Chapter 2

Fundamental and Experimentation

2.1 Introduction:

This chapter deals with a brief description of nanomaterials synthesis methods such as hydrothermal/solvothermal and thermolysis method. The detailed description of design and fabrication of H$_2$S splitting set-up for hydrogen generation is presented. Also, the discussion on characterization of structural, optical, and magnetic properties of the synthesized products is provided.

2.2 Synthesis methods:

Over the past decade, scientists around the world have developed a wide variety of techniques and methods to synthesize nanomaterials of different sizes, shapes and forms. These have been well documented in several reviews in the literature. The synthesis of hierarchical nanostructures with controlled morphology employing the bottom-up approach is one of the major challenges in the field of nanoscience and technology. Particularly, the solution-phase synthesis routes (most commonly referred to as the soft chemistry approach or ‘chimie douce’) are an attractive over the physical routes for several reasons.

Herein, we focus only on the specific methods employed in the present work. These include the ‘hydrothermal’ approach is quite appropriate for well defined hierarchical nanostructures with the excellent control over the structure, morphology and its dimensions. Another important method is ‘thermolysis’, specifically used for controlled synthesis of core-shell nanorod.

2.2.1 Hydrothermal/Solvothermal method:

The hydrothermal technique has emerged as one of the powerful tools for advanced materials processing, particularly processing of nanostructural materials for a wide variety of technological applications. Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/or pressure. The temperature can be elevated above the boiling point of water, reaching saturated vapor pressure. The temperature and the amount of solution
added to the autoclave largely determine the internal pressure produced. The solvothermal method is almost identical to the hydrothermal method except that the solvent used here is non-aqueous. However, under solvothermal conditions, the temperature can be elevated much higher than that in the hydrothermal method, from a variety of organic solvents with high boiling points can be chosen. One of the outstanding characteristics of the solvothermal/hydrothermal method is that, when the starting materials (precursors) are exposed to special treatments, quite unexpected reactions take place, accompanied with the formation of well defined morphologies, which cannot be achieved by the classical reactions.

In literature, many different definitions have been used for hydrothermal synthesis. Byrappa and Yoshimura have defined hydrothermal as “any heterogeneous chemical reaction in the presence of a solvent above room temperature and at a pressure greater than 1 atm in a system” [1,2]. On the other hand according to Lobachev (1973) it is defined as a group of methods in which crystallization is carried out in superheated aqueous solutions at high pressures. Furthermore, Rabenau (1985) has defined hydrothermal reactions as heterogeneous reactions in aqueous media above 100°C and 1 bar pressure.

In the hydrothermal process, water at elevated temperatures plays an essential role in the transformation of the precursor material(s). The solubility and reactivity of the reactants also change at high pressure and high temperatures, and high pressure is favourable for crystallization of products. During the synthesis of nanocrystals, operational parameters such as pressure, temperature, reaction time, and the type of respective precursor-product system can be tuned to maintain a high simultaneous nucleation rate and good size distribution. Moreover, the nanometric morphologies can usually be controlled by varying the parameters in the reaction system, such as the choice of the solvents, capping reagents/surfactants, organometallic additives, reaction temperature, pH value, etc. Of course, there are several differences between solvothermal and hydrothermal methods. For example, the solvothermal method (using non-water as solvents) can effectively prevent the products from being oxidized, which is especially critical in the synthesis of a variety of non-oxides.
Advanced materials processing using hydrothermal technology has lots of advantages owing to the adaptability of the technique, which is also environmentally benign. The use of non-aqueous and a host of other mixed solvents employed in materials processing has brought down the operating temperature-pressure conditions.

Advantages of hydrothermal method are:

1. Powders are formed directly from solutions;
2. Powders can be anhydrous, crystalline or amorphous depending on processing parameters;
3. Good control on particle size and shape of the nanostructures;
4. Chemical composition, stoichiometry etc. can be controlled, and
5. In most of the cases, the as-synthesized powders do not require post treatments like calcination or milling.

To date, various visible light driven nanostructures have been synthesized by a number of researchers using hydrothermal/solvothermal synthesis.

In the present work, we have carried out hydrothermal and/or solvothermal route for synthesize ZnIn$_2$S$_4$ and N-doped TiO$_2$ nanostructures. Hydrothermal reactor is composed of Teflon-lined stainless steel autoclave (shown in Fig. 2.1). The used Teflon liners has a capacity of 200 ml with maximum temperature goes up to 200°C. The reactor was stable in acidic and basic conditions. This Teflon-Liner was easily inserted...
into the stainless steel autoclave. After this Teflon-lined stainless steel autoclave was kept in a laboratory oven with temperature programmable controllable. After completion of reaction, the as-synthesized products and substrate was washed and dried it.

During the hydrothermal synthesis, we varied the precursor’s concentration, solvent concentration, pH modifiers, hydrothermal temperature and period. The Teflon is resistant to many chemicals, outstanding performance at extreme temperatures, low coefficient of friction, non wetting and exceptional dielectric properties.

![Stainless steel autoclave with Teflon liner.](image)

**Fig. 2.1** Stainless steel autoclave with Teflon liner.

**2.2.2 Thermolysis method:**

In the present work we have carried out pyrolysis of Fe-complex to synthesize core-shell Fe$_2$O$_3$ nanomaterials. Thermolysis is a general route for synthesis of various nanostructures [3]. It is the one of the easiest route to synthesize these oxide forms and well control over the shape, size of nanostructures without any burning fuel. The advantage of pyrolysis is that the design of the process is simple, and also the operation of the process developed or adopted is easy. This process is also easily scalable. Control experimentations have been performed to synthesize core-shell $\alpha$-Fe$_2$O$_3$ ($\gamma$-Fe$_2$O$_3$) nanorods. Figure 2.2 shows the photo of a split-tube furnace that has been used for the thermolysis of Fe-complex in the current study.
2.3 Design and fabrication of experimental setup for H$_2$S splitting:

Photodecomposition of H$_2$S:

The photocatalytic reactions were carried out into cylindrical quartz photochemical reactor designed in-house (Fig.3). Reactor has arrangement for circulation of water to maintain the constant temperature throughout the reaction time. Xe lamp (200-500 W, LOT ORIEL GRUPPE, EUROPA, and LSH302) with 420 nm cut off filter ($\lambda \leq 420$ nm) was used as source. Known quantity of photocatalyst powder (0.5 gm) was dispersed in 700 ml KOH solution (0.25 M) and the suspension was homogenized by stirring it using magnetic stirrer. The suspended catalyst was then transferred into reactor followed by purging with argon. At a constant temperature (25°C), the suspended catalyst was flushed with argon gas for half an hour and then H$_2$S was bubbled through the solution at the rate of 1.6 ml min$^{-1}$ for 3 h. All the experiments were carried out under identical conditions. The excess hydrogen sulphide was trapped into the trap containing NaOH solution. The suspension was exposed to visible light for different time intervals. The amount of hydrogen gas evolved was collected into a graduated cylinder and measured. The evolved hydrogen was then analyzed for its purity using a gas chromatograph (Model Shimadzu GC-14B, MS-5 Å column, TCD, Ar carrier). The initial schematic of the photoreactor for the hydrogen generation using H$_2$S splitting is shown in Scheme 2.2.
Scheme 2.2 Design and schematic representation of H$_2$S splitting with photo-reactor

The H$_2$S is prepared using FeS and the HCl. This H$_2$S is collected in the empty trap which is then pass through the calcium chloride (CaCl$_2$) to absorb moisture and the chlorine vapour. Then it is bubbled into the photoreactor, which contained the 0.25 M KOH and 0.5 gm catalyst. In this reactor the K$_2$S and H$_2$ is formed and if the H$_2$S is escaped from this reactor then it is trapped in the next vessel that contains the 10% NaOH solution. The prepare H$_2$ gas is collected into the next trap. The Fig. 2.3 shows the actual photograph of the hydrogen generation set up.

![Photograph of fabricated experimental setup for H$_2$S splitting with indoor visible light source.](image-url)
2.4 Characterization techniques:

Lastly, a brief introduction of the various characterization techniques used for the analysis of structure, surface morphology, chemical composition, and optical properties, such as X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), UV-visible Spectroscopy (UV-Vis), Photoluminescence spectroscopy (PL), FTIR, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Mossbauer spectroscopy, Vibrating sample magnetometer (VSM), TGA/DTA analysis and Gas chromatography (GC) is given.

2.4.1 X-ray diffraction (XRD):

XRD is a non-destructive technique which reveals information about the crystallographic structure and physical properties of materials which are in the form of powder. X-rays have wavelengths of the order of an angstrom (Å =10^{-10} \text{m}), in the range of typical inter atomic distances in crystalline solids. Therefore, X-rays can be diffracted from the repeating patterns of atoms that are characteristic of crystalline materials. X-ray diffraction is based on the elastic scattering (that is the change of direction of the electromagnetic waves without any energy change).

The necessary condition for X-ray diffraction is to satisfy the Bragg’s law,

\[ 2d \sin \theta = n \lambda \]

X-ray radiation directed at the solid provides the simplest way to determine the crystal structure as well as inter atomic spacing that exists. XRD is known to be an absolute technique.

In the present work X-ray diffraction analysis of the as-synthesized products containing various nanostructures were performed using X-ray diffractometer (Model-D8 Advance, Bruker AXS) using CuKα (\lambda= 1.5402 Å) X-ray source.

2.4.2 Scanning electron microscope (SEM):

The SEM is most commonly used characterization technique for surface topographic studies of materials. With the SEM it is possible to obtain a secondary electron image of organic and inorganic materials which allow topographic and morphological studies, by scanning an electron probe across the surface and monitoring emitted secondary electrons. Compositional analysis of a material may also be obtained by monitoring X-
rays produced by the electron-specimen interaction. This detailed map of elemental distribution can be produced.

When the primary electrons hit the specimen, they give away part of their energy to the electrons in the specimen, resulting in emission of secondary electrons. These secondary electrons have lower energies (around 20 eV) and are collected by a suitable collector (an Everhart-Thornley detector). The output of the detector is amplified and used to build up an image. Scanning takes place at lower pressure, so that the electrons are not scattered by gas molecules inside the chamber.

In the present work FESEM analysis was carried out using Hitachi, S-4800. The microscope was operated at a different accelerating voltage namely ~ 5, 10, 15, 20 kV and filament current of ~10 µA.

2.4.3 Transmission Electron Microscope (TEM):

Transmission Electron Microscopy (TEM) is one of the most powerful techniques for obtaining information on the microchemistry, crystal structure on a microscale and defect structure of the crystalline materials. Because of the unique physical and chemical properties of nanomaterials which not only depend on their compositions but also in their structures, TEM provides opportunities for characterizing and understanding of such structures. High resolution TEM (HRTEM) is capable of providing atomic resolution lattice images. In case of HRTEM the images are formed due to the difference in phase of electron waves scattered through a thin specimen. The emergence of HRTEM has allowed the direct reconstruction of Bragg differential electron beams to create interference patterns [4].

A conventional electron microscope operates in a vacuum of $10^{-5}$ torr or less. The most common types of TEM have thermionic guns capable of accelerating the electrons through a selected potential difference in the range of 40-200 kV. The appropriate electron energy depends upon the nature of the specimen and the information required [4]. Typical maximum specimen thickness values are 0.1–0.3 µm for 100 keV [5]. Below the electron gun are two or more condenser lenses. Together, they demagnify the beam emitted by the gun and control its diameter (about 1 to 50 µm) thus the intensity of illumination. As a result parallel, coherent beam of electrons passes through the specimen. The objective lens is so strong that the specimen sits within its pole pieces. The role of the objective lens is to form the first intermediate image and diffraction
patterns, one or other of which is enlarged by the subsequent projector lenses and displayed on the viewing screen. An essential feature of the objective system is the aperture. The objective aperture clearly defines the angular range of scattered electrons which can travel further down the column and contribute to the image. The first image produced by the objective lens usually has a magnification of 50-100 times. This is further magnified by a series of intermediate and projector lenses and is finally projected onto the fluorescent screen. By using three or four lenses, each providing a magnification of up to twenty times, a total magnification of up to one million is easily achieved [4].

Electron emitted from the e-gun can traverse the specimen without any interaction (unscattered electrons) or can be scattered, elastically or inelastically.

2.4.3.1 Bright field imaging:

If a specimen is thin enough to form a useful image in the TEM we can assume that, except for a few which are backscattered, primary electrons that enter the top of the specimen will emerge from the bottom. However, their angular range and energy spread will have been affected by elastic and inelastic scattering within the specimen. The effect of an aperture in the back focal plane of the objective lens is thus to stop all electrons which have been scattered by any mechanism, through an angle greater than $\alpha$ (or to stop all diffracted beams and only permits undeflected electrons to contribute to the image) as shown in Fig. 2.6. If the aperture is centred about the optical axis, as shown in the Fig. 2.6, then in the absence of a specimen a bright background is seen. This is known as bright field imaging [4]. Regions of the specimen which are thicker, or of higher density, will scatter more strongly (i.e. more electrons will be deflected through an angle greater than $\alpha$) and will appear darker in the image.
Fig. 2.6 Schematic diagram of Bright field imaging.

2.4.3.2 Dark field imaging:

On the other hand, if the aperture is displayed it can be used to select a particular diffracted beam. This is known as dark field imaging since in the absence of a specimen the background appears to dark. Thus, the TEM has a capability for creating both electron microscope images (information in real space) and diffraction patterns (information in reciprocal space) for the same region [4].

In the present study TEM and HRTEM analysis was carried out using Technai, G² 20 S – Twin (FEI, Netherlands), at National Chemical Laboratory, Pune, India. The usual method to prepare the specimens for TEM observations was employed. The specimen was scratched and the product thus obtained was sonicated in acetone. A drop of acetone containing the nanostructures was placed on the TEM grid.

2.4.4 X-ray Photoelectron Spectroscopy (XPS):

XPS or more commonly known Electron spectroscopy for chemical analysis (ESCA) is important and powerful technique for the characterization of materials. XPS helps to know the chemical and electronic states in the system, by characterizing first few layers of the specimen. Hence the chemical bond, chemical composition and empirical formulas can be judged by XPS. The XPS principle is based on the photoelectric effect, in which electrons are ejected from the surface by incident X-rays. In the typical XPS, X-rays are produced from Kα emission of magnesium (Kα=1253.56
eV) or aluminium ($K\alpha=1486.58$ eV). The X-rays strike the sample surface and interact with the atomic electrons in the sample via photon absorption [5].

In the present case, analysis of the ZnIn$_2$S$_4$ and N-doped TiO$_2$ nanostructures was carried out using Microtech ESCA-LAB 3000 spectrometer manufactured by VG Scientific, UK. The instrument is with twin anode X-ray source. A concentric hemispherical analyzer was used to analyze the emitted photoelectrons.

2.4.5 **Ultra Violet-Visible Defuse Reflectance Spectroscopy (UV-vis DRS):**

The UV-visible spectrophotometer consists of a light source, a monochromator, and a detector. The light source is usually a deuterium lamp, which emits electromagnetic radiation in the ultraviolet region of the spectrum. A second light source, a tungsten lamp, is used for wavelengths in the visible range of the spectrum. The monochromator is a diffraction grating which splits beam light in the component wavelengths. The present slits focus the desired wavelength on the sample. The light passes through the sample cell and reaches suitable photodetector (photomultiplier tube/photodiodes), which record the intensity of transmitted light. In the typical double beam instrument, light beam splits in two beams, the sample beam and reference beam [6].

The UV-vis DRS measurements of these samples were carried out on a PerkinElmer Spectrum (Model – PerkinElmer, Lambda 950). The spectra recorded in the wavelength range 200-800 nm for each specimen.

2.4.6 **Photoluminescence (PL):**

Photoluminescence (PL) spectroscopy is an effective method to evaluate the nature of transitions and defects in materials. PL is a non-destructive and contact less spectroscopic method. In a typical process light is illuminated on the specimen, which is absorbed by the material (specimen), and upon de-excitation, light is emitted by the specimen known as photo-excitation, and this mechanism is generally known as photoluminescence. As depicted in Fig. 2.7 the corresponding processes are summarized which take place on illumination of light.
Electrons and holes can recombine through a number of processes:

1) electron hole pair photo-generation,

2) recombination through recombination centres,

3) band-to-band (excitons) recombination,

4) hole emission processes which are shown in the Fig. 2.7 given below,

In a typical process if the carriers recombine radiatively, the energy of the emitted light can be analyzed to determine the energy of the defect or impurity level. Levels near to the conduction or the valence band edges are more likely to participate in radiative recombination. Deep levels are involved in non-radiative recombination by providing a stop-over for electrons making their way between the conduction and valence band by emitting photons.

In the detailed experimentation of the PL, high pressure Xenon (Xe) arc lamp is used. The Xe lamp emits an intense and relatively stable continuum from 300 to 1100 nm. A primary filter or excitation monochromator in the excitation path selects specific wavelengths or bands and directs them to the specimen to be analysed. The PL study of this work was done using a Perkin-Elmer-LS-55. The excitation wavelength was ~ 325 nm.

**2.4.7 Fourier Transform Infrared Spectroscopy (FTIR):**

Infrared spectrum appears only when the vibrations amongst bonded atoms produces a change in the permanent electric dipole moment of the molecule/solid. It is reasonable to suppose that the more polar a bond, the more intense will be IR spectrum arising from the vibrations of that bond. IR spectrophotometer consists of mainly source,
monochromator and detector [8,9]. The source is in some form of filament (e.g. Nernst Filament, made of a spindle of rare earth oxides or globar filament, made of carborundum rod) which is maintained at red- or white-heat by an electric current. The monochromator guides IR beam and focuses to the sample. The detectors are based on either temperature (bolometer/thermometer) or conductivity rise at given frequency (PbS).

Fourier Transform IR Spectroscopy: FTIR has considerably speeded and improved the spectroscopy in the IR region in general and in particular far IR region i.e. below 400 cm\(^{-1}\) where good deals of useful molecular information is contained, is usually called as ‘Energy Limited’ region, where sources become weak and detectors insensitive, resulting poor signal to noise ratio.

Figure 2.8 shows the schematic of FTIR spectrophotometer. The apparatus derives from the classical attempt by Michelson to measure the ‘ether wind’ by determining the velocity of light in two perpendicular directions. A parallel beam of radiation is directed from the source to the interferometer, consisting of the beam splitter B and two mirrors, \(M_1\) and \(M_2\). The beam splitter is a plate of suitably transparent material (e.g. KBr) so as to reflect just 50% of the radiation falling on it. Thus half the radiation goes to \(M_1\), and half to \(M_2\), returns from both these mirrors along the same path, and is then recombined to a single beam at the beam splitter (clearly half the total radiation is sent back to the source, but this is immaterial). It is well known (and the essence of the Michelson experiment) that if monochromatic radiation emitted by the source, the recombined
beam leaving B shows constructive or destructive interference, depending on the relative path lengths B to M\textsuperscript{1} and B to M\textsuperscript{2}. Thus if the path lengths are identical or differ by integral multiple of wavelengths, constructive interference gives bright beam leaving B, whereas if the difference is a half integral number of wavelengths, the beam cancels at B. As the mirror M\textsuperscript{2} is moved smoothly away or towards from B, therefore, a detector sees radiation alternating in intensity. It is fairly easy to imagine that if the source emits two separate monochromatic frequencies, υ\textsubscript{1} and υ\textsubscript{2} then interference pattern of υ\textsubscript{1} and υ\textsubscript{2} would overlay the interference caused by M\textsuperscript{1} and M\textsuperscript{2}; the detector would see a more complicated intensity fluctuation as M\textsuperscript{2} is moved, but computing the Fourier transform of the resultant signal is very rapid way of obtaining the original frequencies and intensities emitted by the source. Taking the process further, even white radiations emitted by the source produces an interference pattern which can be transformed back to the original frequency distribution.

The production of a spectrum is a two-stage process: (a) Without a sample in a beam, mirror M\textsuperscript{2} is moved smoothly over period of time (say one second) through a distance of about 1 cm, while the detector signal – the interferogram – is collected into multi-channel computer; the computer carries out the Fourier transformation of the stored data to produce background spectrum. (b) A sample interferogram is recorded in exactly the same way, Fourier transformed, and then ratioed against the background spectrum for plotting as transmittance spectrum. Alternatively, the sample and background spectra may each be calculated in absorbance forms and the latter simply subtracted from the former to give an absorbance spectrum of the sample alone. The advantage of using FTIR is that the whole spectrum is obtained across the entire frequency range at once with constant resolving power over entire range.

Powdered samples were mixed with the standard KBr powder. The FTIR measurements of these samples were carried out on a Perkin Elmer Spectrum One FTIR spectrometer operated in the diffuse reflectance mode at a resolution of 4 cm\textsuperscript{-1} at National Chemical Laboratory, Pune, INDIA.

### 2.4.8 Raman Spectroscopy:

When a beam of visible light is passed through a transparent substance, a small amount of the radiation energy is scattered, the scattering persisting even if all other extraneous matter are rigorously excluded from the substance. If monochromatic
radiation is used, if the scattered energy will consist almost entirely of radiation of the incident frequency then it is so-called Rayleigh scattering but, in addition, certain discrete frequencies above and below that of the incident beam will be scattered, it is referred to as Raman scattering [8].

According to quantum theory of radiation, when photons having energy ‘h\(\nu\)’ undergo collisions with molecules and, if the collision is perfectly elastic, they will be deflected unchanged. A detector placed to collect energy at right angles to an incident beam will thus receive photons of energy ‘h\(\nu\)’, i.e. radiation of frequency ‘\(\nu\)’. However, it may happen that energy is exchanged between photon and molecule during the collision: such collisions are ‘inelastic’. The molecule can gain or lose amounts of energy only in accordance with the quantum laws; i.e. its energy change, \(\Delta E\) joules, must be the difference in energy between two of its allowed states. That is to say, \(\Delta E\) must represent a change in the vibrational and/or rotational energy of the molecule. If the molecule gains energy \(\Delta E\), the photon will be scattered with the energy h\(\nu\)-\(\Delta E\) and the equivalent radiation will have a frequency \(\nu - \Delta E/h\). Conversely, if the molecule loses energy \(\Delta E\), the scattered frequency will be \(\nu + \Delta E/h\). Radiations scattered with a frequency lower than that of the incident beam is referred to as Stokes’ radiation, while that at higher frequency is called anti-stokes’ radiation. Since the former is accompanied by an increases in molecular energy (which can always occur, subject to certain selection rules) while the latter involves a decrease (which can only occur when the molecule is originally in an excited vibrational/rotational state). Stokes’ radiation is generally more intense than anti-Stokes’ radiation.

![Fig. 2.9 Schematic of Raman spectrometer.](image)
Chapter 2

Figure 2.9 shows the schematic of Raman spectrometer. Raman Spectrometer consists of Laser beam (very narrow, monochromatic, coherent and powerful) which when passed through the cell, usually a narrow glass or quartz tube filled with the sample, light get scattered sideways from the sample, which is collected by a lens and passed into a grating monochromator. The signal is measured by a sensitive PMT and after amplification; it is usually processed by a computer which plots the Raman spectrum. Raman spectroscopy measurements were done on instrument (Confocal micro-Raman spectrometer LabRAM ARAMIS Horiba Jobin-Yvon apparatus with laser excitation wavelength of 532 nm) in France.

2.4.9 Mössbauer Spectroscopy:

Mössbauer spectroscopy is a versatile technique that can be used to provide information about the chemical, structural and magnetic properties of a material [10]. Key to the success of the technique is the discovery of recoilless $\gamma$-ray emission and absorption, referred to as the “Mössbauer Effect” [11]. Certain nuclei embedded in a solid matrix can emit or absorb $\gamma$-rays with no recoil, giving rise to resonant nuclear $\gamma$-ray absorption. Nuclei in atoms undergo a variety of energy level transitions, often associated with the emission or absorption of $\gamma$-rays. These energy levels are influenced by their surrounding environment, both electronic and magnetic, which can change or split these energy levels (Fig. 2.10). These changes in energy levels can be probed using Mössbauer spectroscopy as the sensitivity of this technique is 1 eV in 1013 eV.

When source and absorber atoms are in different local environments, their nuclear energy levels are different (Fig. 2.10). At its simplest (blue), this appears in the transmission spectrum as a shift of the minimum away from zero velocity; this shift is called isomer shift (IS or $\delta$). The 1/2 and 3/2 labels represent the nuclear spin, or intrinsic angular moment, quantum numbers, ‘I’. Interaction of the nuclear quadrupole moment with the electric field gradient leads to splitting of the nuclear energy levels (red). For $^{57}$Fe, this causes individual peaks in the transmission spectrum to split into doublets (red) having a quadrupole splitting (QS or $\Delta$). When a magnetic field is present at the nucleus, Zeeman splitting takes place, yielding a sextet pattern (green) and the internal magnetic field $B_{hf}$; in the simplest case, the areas of the lines vary in the ratio of 3:2:1:1:2:3.
So Mössbauer spectra are described using three parameters: isomer shift ($\delta$), which arises from the difference in s electron density between the source and the absorber, quadrupole splitting ($\Delta$ which is a shift in nuclear energy levels that is induced by an electric field gradient caused by nearby electrons, and hyperfine splitting (for magnetic materials only). Graphically, quadrupole splitting is the separation between the two component peaks of a doublet, and isomer shift is the difference between the midpoint of the doublet and zero on the velocity scale (Figure). So, these changes in the energy levels can provide information about the atom's local environment within a system. Mössbauer spectroscopy can only be applied to a relatively small group of atoms $^{57}$Fe is by far the most common element studied using the technique.

*Fig. 2.10 shows the schematics of Mossbauer spectrometer and nuclear energy level splitting.*

Figure 2.10 shows the schematics of Mossbauer spectrometer and nuclear energy level splitting. The experiment was performed in transmission mode with a $^{57}$Co(Rh) source in a Wissel spectrometer. The solid sample is exposed to the beam of $\gamma$ radiation, and a detector measures the intensity of the beam that is transmitted through the sample. The $\gamma$-ray energy is varied by accelerating the gamma-ray source through a range of velocities with a linear motor. The relative motion between the source and sample results in an energy shift due to the Doppler effect (change in the apparent frequency of a wave as observer and source move toward or away from each other).
In the resulting spectra, gamma-ray intensity is plotted as a function of the source velocity. The source velocity is calibrated by means of a reference sample, metallic iron \( (B_{hf} = 33T) \). At velocities corresponding to the resonant energy levels of the sample, some of the gamma-rays are absorbed, resulting in a drop in the measured intensity and a corresponding dip in the spectrum. The number, positions, and intensities of the peaks provide information about the chemical environment of the absorbing nuclei and can be used to characterize the sample. The spectra as then computer-fitted assuming a Lorentzian line shape and isomer shifts are given relative to metallic iron. Mössbauer parameters are temperature-sensitive, and this characteristic is exploited by using lower temperatures to improve peak resolution and induce interesting magnetic phenomena. A Janis cryostat was used. Mossbauer spectroscopy was performed using \(^{57}\)Co(Rh) \( \gamma \)-ray source and \( \alpha \)-Fe foil as the standard for calibration. Measurements on magnetite-oxide composite were done at Dept. of Physics, Rouv University, France.

### 2.4.10 BET Surface Area Measurement:

The specific surface area of a material can be analyzed by BET surface area analyzer. The BET theory accounts for the physical adsorption of gas molecules on a solid surface and thereby serves as an important analysis technique for the measurement of the specific surface area of a material [12]. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory. The word “BET” consists of the first initials of their family names. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by following equation.

\[
\frac{1}{v \left( \frac{P}{P_0} \right) - 1} = \frac{e - 1}{v_m c} \left( \frac{P}{P_0} \right) + \frac{1}{v_m c}
\]

Where \( P \) and \( P_0 \) are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, \( v \) is the adsorbed gas quantity (for example, in volume units), \( v_m \) is the monolayer adsorbed gas quantity and \( c \) is the BET constant, which is expressed by following equation.

\[
e = \exp \left( \frac{E_1 - E_L}{RT} \right)
\]

\( E_1 \) is the heat of adsorption for the first layer, and \( E_L \) is that for the second and higher layers and is equal to the heat of liquefaction. Equation (1) is an adsorption...
isotherm and can be plotted as a straight line with $1/v[(P_0/P)-1]$ on the $y$-axis and $\phi = P/P_0$ on the $x$-axis according to experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of $0.05 < P/P_0 < 0.35$. The value of the slope ($A$) and the $y$-intercept ($I$) of the line are used to calculate the monolayer adsorbed gas quantity $v_m$ and the BET constant $c$. The following equations can be used.

$$v_m = \frac{1}{A + I} \quad c = 1 + \frac{A}{I}$$

Total surface area $S_{\text{total}}$ and a specific surface area ($S$) are evaluated by the following equations, where $v_m$ is in units of volume which are also the units of the molar volume of the adsorbate gas, $N$ is Avogadro's number, $s$ is adsorption cross section of the adsorbing species, $V$ is molar volume of adsorbate gas and $a$ is mass of adsorbent (in g).

$$S_{\text{BET, total}} = \frac{(v_m N_s)}{V} \quad S_{\text{BET}} = \frac{S_{\text{total}}}{a}$$

BET surface area measurements of different samples were carried out on a Quadrasorb-SI instrument at National Chemical Laboratory, Pune. This is a state-of-the-art, high-performance Surface Area Analyzer and Pore Size Analyzer with four independent analysis stations.

### 2.4.11 Thermogravimetric Analysis (TGA/DTA):

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% $O_2$ in $N_2$ or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry, or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process. In the particular case of carbon nanotubes, the weight change in an air atmosphere is typically a superposition of the weight loss due to oxidation of carbon...
into gaseous carbon dioxide and the weight gain due to oxidation of residual metal catalyst into solid oxides.

Materials analyzed by TGA include polymers, plastics, composites, laminates, adhesives, food, coatings, pharmaceuticals, organic materials, rubber, petroleum, chemicals, explosives and biological samples.

**2.4.12 Vibrating Sample Magnetometer (VSM):**

A vibrating sample magnetometer or VSM is instrument that measures magnetic properties. A sample is placed inside a uniform magnetic field to magnetize the sample. The sample is then mechanically vibrated at constant frequency of 1 kHz frequent in vertical plane. The induced voltage in the pickup coil is proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup shown in Fig. 2.9, the induced voltage is measured through the use of a lock-in amplifier using the vibrating frequency signal as its reference signal. By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material [12].

VSM operates by first placing the sample to be studied in a constant magnetic field. If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins, with the field. The stronger the constant field, the larger the magnetization will be.
The magnetic dipole moment of the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. As the sample is moved up and down, this magnetic stray field is changing as a function of time and can be sensed by a set of pick-up coils. The alternating magnetic field will cause an electric field in the pick-up coils according to Faraday's Law of Induction. This current will be proportional to the magnetization of the sample. In present study VSM was performed on a Lakeshore 7307.

2.4.13 Gas Chromatography (GC):

Gas-chromatographic analysis of gaseous mixtures containing hydrogen with helium as a carrier gas is easily achieved qualitatively, as well as quantitatively. Hydrogen has a very high thermal conductivity, higher than the other gases used as carriers in gas chromatography. It is based on the comparison of two gas streams, one containing only the carrier gas, the other one the carrier gas and the compound. Naturally, a carrier gas with a high thermal conductivity e.g. helium or hydrogen is used in order to maximize the temperature difference (and therefore the difference in resistance) between two thin tungsten wires. The large surface-to-mass ratio permits a fast equilibration to a steady state. The temperature difference between the reference cell and the sample cell filaments is monitored by a Wheatstone bridge circuit.

In the present study the photocatalytic hydrogen evolved in the quartz reaction cell was sampled in a gas tight syringe and analyzed periodically by using a gas chromatograph (Model Shimadzu GC-14B, Ar carrier), equipped with a 2.5 m column packed with MS-5Å and thermal conductivity detector maintained at 355 K.

2.4.14 Gas Chromatography-Mass Spectroscopy (GC-MS):

Gas chromatography coupled to mass spectrometry is a versatile tool to separate, quantify and identify unknown (volatile) organic compounds and permanent gases. By combining sensitivity and a high resolving power, complex mixtures can be analyzed. The information obtained can be used for detection of impurities, contamination control and improvement of, for example, semiconductor manufacturing processes. GC can separate volatile and semivolatile compounds with great resolution, but it cannot identify them. MS can provide detailed structural information on most compounds such that they can be exactly identified, but it cannot readily separate them. Therefore, it was not surprising that the combination of the two techniques was suggested shortly after the
development of GC in the mid-1950s. Gas chromatography and mass spectrometry are, in many ways, highly compatible techniques. In both techniques, the sample is in the vapor phase, and both techniques deal with about the same amount of sample.
References


