room temperature to very high temperatures. To control the morphology of the materials to be prepared, either low-pressure or high-pressure conditions can be used depending on the vapor pressure of the main composition in the reaction. Many types of nanomaterials have been successfully synthesized by the use of this approach. Hydrothermal synthesis can generate nanomaterials which are not stable at elevated temperatures. Nanomaterials with high vapor pressures can be produced by the hydrothermal method with minimum loss of materials.[5] The compositions of nanomaterials to be synthesized can be well controlled in hydrothermal synthesis through liquid phase or multiphase chemical reactions. This special issue serves as a forum presenting the recent research results of hydrothermal synthesis of nanomaterials.

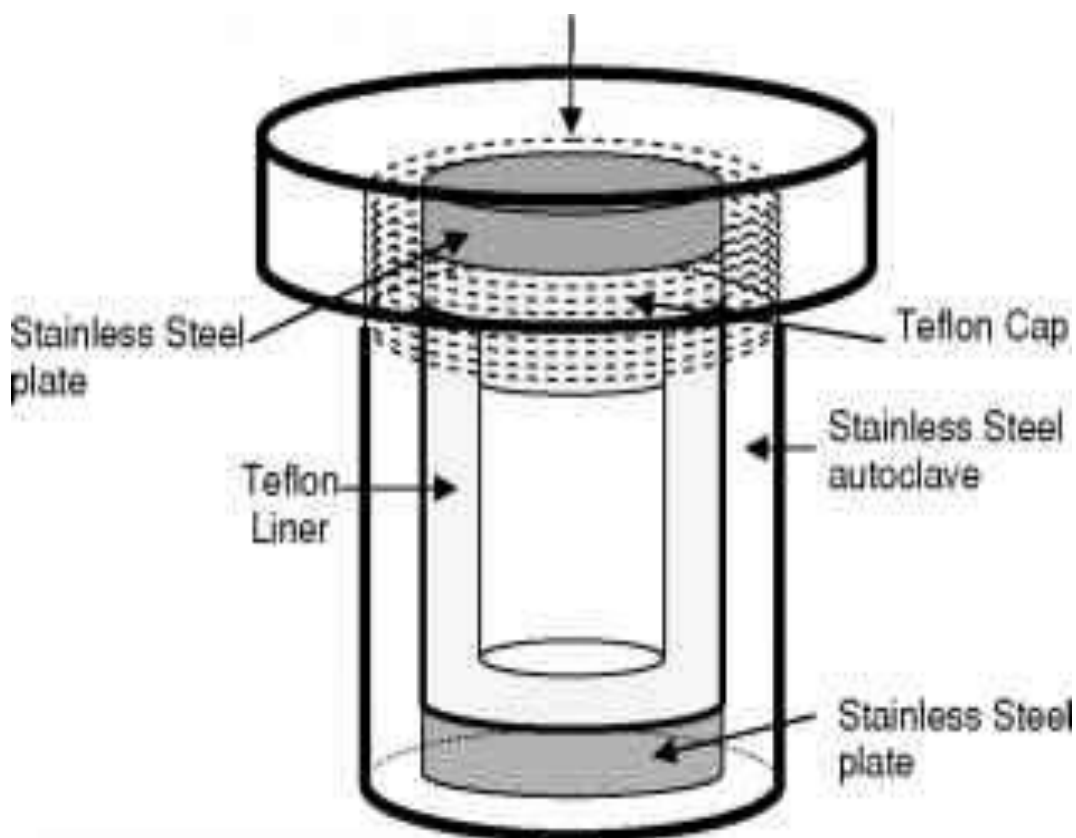


Figure 1.5 Hydrothermal synthesis

Hydrothermal method is appropriate preparation method specially for powdery nanostructure. The hydrothermal process includes mixing of precursors and agents into the solvent that enables the synthesis of crystalline nanostructure with correct ratio. The procedure includes the transfer of mixture into the sealed autoclave made of stainless steel lined with Teflon and heated in an oven at specific temperature, time and pressure. The temperature determines the internal pressure and the total amount of solution added to the autoclave. The advantage of hydrothermal method that materials are dissolved in appropriate solvent by exact temperature and pressure when compared to solvothermal method. The difference between the solvothermal method and hydrothermal method is the distilled water used as a primary solvent instead of an organic solvent.

1.7 PHOTOCATALYST

Photocatalyst is phenomena, which occurs in catalysis by influence of photons. A photocatalyst employ the catalyst for speeding up chemical reactions in the presence of UV light. An efficient photocatalyst is conductive nanomaterial, which directly absorbs incident light to bring up to higher energy states, which provides such energy to a reacting substance to make a chemical reaction occur [6]. Photocatalysis, generally is used to design, characterize, and potential photocatalytical applications with doped or undoped nanostructural materials especially considering their particles sizes as well as shapes. Accelerated photo- reaction in the presence of a catalyst is called photo-catalysis. In the reaction, light is absorbed by the substrate. Reaction rate or activity of catalyst depends on the ease by which the catalyst is creating electron-hole pair. These electron-hole pairs react with the substrate to produce free radical [7]. The effect of photocatalysts is explained by the following example of photocatalytic decomposition of surface stains, which occurs in photocatalytic self-cleaning coatings. Pairs of electron and hole are excited by UV lights. The photo-generated electrons produce anion radicals like by reacting with O_2 . [8]

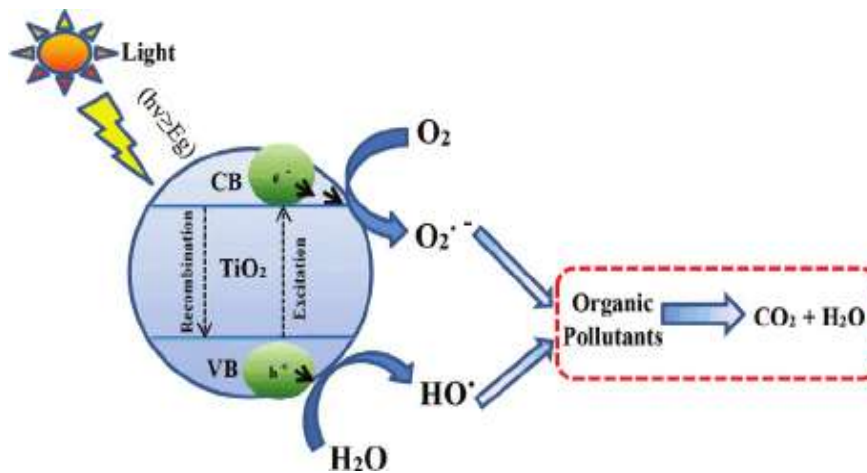


Figure 1.6 Mechanism for photocatalyst

Photocatalyst can be categorized into two types

- Homogeneous photocatalysis
- Heterogeneous photocatalysis

1.7.1 HOMOGENEOUS PHOTOCATALYSIS

When both the semiconductors and the reactants are in the same phase. Liquid, solid or gas such photocatalytic reaction are termed as homogeneous photocatalysis

1.7.2 HETEROGENEOUS PHOTOCATALYSIS

When both semiconductors are in different phases then it is called as heterogeneous photocatalysis [9]

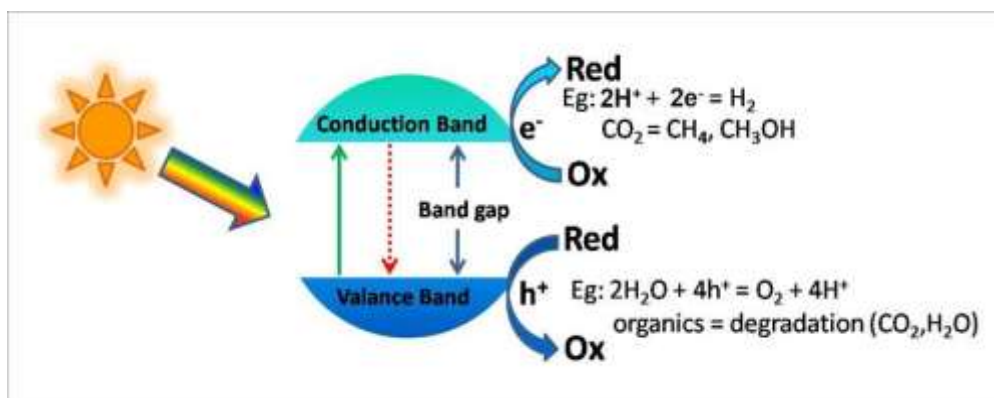


Figure 1.7 photocatalyst

CHAPTER- 2

LITERATURE SURVEY

Yousef Fazli, Seied Mahdi Pourmortazavi, Iraj Kohsari, Meisam Sadeghpour Karimi, Majid Tajdari, were synthesized nickel sulfide and also studied the characterization of sample by field scanning electron microscope (FE-SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), UV-Vis spectroscopy. Synthesis, characterization and photocatalytic property of nickel sulfide nanoparticles. Photocatalytic for synthesized Nickel sulfide also studied [10]

Ye Yuan^{1,2,3}, Liping Wang^{1,2} and Lizeng Gao³, synthesized that Nano-Sized Iron Sulfide: Structure, Synthesis, Properties, and Biomedical Applications. The synthesized samples were characterization done also the properties and biomedical applications were studied [11]

Matjaz Kristl, Brina Dojer, Saso Gyergyek a, Janja Kristl have synthesized Nickel and Cobalt sulfide nanoparticles using a low cost sonochemical method. The characterisation of nickel and cobalt sulfides by X-ray diffraction, transmission electron microscopy (TEM) including EDX analysis, IR and UV–Vis spectroscopy and elemental analysis [12]

E. Sathiyaraj, S. Thirumaran have studied that Structural, morphological and optical properties of iron sulfide, cobalt sulfide, copper sulfide, zinc sulfide and copper-iron sulfide nanoparticles synthesized from single source precursors. The synthesized samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), UV-Vis, photoluminescence and Fourier transform infrared (FT-IR) spectroscopy techniques [13]

G. Gurumoorthy have synthesized the cobalt sulfide and cobalt iron sulfide. The synthesized samples of Cobalt sulfide and cobalt-iron sulfide nanoparticles were characterized using Transmission electron microscope (TEM), EDS, UV-vis, Photoluminescence and IR spectroscopy [14]

Subbiah Thirumaran, Govindasamy Gurumoorthy, Rajaram Arulmozhi, Samuele Ciattini have synthesized the nickel sulfide and nickel- iron sulfide nanoparticles. The characterization was also done by X- ray diffraction (XRD), NMR, UV-Vis, Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR). The photocatalytic application of the samples of nickel sulfide and nickel- iron nanoparticles also studied [15]

CHAPTER- 3

AIM AND SCOPE OF PRESENT INVESTIGATION

This project work is mainly focused on the following objectives:

- To synthesis novel Fe-Co-Ni nanocomposite by a hydrothermal method
- Characterization of the nanocomposite using XRD, UV, FT-IR, SEM
- Determine morphology and size of the nanocomposites
- Photocatalytic degradation of the *Acid yellow-36* dye using Fe-Co-Ni nanocomposite
- Summarize the obtained results

CHAPTER- 4

4.1 EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

4.1.1 MATERIALS

Iron (II) chloride were purchased from, Nickel chloride was purchased from Merch, sodium sulfide was purchased from Loba chemicals, cobalt nitrate was purchased from Alfa Aesar, ethanol and acetone were purchased from SRL. All these solutions were prepared using distilled water.

4.1.2 SYNTHESIS OF (Fe- Ni-Co-S) NANOCOMPOSITE

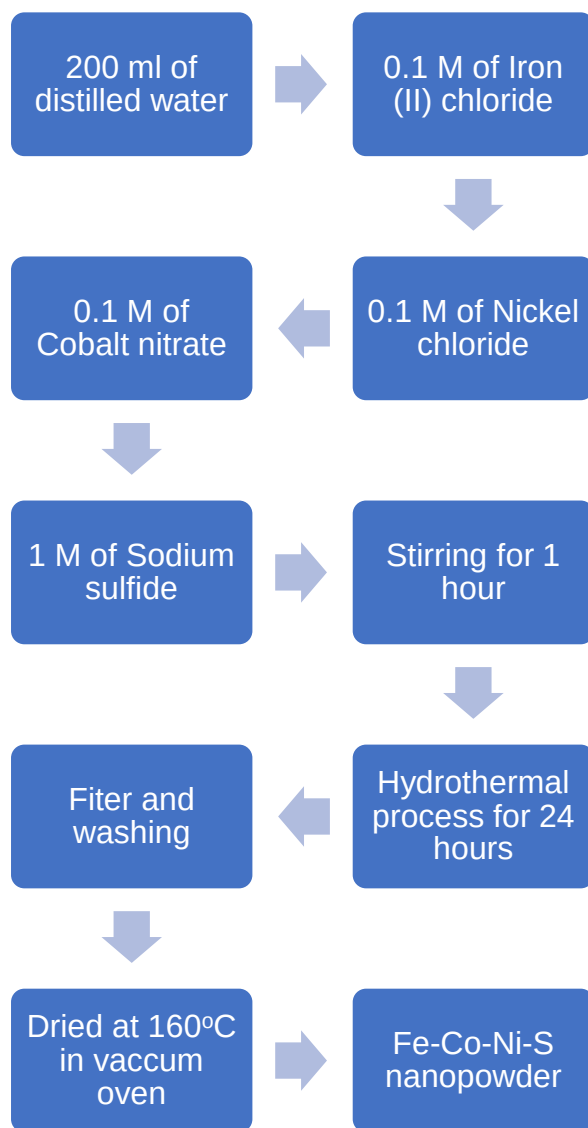


Figure 4.1 Synthesis of Fe-Ni-Co-S nanocomposite

About 0.1M of Iron (II) chloride is taken in a 500 ml beaker to which 200ml of deionized water is added to the beaker. To that mixture 0.1M of Nickel chloride is added. Then 0.1 M of Cobalt nitrate also added to the mixture and then add 0.1 M Iron (II) chloride is also added to the mixture. Finally add 1 gram of polyvinyl pyrrolidone to the mixture. Then 50 ml of distilled water taken and add 1 M sodium sulfide flakes added and stir well. Then add the sodium sulfide solution to the mixture. The reaction mixture is stirred in a magnetic stirrer for almost 1 hours at room temperature. After stirring, the reaction is transferred into the Teflon tube. Teflon tube along with mixture is tightly enclosed in autoclave. Then it is kept in hot air oven and set the temperature at 170 ° C. it is kept in hot air oven around 24 hours (1 day). After 24 hours, the autoclave is taken out from the hot air oven and kept it for cool. Around 2 hours it kept for cool, it will come to room temperature. After that the Teflon tube taken from the autoclave and transferred the mixture into 500 ml beaker. Add enough amount of distilled water to the mixture. kept it for settle down. The product thus obtained is washed thoroughly with deionized water, to remove all the residues which is followed by washing with acetone. Finally, the sample is dried in air oven at 120°C. After drying of sample taken out and grain it using the mortar piston. The colour of the sample changes from green to red when calcinated. The resultant thus obtained is the Fe- Ni-Co-S nanoparticle.

4.2 CHARACTERIZATION TECHNIQUES

The nanoparticle characterisation is carried out by various measurement techniques [16]. In characterization techniques the study of crystal structure by using X-ray Diffraction, morphology by using Scanning Electron Microscope (SEM), wavelength by using UV- Visible spectroscopy, to determine the functional groups by using FTIR.

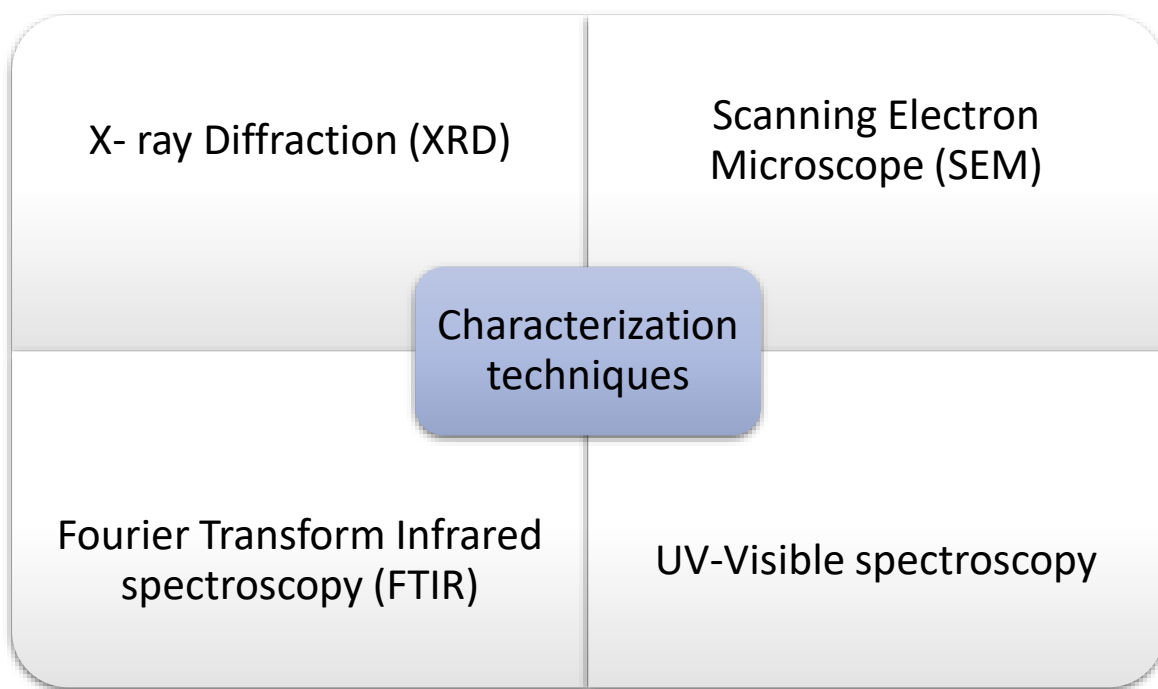


Figure 4.2 Characterization techniques

4.2.1 X- RAY DIFFRACTION (XRD)

X-ray diffraction (XRD) is a logical method in view of the diffraction of X-rays by matter, particularly for crystalline materials. X-ray diffraction (XRD) is a materials characterization technique that is widely used for all kinds of solid particles including nanoparticles of all sizes. The theory of XRD is well developed for single crystals and powders of solids with a large number of crystalline planes. XRD is used for characterization of Nano powders of any sizes, and the observed changes in positions of diffraction peaks are used to make conclusions on how crystal structure and cell parameters changes with the change in nanoparticles size and shape [17]. XRD is to study the grain and particle size of the nanomaterials. X-ray diffraction spectroscopy as rapid analysis technique is used to identify the type of material as well as its phase and crystalline properties. The structural properties of nanocomposites can be characterized by X-ray diffraction. XRD is also used to determine possible changes in the crystal structure of the matrix after adding nanoparticles. [19]

When monochromatic x-rays scatter from a substance with a structure on this scale, it causes interferences. This results in a pattern of lower and higher intensities due to constructive and destructive interferences according to Braggs law. With crystalline

substances, the pattern creates three-dimensional shavings of diffraction in response to x-ray wavelengths, like the spacing of planes in a crystal lattice. This process is known as constructive interference and is used as a technique for studying crystal structures and atomic spacing. All diffraction methods start with the emission of x-rays from a cathode tube or rotating target, which is then focused at a sample. By collecting the diffracted x-rays, you can analyse the sample's structure. This is possible because each mineral has its unique set of d-spacings.[20] D-spacings are the distances between planes of atoms, which cause diffraction peaks. There are standard reference patterns of d-spacings, which act as a comparison when using XRD to identify the structure of a sample substance. The way that x-rays reveal the atomic structure of crystals is based on Bragg's law.

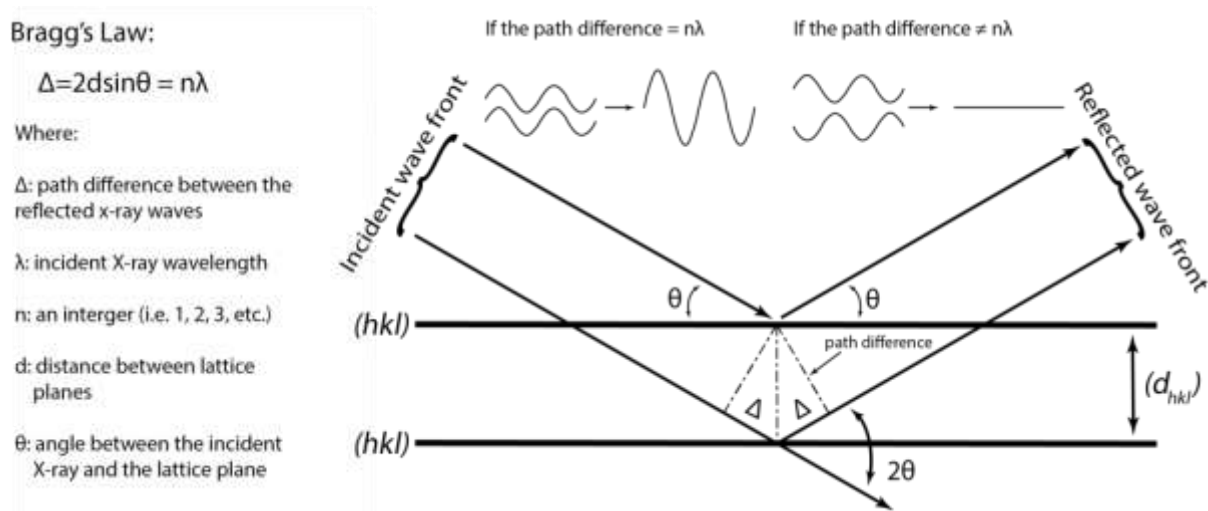


Figure 4.3 schematic representation of Bragg's law

4.2.2 SCANNING ELECTRON MICROSCOPE (SEM):

Scanning electron microscope (SEM) is a very useful for the characterization of size and shape of the nanoparticle. Scanning electron microscope (SEM) projects and scans a focused stream of electrons over a surface to create an image. The electrons in the beam interact with the sample, thereby producing various signals that can be used to obtain information about the surface's topography and composition. The main SEM components include:

- Source of electrons
- Column down which electrons travel with electromagnetic lenses
- Electron detector
- Sample chamber
- Computer and display to view the images

Electrons are produced at the top of the column, accelerated down, and passed through a combination of lenses and apertures to produce a focused beam of electrons which then strikes the surface of the sample [21]. The sample itself is mounted on a stage in the chamber area and (unless the microscope is designed to operate at low vacuums) both the column and the chamber are evacuated by a combination of pumps. The level of the vacuum will depend on the design of the microscope.



Figure 4.4 SEM instrument

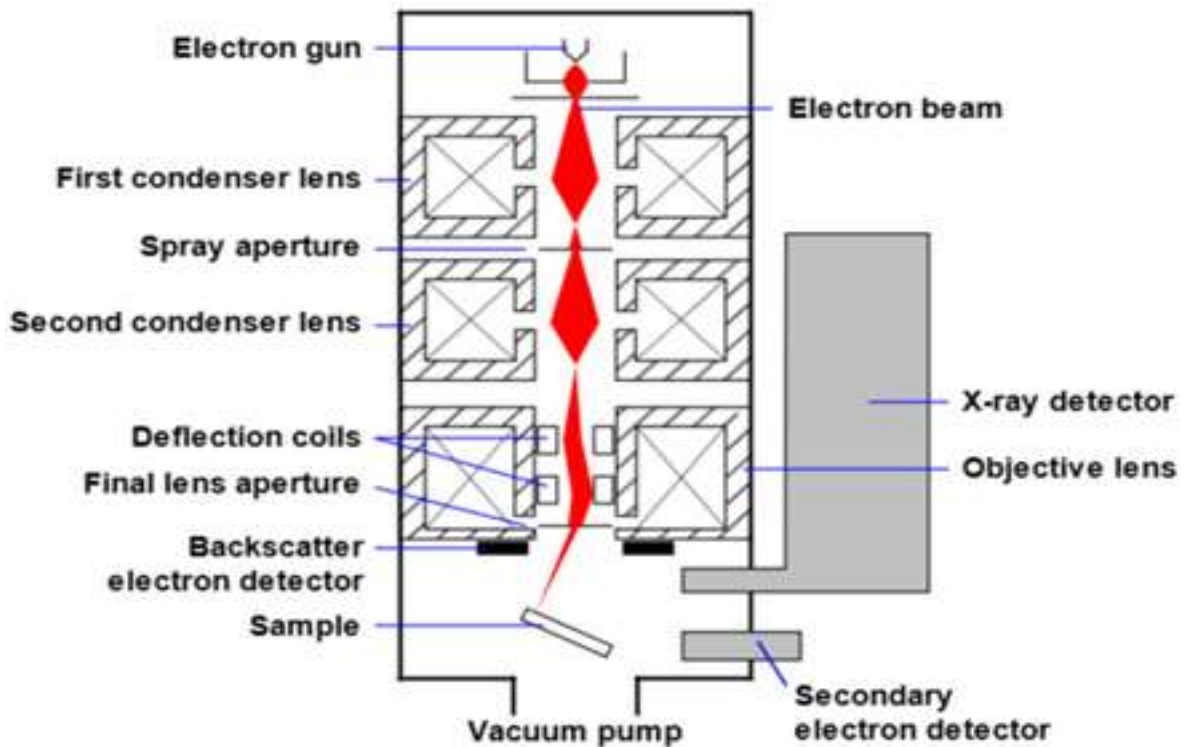


Figure 4.5 working of SEM

The position of the electron beam on the sample is controlled by scan coils situated above the objective lens. These coils allow the beam to be scanned over the surface of the sample. This beam restoring or scanning enables information about a defined area on the sample to be collected. As a result of the electron-sample interaction, a number of signals are produced. These signals are then detected by appropriate detectors.[22]

The scanning electron microscope (SEM) produces images by scanning the sample with a high-energy beam of electrons. As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by one or more detectors to form images which are then displayed on the computer screen. When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. Many signals like secondary electrons and X-rays are produced as a result of this interaction inside the sample. The maximum resolution obtained in an SEM depends on multiple factors like the electron spot size and interaction volume of the electron beam with the sample[23]. While it cannot provide atomic resolution, some SEMs can achieve resolution below 1

nm. Typically, modern full-sized SEMs provide resolution between 1-20 nm, whereas desktop systems can provide a resolution of 20 nm or more.

4.2.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared (FTIR) spectroscopy is a very efficient non-destructive characterization technique for surface characterization of nanoparticles' surfaces, providing a specific setup is connected to the spectrometer. It is to determine the functional groups. The chemical structure of the nanoparticles' surface and the surface reactive sites responsible for surface reactivity can be determined under particular conditions.[24]

The structure and bands of the synthesised nanoparticles, as well as the stretch of bonds, were revealed by FTIR. FTIR may be used to test a variety of components, including bulk or thin films, liquids, solids, pastes, powders, fibres, and other materials. FTIR analysis may be used for quantitative (amount) analysis as well as qualitative (identification) analysis of materials where appropriate criteria are used. FTIR can test samples up to 11 mm in diameter and weigh in bulk or the top 1 mm of the sample. [25]

The difficulty in FTIR characterization is mainly because of high degree of overlapping of the IR absorption bands which makes difficult for the attribution of certain functional groups, despite the fact that up to date computer-searchable databases are available.[26]

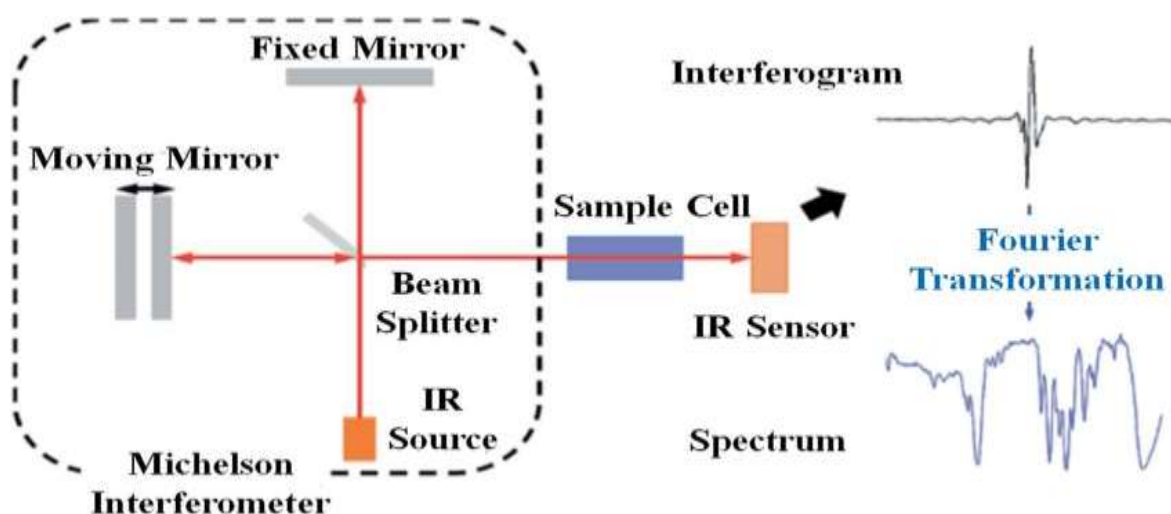


Figure 4.6 Working of FTIR

4.2.4 UV-VISIBLE SPECTROSCOPY

UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample.[27]

The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions of electrons from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

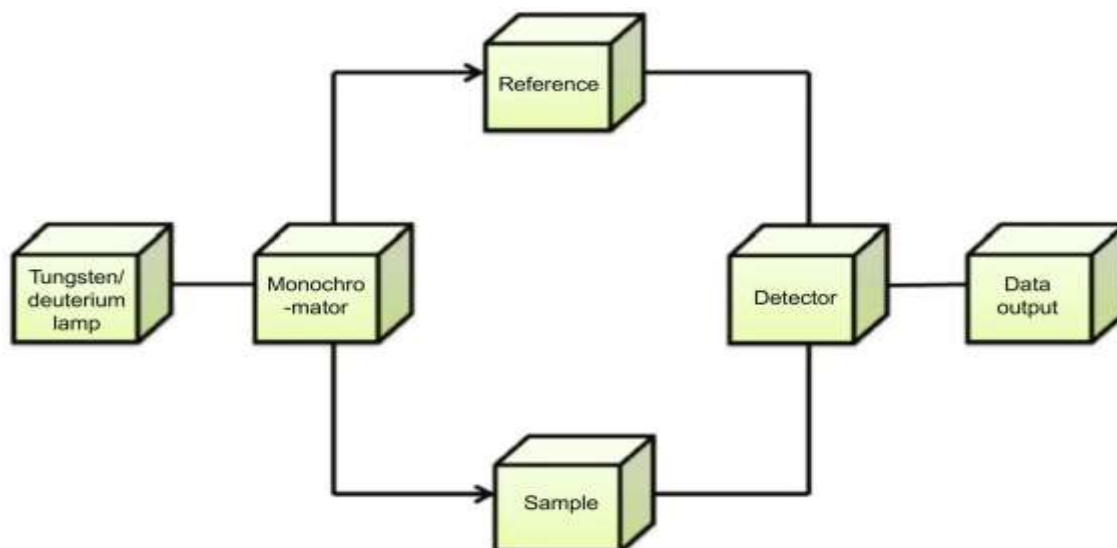


Figure 4.7 Working of UV- Visible spectroscopy

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals.

The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. There are four possible types of transitions ($\pi\text{--}\pi^*$, $n\text{--}\pi^*$, $\sigma\text{--}\sigma^*$, and $n\text{--}\sigma^*$), and they can be ordered as follows: $\sigma\text{--}\sigma^* > n\text{--}\sigma^* > \pi\text{--}\pi^* > n\text{--}\pi^*$. UV/Vis spectroscopy

is routinely used in analytical chemistry for the quantitative determination of different analytes or sample, such as transition metals ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

- Solutions of transition metal ions can be coloured (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another.
- The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption (λ_{max}).
- organic compounds especially those with a high degree of conjugation also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy.
- Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.
- While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

The Beer- Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV-Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a Calibration curve.

A UV- Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For

accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward- Fieser rules, for instance, are a set of empirical observations used to predict λ_{max} , the wavelength of the most intense UV- Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample.

The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectrum. Experimental variations such as the slit width (effective bandwidth) of the spectrophotometer will also alter the spectrum. To apply UV/Vis spectroscopy to analysis, these variables must be controlled or accounted for in order to identify the substances present.

The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer-Lambert law:

where A = absorbance

I = intensity of the incident is the transmitted intensity,

L = the path length

c = concentration of absorbing species

ϵ = molar absorptivity coefficient.

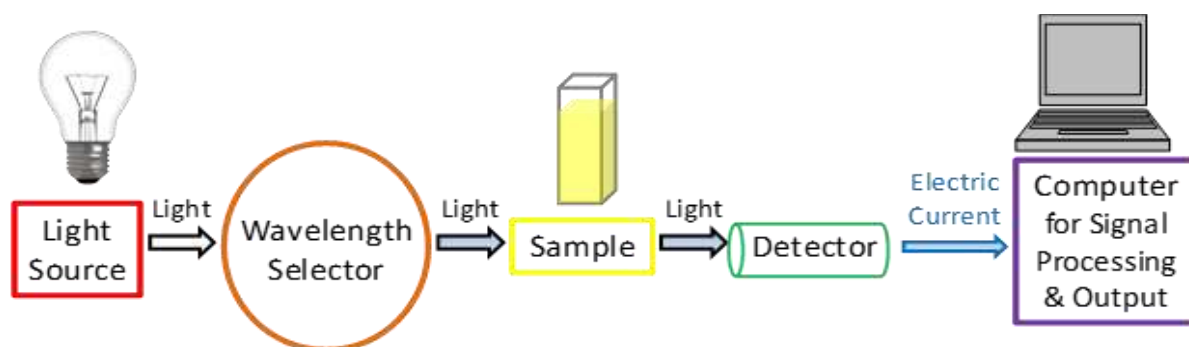


Figure 4.8 Schematic representation of UV-visible spectroscopy

CHAPTER – 5

5.1 RESULTS AND DISCUSSION

Crystal structure, morphology, compositional information, presence of organic functional groups on the surface and photocatalytic application of the synthesized nanoparticles were characterized using the following techniques such as X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infra-red spectroscopy (FTIR). These highlighted techniques are presented in this chapter. A brief information about these characterization techniques are discussed herein.

5.1 X-RAY DIFFRACTION (XRD)

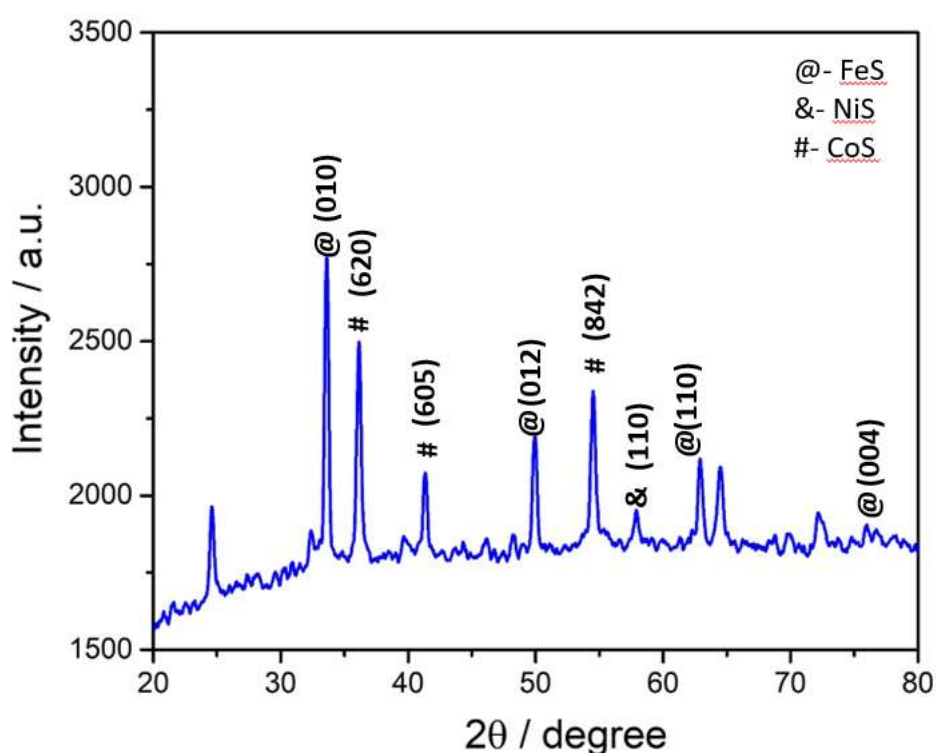


Figure 5.1 XRD FOR Fe-Ni-Co-S

Figure 5.1 depict the powder X-ray diffraction pattern obtained for the sample. FeS phase of the sample was identified from the diffraction peaks(2theta) at 33.50,

50.00, 62.80 and 76.40 which correspond to miller indices (010), (012), (110), and (004) respectively. Further the peak at 57.4, corresponding to miller index (110) represents the presence of NiS phase in the sample. Also the peaks at 36.2, 42.4, 55.2 with miller indices (620), (605), (824) correspond to CoS phase of the sample. Thus, the indexing of powder XRD pattern confirms the presence of all the phases FeS, NiS, CoS in the sample.

5.2 SCANNING ELECTRON MICROSCOPE (SEM)

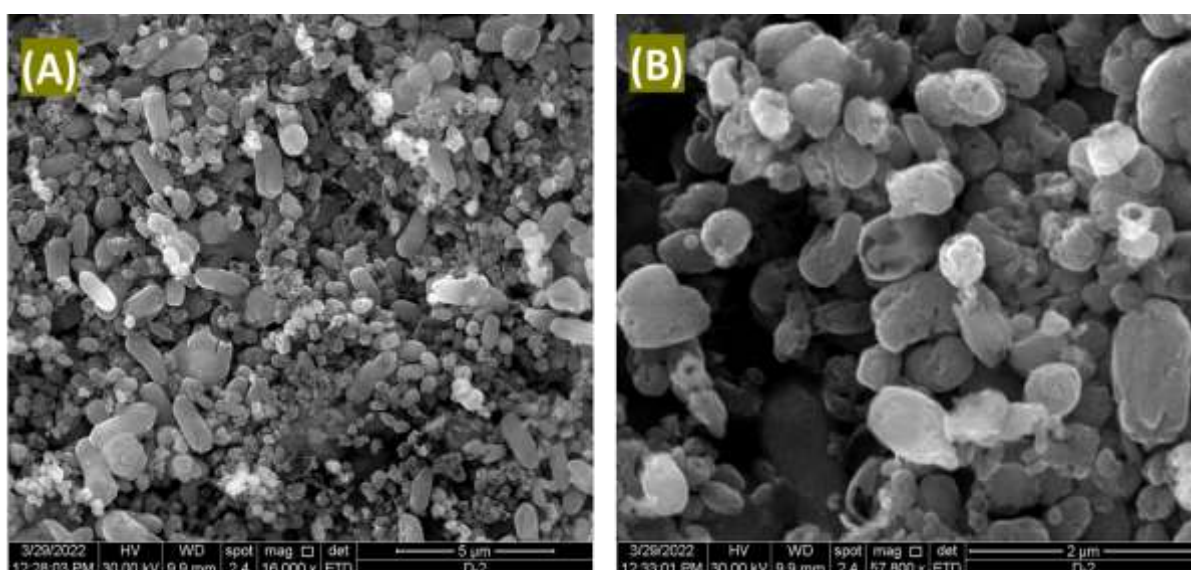


Figure 5.2 SEM images of the Fe-Ni-Co-S at 5 micron and 2 micron scale

Figure 5.2 shows that the morphology of annealed Fe-Ni-Co-S nanocomposite analysed using SEM. Figure 5.2 a and b having different magnifications of nanocomposite at 5 micron and 2 micron respectively. As shown in SEM images, the sample exhibits spherical structure and has particle size ranging between 0.1 to 0.2 micron. The average diameter 9.9 nm for Fe-Ni-Co-S

5.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

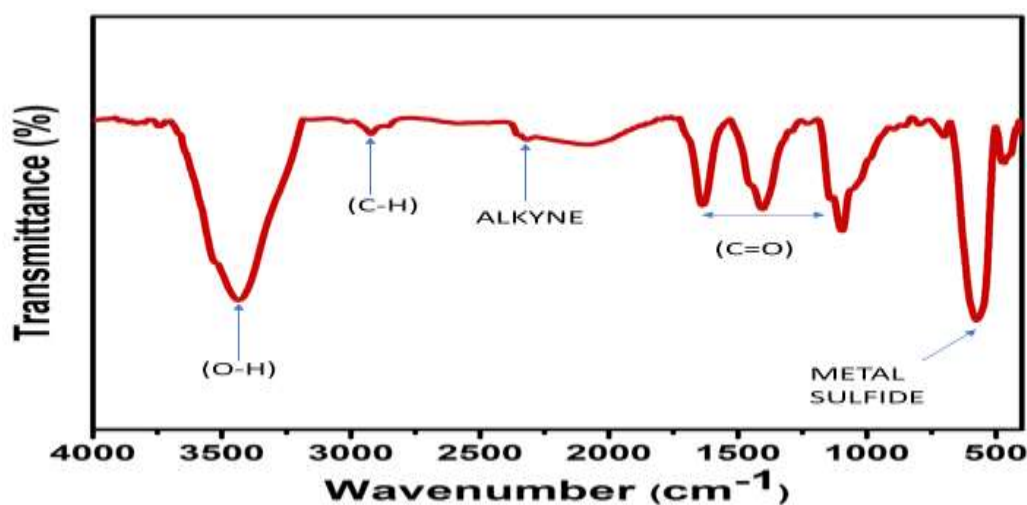


Figure 5.3 FTIR FOR Fe-Ni-Co-S

TABLE 5.1 FTIR FOR Fe-Ni-Co-S

S.NO	FUNCTIONAL GROUP	WAVENUMBER (cm ⁻¹)
1	O-H	3450
2	C-H	2950
3	ALKYNE	2480
4	C=O	1750
5		1350
6	METAL SULFIDE	550

The FTIR spectrum of Fe-Ni-Co-S nanocomposite are shown in Figure 5.3. Strong peaks shown around 3450 cm⁻¹ corresponds to O-H stretching respectively. The presence of water molecule peaks in the annealed samples is due to adsorption of water when FT-IR sample disks were prepared in an open air. The three peaks between 1650 and 1090 cm⁻¹ shows (C=O) respectively. Metal sulfide are present in 550cm⁻¹.

5.4 UV- VISIBLE SPECTROSCOPY

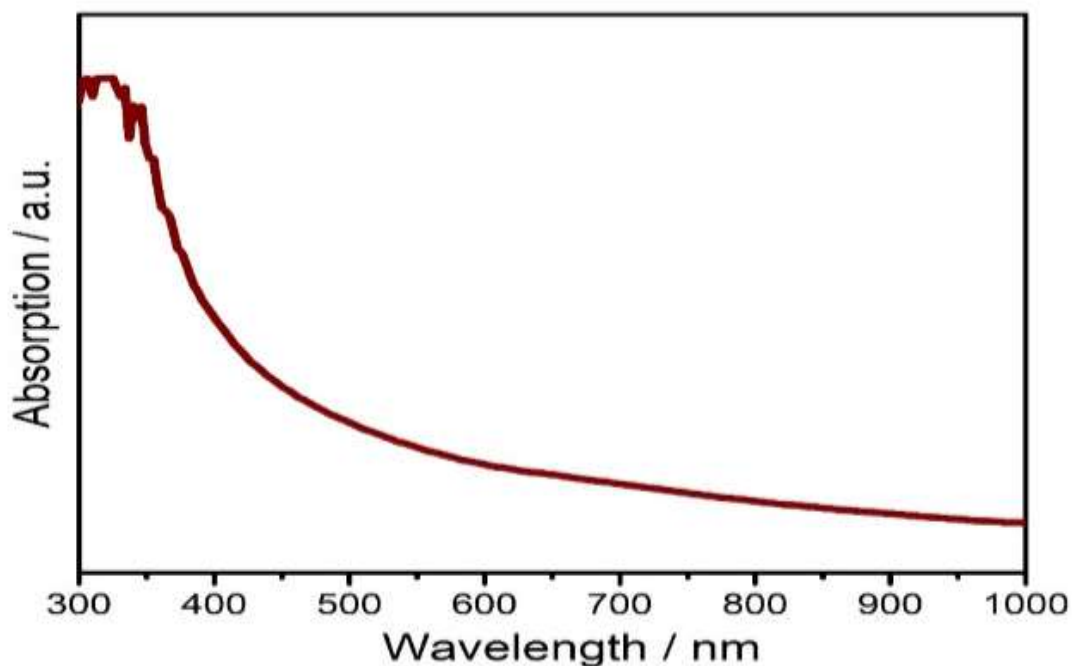


Figure 5.4 a UV FOR Fe-Ni-Co-S

From the figure 5.4 a, the graph shows that the absorption peak was obtained at 350nm.

5.4.1 BAND GAP

The band gap (E_G) is the gap in energy between the bound state and the free state, between the valence band and conduction band. Therefore, the band gap is the minimum change in energy required to excite the electron so that it can participate in conduction. Schematic of the energy bands for electrons in a solid.

As the electronegativity difference $\Delta\chi$ increases, so does the energy difference between bonding and antibonding orbitals. The band gap is a very important property of a semiconductor because it determines its colour and conductivity

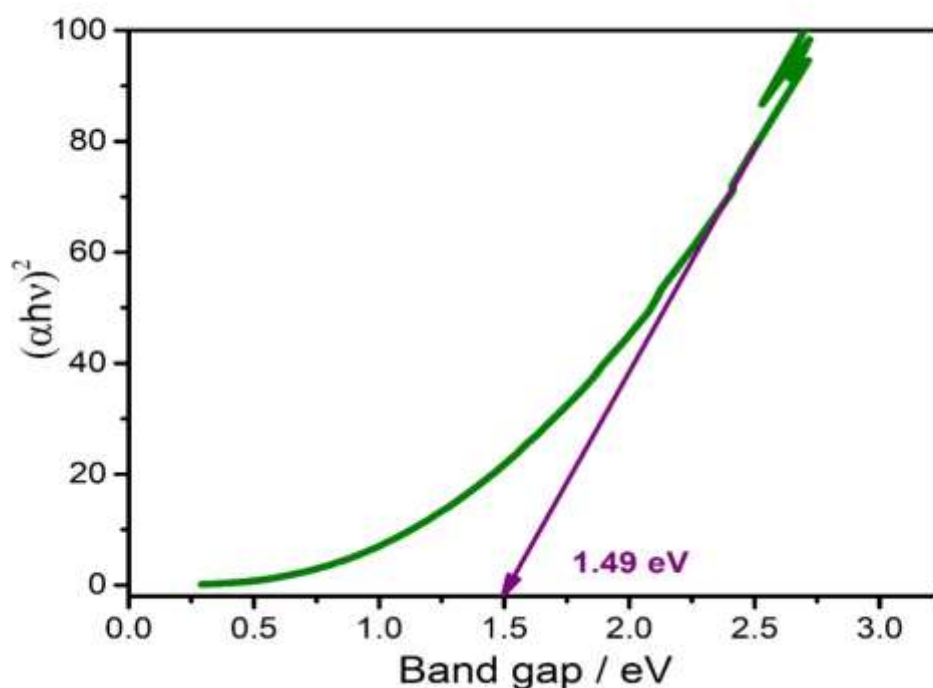


Figure 5.4 b UV BAND GAP FOR Fe-Ni-Co-S

The figure 5.4 b shows the band gap of nanocomposite band gap and this nanocomposite shows the band gap at 1.49 eV. This means our compound shows that the good conductivity and good electron absorber.

5.5 Photodegradation study

5.5.1. Photocatalytic activity test

Acid yellow-36 (AY) was chosen as the model organic pollutants to test the photocatalytic dye degradation analysis for the catalyst. Typically, a catalysts (20 mg) was added into the 50 ml of aqueous dye solution (20 mg L^{-1}) then, the dye solution was kept in dark room to attain the adsorption and desorption equilibrium of dyes on surface of catalyst. Then, the dye solution was irradiated on sunlight for overall time period of 120 minutes. 2 ml of solution was taken at appropriate interval of time. The collected solution was centrifuged and filtered using a $0.2 \mu\text{m}$ syringe filter. The

degradation efficiency is determined by the degradation of organic dyes on UV-Vis spectrophotometer. The degradation efficiency is calculated by the formula,

$$\text{Degradation efficiency (\%)} = (C_0 - C)/C_0 \times 100 \quad (1)$$

Where C and C₀ are initial and final concentration of dye molecules. After 1st completed the photocatalytic reaction, the catalyst was collected by centrifuge and washed with water and dried at 70°C. The regenerated catalyst was used to evaluate the stability and reusability of catalyst by degradation the dye solution.

The first order kinetic reaction value were used to determine the correct degradation rate of MB as follows;

$$-\ln(C/C_0) = kt \quad (2)$$

Where, k = rate of reaction constant and t is time. The Photocatalytic dye degradation activity were performed during the well sun shining between 11:00 AM to 2:00 PM in clear sky. The average solar light intensity was measured about 1.00 x 10⁵ lux

5.5.2. Photocatalytic activity

The photocatalytic degradation efficiency of as prepared catalysts of Fe-Ni-Co-S nanoparticle was resolute by the deprivation of AY dye under irradiation of Sun light. When irradiating the AY dye solution, the concentration of the dye was noticeably reduced and it was confirmed by the significant color variation. For Fe-Ni-Co-S catalyst, the catalyst influences the organic molecule to achieve the efficiency of about 94.5 % within 120 mins. The rate of electron-hole pair recombination was delayed and higher absorption by incorporation of trimetalsulphide nanoparticle structure results increased the degradation efficiency.

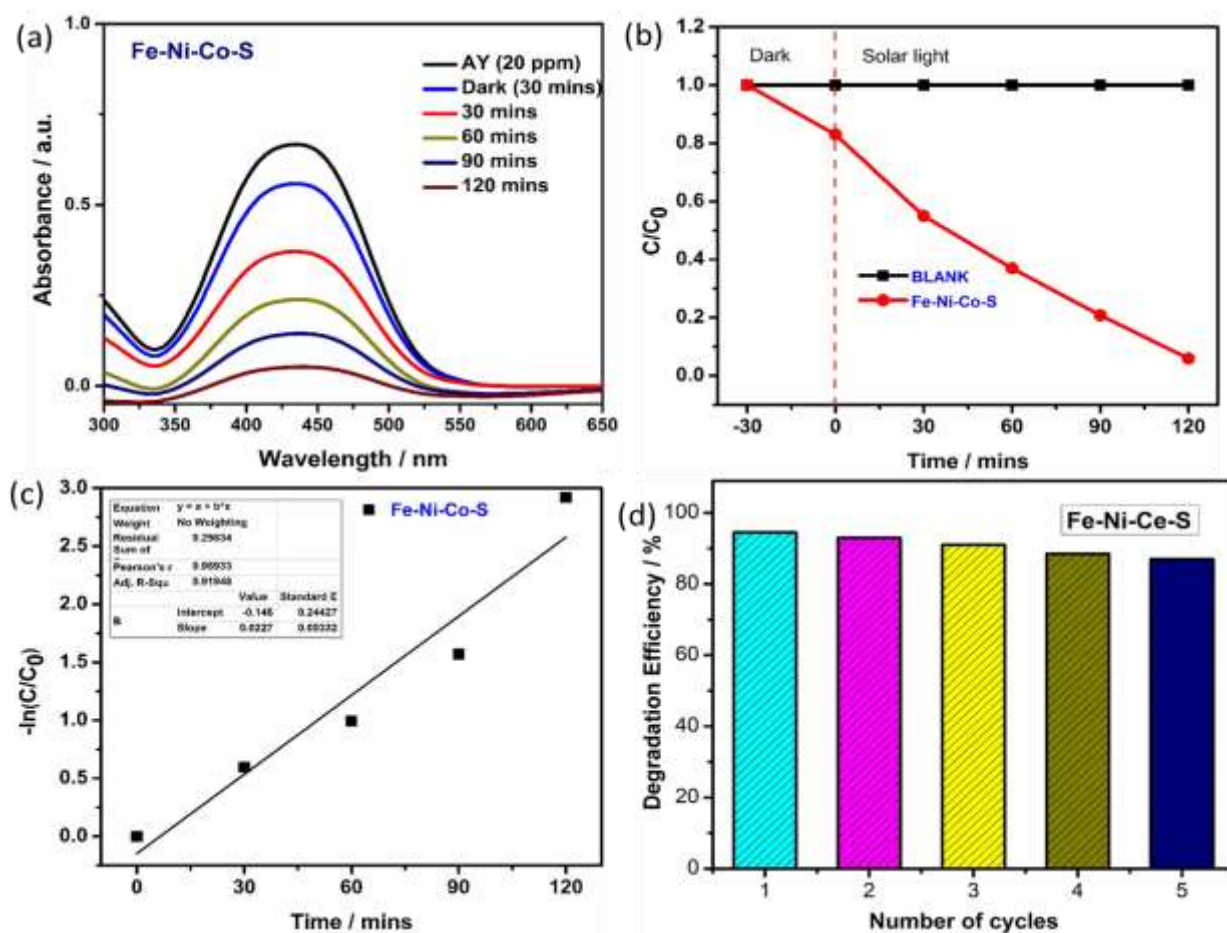


Figure.5.5 (a) represents the UV-visible spectra for the AY with occurrence of catalysts Fe-Ni-Co-S was irradiated by sun light for 120 minutes. (c) C/C_0 versus time interval plot of AY dye (d) $-\ln(C/C_0)$ versus time interval plot of AY dye (d) reusability test of AY dye solution

The significant improvement of the degradation efficiency is due to the presence of different metal and effective incorporation and energy level matching. Hence reduce the recombination of excited charge carriers (electron-hole pair) and higher energy absorption to produce large number of reactive oxygen species (ROS radicals).

Figure. 5.5 b depicts the changes in initial and final concentration of dye in the presence and absence of photocatalyst against the light irradiation with respect to time (t) for the AY dye solution. Addition investigation of pseudo-first order kinetics studies shown in Figure. 5.5c the degradation rates was 0.052 min^{-1} for Fe-Ni-Co-S nanoparticles against AY dye, respectively. From the studies rate constant value and R^2 values are listed in the Table.5.2. The Figure 5.6 showed schematic diagram

illustrating the mechanism of charge separation, generation of reactive oxygen species (ROS) and photocatalytic activity of photocatalyst under the sunlight irradiation [2].

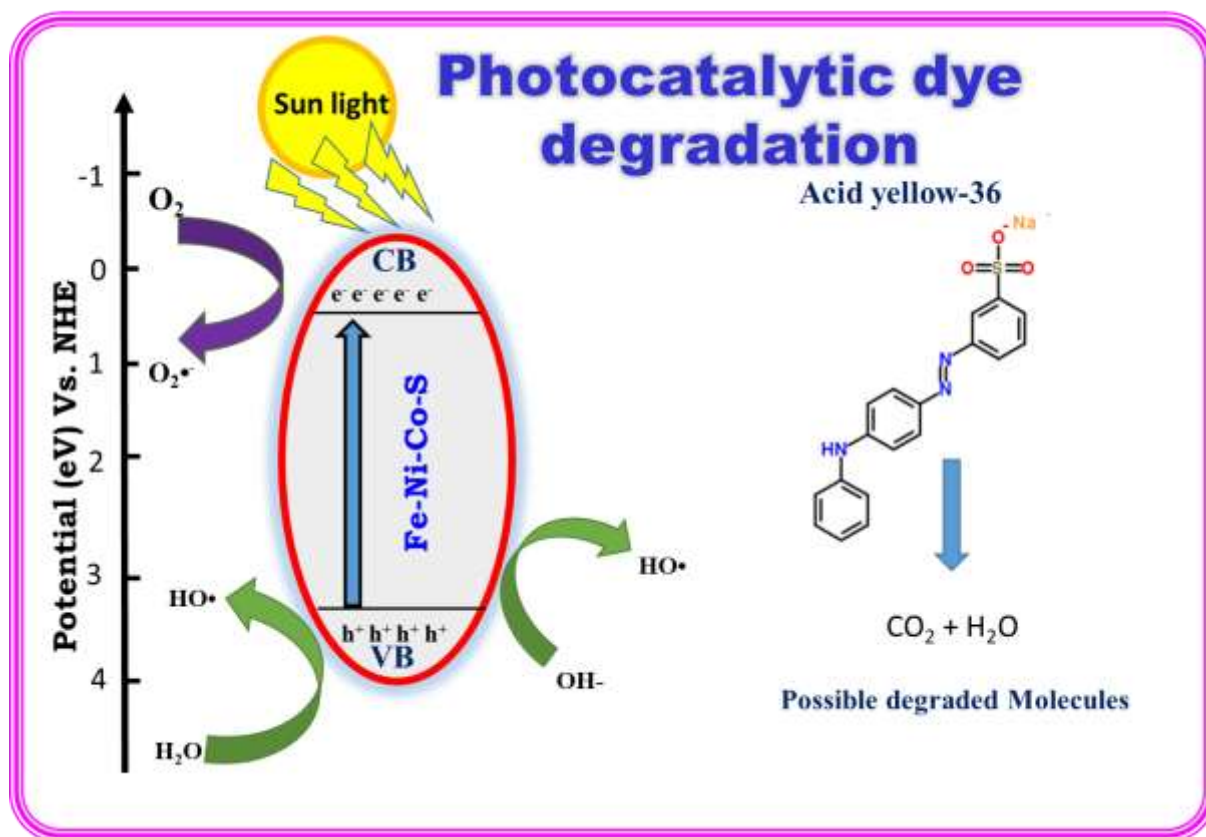


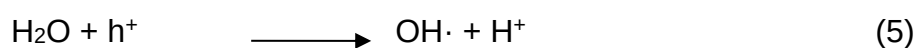
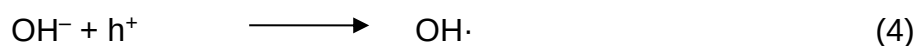
Figure. 5.6 Schematic diagram illustrating the mechanism of charge separation and photocatalytic activity of photocatalyst under the sunlight irradiation

The mechanism of AY dye degradation for the Fe-Ni-Co-S catalyst is described as follows,

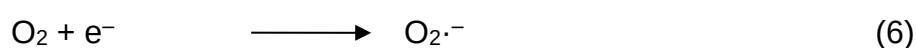
(i) Formation of electron hole pair



(ii) Formation of hydroxyl radicals



(iii) Formation of superoxide radicals



(iv) Photo degradation of AY dye



Table 5.2 photocatalytic activity result of NiO, and Ag/ Ni(OH)₂ nanoparticles.

S.No	Catalyst	Band gap (eV)	Degradation efficiency (%) (120 minutes)	K (min ⁻¹)	R ²
Acid yellow-36 (20 ppm)					
1	Fe-Ni-Co-S	1.49	94.5	0.052	0.91

SUMMARY AND CONCLUSION

- Sulfide nanocomposite have attracted much attention due to its applications in catalysis, dye degradation, electrode materials in battery and optoelectronic devices.
- Polyvinylpyrrolidone was used as surfactant to reduce particle size.
- Herein, low temperature based Fe-Ni-Co-S nanocomposite was
- Synthesized by a “one-pot” hydrothermal method.
- Equal concentration of precursors were used.
- Crystallite structure and size were confirmed by XRD. The size of the crystallite was calculated using Debye Scherrer formula, the size was found to be 21.3 nm
- The SEM microscopy demonstrated the synthesized nanoparticles were in nanoscale region with asymmetric surface morphology structure.
- Organic functional groups presence on the surface of the nanoparticles were identified using FT-IR spectroscopy.
- The investigated photocatalytic result demonstrated that Fe-Ni-Co-S nanocomposite showed excellent dye degradation of *Acid yellow-36* which is due to its effective charge carriers creation and followed by the free radical formation during the light irradiation.
- Thus, the prepared cost effective and low temperature Fe-Ni-Co-S could be the suitable candidate for water purification, through the photocatalysis process.

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