The synthesis and characterization of material is the first and foremost important step during the experimental research. This chapter describes the preparation of various nanocomposites and the experimental techniques employed for their physico-chemical characterization. This chapter will focus on the most effective and widely used techniques available to characterize solid-state compounds. The primary objective of this chapter is to provide a practical description of the methods used to characterize a broad range of materials.

2.1. Introduction

Characterization of materials regarding composition, trace impurities, structural phase and crystallographic perfection is vital for repeated reproduction of materials with stringently defined specifications, their applications as well as for fundamental research [1, 2]. The synthesis and characterization of material is the first and foremost step during the experimental research in materials science. The quality of samples depends to a great extent on the synthesis method used. In addition, the proper selection of synthesis parameters helps to carry out desired properties in the samples to be characterized along with desired potentials. Structure, surface morphology,
grain growth, transport of electrons within material and magnetic properties depend on material synthesis. When a material is fabricated in the lab, how are we able to assess whether our method was successful? Depending on the nature of the material being investigated, a suite of techniques may be utilized to assess its structure and properties. Whereas some techniques are qualitative, such as providing an image of a surface, others yield quantitative information such as the relative concentrations of atoms that comprise the material.

2.2. Synthesis of the Hybrid Nanocomposite

2.2.1. Chemicals used for the synthesis

The chemicals used for the synthesis are listed below in Table 2.1.

<table>
<thead>
<tr>
<th>SI.No.</th>
<th>Chemical</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Titanium tetra Isopropoxide</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2</td>
<td>Glacial Acetic acid</td>
<td>MERCK</td>
</tr>
<tr>
<td>3</td>
<td>Ammonia solution (28%)</td>
<td>Qualigen</td>
</tr>
<tr>
<td>4</td>
<td>P-123- poly(ethylene oxide)-poly(propylene oxide)- poly(ethylene oxide)Pluronic 123</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>5</td>
<td>Con.HCl</td>
<td>SDFCL</td>
</tr>
<tr>
<td>6</td>
<td>Aniline</td>
<td>SD Fine Chemicals</td>
</tr>
<tr>
<td>7</td>
<td>Pyrrole</td>
<td>SPECTROCHEM</td>
</tr>
<tr>
<td>8</td>
<td>Thiophene</td>
<td>SPECTROCHEM</td>
</tr>
<tr>
<td>9</td>
<td>Ammonium peroxodisulphate(APS)</td>
<td>MERCK</td>
</tr>
<tr>
<td>10</td>
<td>Anhydrous FeCl₃</td>
<td>MERCK</td>
</tr>
<tr>
<td>11</td>
<td>Acetonitrile</td>
<td>SPECTROCHEM</td>
</tr>
<tr>
<td>12</td>
<td>Methanol</td>
<td>SPECTROCHEM</td>
</tr>
</tbody>
</table>

2.2.2. Synthesis of mesoporous TiO₂

Pure titania is prepared by surfactant assisted hydrothermal route. In this method a fixed amount of the surfactant, P123 is dissolved in a calculated amount of distilled water. Titania sol is prepared by taking 10 ml of titanium
Materials and Methods

tetraisopropoxide along with 20 ml of acetic acid in a beaker with addition of
100 ml of distilled water dropwise and the system is under stirring. The titania
sol is then added to the surfactant solution dropwise under stirring. The
mixture is then sonicated for one hour. It is then transferred into an autoclave
and kept in an oven at 110°C for overnight. After that the mixture is filtered,
washed with water, dried at 110°C and calcined at 500°C for 5 hrs. It is then
powered to get mesoporous titania.

2.2.3. Synthesis of Polyaniline - TiO₂ hybrid nanocomposite

*Titania-Polyaniline Composites (TP)*

2 g TiO₂ was taken in a beaker along with 100 ml 1 M HCl solution and
3.3 ml of distilled aniline. The mixture was kept under stirring in an ice bath
with a magnetic stirrer and ammonium peroxodisulphate solution (12.5 g in
100 ml distilled water) was added drop by drop. The mixture was sonicated for
about 1 hour and then transferred to an autoclave and placed in an oven for
overnight at 110°C. It was filtered, washed with water and acetone to remove
unreacted aniline, dried in an oven at 110°C. Different compositions were
prepared by changing the amount of aniline (TP1, TP2 and TP3).

2.2.4. Synthesis of Polypyrrole- TiO₂ hybrid nanocomposite

*Titania-Polypyrrole Composites (TPpy)*

2 g TiO₂ was taken in a beaker along with 3.6 ml of distilled pyrrole in
10 ml of distilled water. The mixture was kept under stirring in an ice bath
with a magnetic stirrer and FeCl₃ solution (8.415g in 100 ml distilled water)
was added drop by drop. The mixture was sonicated for about 1 hour and then
transferred to an autoclave and placed in an oven for overnight at 110°C. It
was filtered, washed with water and acetone to remove unreacted pyrrole,
dried in an oven at 110°C. Different compositions were prepared by changing the amount of pyrrole (TPpy1, TPpy2 and TPpy3).

2.2.5. Synthesis of Polythiophene- TiO₂ hybrid nanocomposite

*Titania-Polythiophene Composites (TPth)*

2 g TiO₂ was taken in a beaker along with 3.1 ml of distilled thiophene in 5 ml of acetonitrile. The mixture was kept under stirring in an ice bath with a magnetic stirrer and FeCl₃ solution (6.275 g in 100 ml acetonitrile) was added drop by drop. The mixture was sonicated for about 1 hour and then transferred to an autoclave and was kept in an oven for overnight at 110°C. It was filtered, washed with water and acetone to remove unreacted thiophene, dried in an oven at 110°C. Different compositions were prepared by changing the amount of thiophene (TPth1, TPth2 and TPth3).

The nanocomposite systems prepared for the present work with its notations are listed in Table 2.2.

<table>
<thead>
<tr>
<th>SI.No.</th>
<th>System</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO₂</td>
<td>T</td>
</tr>
<tr>
<td>2</td>
<td>Polyaniline- TiO₂ (1:4 molar ratio of aniline and TiO₂)</td>
<td>TP1</td>
</tr>
<tr>
<td>3</td>
<td>Polyaniline- TiO₂ (1:2 molar ratio of aniline and TiO₂)</td>
<td>TP2</td>
</tr>
<tr>
<td>4</td>
<td>Polyaniline- TiO₂ (1:1 molar ratio of aniline and TiO₂)</td>
<td>TP3</td>
</tr>
<tr>
<td>5</td>
<td>Polypyrrole- TiO₂ (1:4 molar ratio of pyrrole and TiO₂)</td>
<td>TPpy1</td>
</tr>
<tr>
<td>6</td>
<td>Polypyrrole- TiO₂ (1:1 molar ratio of pyrrole and TiO₂)</td>
<td>TPpy2</td>
</tr>
<tr>
<td>7</td>
<td>Polypyrrole- TiO₂ (1:1 molar ratio of pyrrole and TiO₂)</td>
<td>TPpy3</td>
</tr>
<tr>
<td>8</td>
<td>Polythiophene- TiO₂ (1:1 molar ratio of thiophene and TiO₂)</td>
<td>TPh1</td>
</tr>
<tr>
<td>9</td>
<td>Polythiophene- TiO₂ (1:1 molar ratio of thiophene and TiO₂)</td>
<td>TPh2</td>
</tr>
<tr>
<td>10</td>
<td>Polythiophene- TiO₂ (1:1 molar ratio of thiophene and TiO₂)</td>
<td>TPh3</td>
</tr>
<tr>
<td>11</td>
<td>Polyaniline</td>
<td>PANI</td>
</tr>
<tr>
<td>12</td>
<td>Polypyrrole</td>
<td>Ppy</td>
</tr>
<tr>
<td>13</td>
<td>Polythiophene</td>
<td>Pth</td>
</tr>
</tbody>
</table>
2.3. Material Characterization Techniques

The properties of hybrid nanocomposites result from the complex cooperation between the organic and inorganic species constituting the nanocomposites. Continuously, increasing demand for the detailed knowledge of such properties at the nanoscale has contributed to the development of the characterization techniques. By using appropriate combination of analysis techniques, the desired characterization on the atomic as well as bulk scale is certainly possible. A thorough characterization of the prepared nanocomposites was undertaken using different spectroscopic as well as quantitative methods. A brief discussion of the characterization method along with its experimental aspects is given in the following sections.

2.3.1. X-Ray Diffraction Analysis

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions [3]. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. The analyzed material is finely ground, homogenized, and average bulk composition is determined [4]. About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline substance (Phase), one gets a diffraction pattern [5].
In 1919 A.W.Hull gave a paper titled, “A New Method of Chemical Analysis”. Here he pointed out that “….every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others [6]. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance [5]. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample [7]. An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions we will have destructive interference, that is, the combining waves are out of phase and there is solid sample [8]. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions we will have constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another.
Materials and Methods

Fig. 2.1. Schematic of X-Ray Diffractometer

Only crystallites having reflecting planes \((h, k, l)\) parallel to the specimen surface will contribute to the reflected intensities. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of \(2\theta\) angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

Fig. 2.2. Schematic diagram of XRD process
Applications

The most common use of powder (polycrystalline) diffraction is chemical analysis. This can include phase identification (search/match), investigation of high/low temperature phases, solid solutions and determinations of unit cell parameters of new materials. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology. Other applications include: characterization of crystalline materials, identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions, measurement of sample purity etc. Some of the strengths and limitations of XRD technique are listed below [9].

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Powerful and rapid (&lt; 20 min) technique for identification of an unknown mineral.</td>
<td>1. Homogeneous and single phase material is best for identification of an unknown sample.</td>
</tr>
<tr>
<td>2. In most cases, it provides an unambiguous mineral determination.</td>
<td>2. Must have access to a standard reference file of inorganic compounds (d-spacings, hkl’s).</td>
</tr>
<tr>
<td>3. Minimal sample preparation is required.</td>
<td>3. Requires tenths of a gram of material which must be ground into a powder.</td>
</tr>
<tr>
<td>4. XRD units are widely available.</td>
<td>4. For mixed materials, detection limit is ~ 2% of sample.</td>
</tr>
<tr>
<td>5. Data interpretation is relatively straight forward.</td>
<td>5. For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated.</td>
</tr>
<tr>
<td></td>
<td>6. Peak overlay may occur and worsens for high angle 'reflections'.</td>
</tr>
</tbody>
</table>
Materials and Methods

For mesoporous materials reflections are observed in X-ray powder patterns at low 2θ angles (0.5 20 10°). These reflexes are due to the long range order induced by the very regular arrangement of the pores. Generally the d-spacing of the mesopores are rather big so the X-ray diffraction at low angles are observed.

XRD patterns were recorded in Bruker AXS D8 Advance X-Ray Diffractometer using Ni filtered CuKα radiation (λ=1.5406 Å) in the range 5-70° at a scan rate 2°/ min. Low angle XRD measurements of the samples were taken on a Panalytical Xpert PRO MPD model with Ni filtered Cu Kα radiation (λ= 1.5406 Å) within the 2θ range 0.1-5° at a speed of 0.25°/min. at room temperature.

2.3.2. UV-Visible Diffuse Reflectance Spectroscopy

Optical properties of un-supported or powdered nanostructures are frequently determined through UV-Vis absorption spectroscopy of their dispersed solutions in liquid media. Though the peak position of the absorption band of semiconductor nanostructures could be defined well from such measurements, precise determination of their band gap energies (Eg) is difficult. However, using the Kubelka-Munk treatment on the diffuse reflectance spectra of such powdered semiconductor nanostructures, it is possible to extract their Eg unambiguously. Effects of light scattering in the absorption spectra of powder samples dispersed in liquid media can be avoided using DRS [10]. Spectroscopic investigations of
Chapter 2

solutions, gas phase and individual crystals usually take place in transmission, but it is very difficult to obtain transparent films of powders and solids (e.g., heterogeneous catalysts), making transmission experiments almost impossible. Alternatively, diffuse reflected light can be collected and this technique has been named diffuse reflectance spectroscopy (DRS) [11]. One of the advantages of DRS is that the obtained information is directly chemical in nature since outer shell electrons of the transition metal ions are probed. This provides information about the oxidation state and coordination environment of transition metal ions in catalytic solids. DRS is quantitative and can be used under in-situ conditions. The main disadvantage of the technique is that DRS spectra are complex, and usually encompass several broad and overlapping bands [12]. When electromagnetic radiation in the UV/Visible wavelength range interacts with a sample, four results are possible: the radiation is absorbed, transmitted, reflected or scattered. When equipped with the proper accessories, UV/Vis. instruments can measure the reflected and scattered energy from a sample. Reflected radiation can be either specular or diffuse. An integrating sphere, when used in combination with the Lambda 35 spectrometer, is a valuable tool for collecting and measuring specular and/or diffuse reflectance [13]. The interaction of light of the UV-Vis-NIR region with catalytic solids is considered to be a complex process due to absorption and scattering phenomena.

These phenomena are largely overcome by the application of techniques such as DRS spectroscopy. DRS is based on the reflection of light by a powdered sample, and the dimensions of the individual particles in such powdered samples are comparable to the wavelength; i.e., 0.2-3µm. This makes it impossible to distinguish the phenomena of reflection, refraction and
Materials and Methods

diffraction; the light is scattered. Diffuse reflected light from a non-absorbing medium involves photons, which are scattered in all directions [14]. Excellent reference materials are totally reflecting over an as-wide-as-possible wavelength range. All reference materials (MgO, BaSO₄, Spectralon®, etc.) have reflectance losses at wavelengths below 250 nm. This leads to artefacts, which implies that recording spectra below 250 nm is not really reliable [15, 16]. In addition, reference materials must be stable toward water and other chemical compounds. Absorbance measurements as well as onset absorption were taken in Spectrophotometer UV-Vis. Double beam UVD-3500, labomed, Inc.

2.3.3. FT-IR Spectroscopy

During the past years, the technique of infrared Fourier Transform Spectroscopy has become more and more important as an instrument for obtaining high quality IR spectra in analytical research and process control. There are two reasons for this development, viz. the capability of Infrared Fourier Transform Spectrometers of producing routine spectra in shorter times and of better quality than those from conventional grating systems and the extension of the possibilities of performing measurements which would be impossible with grating systems. Superior sensitivity and resolution, rapid sample measurement, absolute wavelength accuracy, versatile spectra processing, and total automation of complex analysis are fundamental reasons why one is turning to Fourier Transform Infrared (FT-IR).

Infrared Spectroscopy gives information on the vibrational and rotational modes of motion of a molecule and hence an important technique for identification and characterization of a substance. The infrared spectrum originates from the vibrational motion of the molecule. The vibrational frequencies are a kind of fingerprint of the compounds. This property is used
for characterization of organic, inorganic and biological compounds [17,18]. The band intensities are proportional to the concentration of the compound and hence qualitative estimations are possible. Generally organic compounds and many inorganic compounds give useful results. Hence FTIR is an important technique for identification and characterization of a substance.

Applications:

Fourier Transform Infrared Spectroscopy is exceptionally suitable for obtaining spectra in energy limited situations (small quantities of samples, trace impurities in mixtures, weakly absorbing samples etc.) and conditions under which conventional dispersive instruments fail to produce the desired spectra.

The use of FT-IR in research, analytical and quality control laboratories has brought new and extended capabilities to all users.

Physical Properties: Thickness, Crystallinity, Polymerisation, Vulcanisation, Phase change, hydrogen bonding.

Materials and Methods

Theoretical: Molecular orientation. Molecular Interactions, Pure rotation.

Low Energy: ATR. Highly scattering, strongly absorbing. Typical application includes Chemistry & Chemical Engineering, Polymer & Rubber Industries, Forensic Labs, Pharmaceutical Labs Food Industries, Agriculture, Petroleum Industries and Nanotechnology.

The Infrared induced vibrations of the samples were recorded using Thermo NICOLET 380 FTIR Spectrometer by means of KBr pellet procedure. Spectra were taken in the transmission mode under atmospheric pressure and room temperature. The changes in the absorption bands were investigated in the 400-4000 cm\(^{-1}\) range. The resolution and acquisition applied were 4 cm\(^{-1}\) and 60 scans respectively.

2.3.4. Transmission Electron Microscopy

It is a microscopic technique whereby a beam of electrons is transmitted through an ultra thin specimen and interacts as it passes through the sample. An image is formed from the electrons transmitted from the specimen are magnified and focused by an objective lens and appears on an imaging screen [19]. TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to 1,000,000x with resolution better than 10 Å. The images can be resolved
over a fluorescent screen or a photographic film. Furthermore, the analysis of the X-ray produced by the interaction between the accelerated electrons with the sample allows determining the elemental composition of the sample with high spatial resolution [20]. In TEM, the crystalline sample interacts with the electron beam by diffraction rather than by absorption. The intensity of diffraction depends upon the orientation of the planes of atoms in a crystal relative to the electron beam; at certain angles, the electron beam is strongly diffracted from the axis of the incoming beam, while at other angles, the beam is largely transmitted. Therefore, a highly contrasted image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through it.

This produces a variation in electron intensity that reveals information on the crystal structure [19]. The specimens must be prepared as a thin foil so that the electron beam can penetrate. In the case of materials that are in the form of powders or nanotubes, which are electron transparent, the specimens were prepared by deposition of the diluted sample onto the support grids [19].

**Applications**

It is used both in material science and biological science. It also finds application in the field of Nanotechnology, Ceramics, Pharmaceuticals and Semiconductors etc.

Morphology of all samples was observed on a PHILIPS, CM200 Transmission Electron Microscope, Operating voltages: 20-200kv Resolution: 2.4 Å°.
2.3.5. Raman Spectroscopy

Raman Spectroscopy is a spectroscopic technique used to study vibrational, rotational and other low frequency modes in a system. Raman spectroscopy results from inelastic scattering (Raman scattering) of radiation from molecules. The difference in frequencies of the incident and scattered light corresponds to the vibrational and rotational energies of the molecule. It is the change in the polarisability of the molecule that is responsible for the transitions. Symmetry selection rules predict that for centro-symmetric molecules, the Raman active vibrations will be IR inactive and vice versa (mutual exclusion principle) [21]. The laser light interacts with phonons or other excitations in the system resulting in the energy of the laser photons shifted up or down and the shift in energy gives information about the vibrational modes in the system [22].

When light impinges on a molecule it interacts with electron cloud of the bonds and the incident photon excites one of the electrons in to a virtual state. For the spontaneous Raman effect the molecule will be excited from the ground state to a virtual energy state and relax in to a vibrational excited state which generates stokes Raman scattering. If the molecule was already in an elevated vibrational excited state, it is then called antistokes Raman scattering. The amount of deformation of electron cloud or the polarisability change will determine the Raman scattering intensity whereas Raman shift is equal to the vibrational level that is involved [23].
Chapter 2

Applications

It is widely used in chemistry since vibrational information is very specific for chemical bonds in molecules. It provides a fingerprint by which molecules can be identified in the range of 500-2000 cm\(^{-1}\). Raman gas analysers are used in medicine for real time monitoring of anaesthetic and respiratory gas mixtures during surgery. The polarisation of Raman scattered light with respect to the crystal and the polarisation of laser light can be used to find the orientation of the crystal [19, 22].

Raman spectra were recorded on Horiba Jobin Yvon Lab Ram HR system at a spatial resolution of 2 mm in a backscattering configuration. The 514.5 nm line of Argon ion laser was used for excitation.

2.3.6. Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is the most widely used thermal method. It is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimens is subjected to a controlled temperature programme in a controlled atmosphere. It is based on the measurement of mass loss of material as a function of temperature. In thermogravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. A plot of mass change versus temperature \((T)\) is referred to as the thermogravimetric
Materials and Methods

curve (TG curve). For the TG curve, we generally plot mass \( m \) decreasing downwards on the \( y \) axis (ordinate), and temperature \( T \) increasing to the right on the \( x \) axis (abscissa). Sometimes we may plot time \( t \) in place of \( T \) \cite{24}. TG curve helps in revealing the extent of purity of analytical samples and in determining the mode of their transformations within specified range of temperature. A TGA consists of a sample pan that is supported by a precision balance. The pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. In most cases, TGA analysis is performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp. The maximum temperature is selected so that the specimen weight is stable at the end of the experiment, implying that all chemical reactions are completed (i.e., all of the carbon is burnt off leaving behind metal oxides). This approach provides two important numerical pieces of information: ash content (residual mass, \( M_{\text{res}} \)) and oxidation temperature \( T_o \). 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% \( \text{O}_2 \) in \( \text{N}_2 \) or \( \text{He} \)) 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). Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures
up to 1000°C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.

Applications

TGA can be used to understand the chemistry of decomposition of a particular compound. TGA also provides information about the temperature range over which a particular sample appears to be stable or unstable. We have also interpreted TG curves qualitatively. Beside these there are many other applications of thermogravimetric analysis. Some are listed below [25].

i) Purity and thermal stability.
ii) Solid state reactions.
iii) Decomposition of inorganic and organic compounds.
iv) Determining composition of the mixture.
v) Corrosion of metals in various atmospheres.
vi) Pyrolysis of coal, petroleum and wood.
vii) Roasting and calcinations of minerals.
viii) Reaction kinetics studies.
ix) Evaluation of gravimetric precipitates.
x) Oxidative and reductive stability.
xi) Determining moisture, volatile and ash contents.

xii) Desolvation, sublimation, vaporizations, sorption, desorption, chemisorptions.

TG/DTA analysis was done on a Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer instrument under nitrogen atmosphere at a heating rate of 5-10°/min from room temperature to 1000°C with samples mounted on analyser.
2.3.7. X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy –XPS (also known as ESCA-Electron Spectroscopy for Chemical Analysis) is a non-destructive technique which provides chemical analysis of the outermost 5-10 nm of any vacuum compatible solid. The sample is illuminated with monochromatic X-rays which have sufficient photon energy to cause the photoemission of the core level electrons whose binding energies are characteristic of the elements present. The position and intensity of the peaks provide both chemical (e.g. oxidation state) and quantitative (> ~0.1 atom %) information for all elements except hydrogen. Underlying layers can be examined by the use of XPS in conjunction with argon-ion bombardment providing elemental depth information due to the destructive nature of the ion bombardment [26].

X-ray Photoelectron Spectroscopy (XPS) is one of a number of surface analytical techniques that bombards the sample with photons, electrons or ions in order to excite the emission of photons, electrons or ions. It is also known as electron spectroscopy for chemical analysis (ESCA). A semi-quantitative technique for determining composition based on the photoelectric effect. XPS measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS is based on the principle that X-rays hitting atoms generate photoelectrons. It is a typical example of a surface-sensitive technique. Only electrons that are generated in
the top few atomic layers are detected. In this way quantitative information can be obtained about the elemental composition of the surface of all kinds of solid material (insulators, conductors, polymers). An important strength of XPS is that it provides both elemental and chemical information. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions. Bombarding a sample in vacuum with X-rays gives rise to the emission of electrons. If monochromatic X-rays are used with a photon energy $h\nu$, the kinetic energy of the emitted electrons $K_e$ is given by:

$$K_e = h\nu - B_e$$

where $B_e$ is the binding energy of the atomic orbital from which the electron originates and $\phi$ is the work function. The work function is the minimum amount of energy an individual electron needs to escape from the surface. Each element produces unique set of electrons with specific energies. By measuring the number of these electrons as a function of kinetic (or binding) energy, an XPS spectrum is obtained. All elements can be detected, except H and He because the diameter of these orbitals is so small, to reduce the catch probability to almost zero. The sample analysis is conducted in a vacuum chamber, under the best vacuum conditions achievable, typically $\sim 10^{-10}$ torr. This facilitates the transmission of the photoelectrons to the analyzer but more importantly minimizes the re-contamination rate of a freshly cleaned sample. This is crucial because XPS is very surface-sensitive, with a typical “sampling depth” of only a few nanometers.
Materials and Methods

Application

- Characterization of thin layers (< 10 nm)
- Characterization of thick layers by sputtering
- Contamination
- Cause of bad adherence
- Chemical information

XPS measurement was done using SPECS XPS system with 150W achromatic Al Ka X-ray source at 1486.6 eV energy. The survey scans were obtained at 70eV pass energy and composition was obtained from survey scan. Core level spectra of C1s and S 2p were obtained at 25 eV pass energy and Ti 2p and O1s core levels at 40eV pass energies. C1s, S 2p and Ti 2p core levels were deconvoluted with Gaussian-Lorenztian to get component peaks.

2.3.8. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) enables the investigation of specimens with a resolution down to the nanometer scale. It is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. Here an electron beam is generated by an electron cathode and the electromagnetic lenses of the column and finally swept across the surface of a sample. The path of the beam describes a raster which is correlated to a raster of gray level pixels on a screen. As a consequence the magnification is simply computed by the ratio of the image width of the output medium divided by the field width of the scanned area.
Chapter 2

Fig. 2.5. Principle of SEM Imaging

The electrons interact with the atoms that make up the sample producing signals that contains information about the sample's surface topography, composition, and other properties such as conductivity. The main signals which are generated by the interaction of the primary electrons (PE) of the electron beam and the specimen’s bulk are secondary electrons (SE) and backscattered electrons (BSE) and furthermore X rays. Accelerated electrons in SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photon characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence–CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination[28].
Materials and Methods

SEM gives high resolution surface morphological images, and also has the analytical capabilities such as detecting the presence of elements down to boron (B) on any solid conducting materials through the energy dispersive X-ray spectrometry (EDX) providing information about crystallinity from the few nanometer depth of the material surface via electron back scattered detection (BSD) system attached with microscope and advanced technological PBS (WDS) for elemental analysis. Liquid samples and solid samples which are magnetic/ferrite cannot be measured.

In the conventional scanning electron microscope, which operates in high vacuum, the specimen has to be electrically conductive or has to be coated with a conductive layer (e.g. Carbon, Gold etc.).

Applications

The SEM is routinely used to generate high-resolution images of shapes of objects and to show spatial variations in chemical compositions: (1) acquiring elemental maps or spot chemical analyses using EDS,(2) discrimination of phases based on mean atomic number (commonly related to relative density) using BSE, and (3) compositional maps based on differences in trace element "activitors" (typically transition metal and Rare Earth elements) using cathodoluminescence (CL). The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure [28].

The main features and benefits of the SEM are:-

- Image magnification and resolution
- Magnification range X 15 - X 200,000
- Resolution 2 nm
Chapter 2

- Accelerating voltage 1 - 30 keV
- Secondary and backscattered electron imaging
- Stereo imaging and stereo height measurement
- EDX analysis of known or unknown materials
- Automatic particle counting and characterisation
- Qualitative and quantitative analysis for all elements from carbon upwards
- Quantitative analysis of bulk materials and features $\geq 2 \mu m$
- Qualitative analysis of features $\geq 0.2 \mu m$
- Detection limits typically 0.1 - 100 wt% for most elements
- Multi-element X-ray mapping and line scans
- Multi-layer, multi-element thin film analysis - Thickness and composition
- Particle / Phase analysis - Detection, analysis, morphology and size
- Image Analysis
- Automatic particle counting and characterization[29]

The scanning electron micrographs of the samples were taken using JEOL Model JSM-6390LV scanning electron microscope with a resolution of 1.38 eV. The powdered samples were dusted on a double sided carbon tape, placed on a metal stub and was coated with a layer of gold to minimize charge effects.

2.3.9. Energy Dispersive X-ray Spectrometry (EDX)

Energy dispersive X-ray analysis is a technique to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample. EDS makes use of the X-ray spectrum emitted
by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements (Z < 10). Energy Dispersive Spectroscopy (EDS) allows one to identify particular elements and their relative proportions (Atomic % for example).

The electron beam excites the atoms in the sample that subsequently produce X-rays to discharge the excess energy. The energy of the X-rays is characteristic of the atoms that produced them, forming peaks in the spectrum. The EDS- X-ray detector measures the relative abundance of emitted X-rays versus their energy. The detector is typically lithium-drifted silicon, solid-state device. When an incident X-ray strikes the detector, it creates a charge pulse that is proportional to the energy of the X-ray. The charge pulse is converted to a voltage pulse (which remains proportional to the X-ray energy) by a charge-sensitive preamplifier. The signal is then sent to a multichannel analyzer where the pulses are sorted by voltage. The energy, as determined from the voltage measurement, for each incident X-ray is sent to a computer for display and
further data evaluation. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume. Many elements will have overlapping peaks (e.g., Ti K$_\beta$ and V K$_\alpha$, Mn K$_\beta$ and Fe K$_\alpha$). The accuracy of the spectrum can also be affected by the nature of the sample.

**Typical Applications**

- Foreign material analysis
- Corrosion evaluation
- Coating composition analysis
- Rapid material alloy identification
- Small component material analysis
- Phase identification and distribution

Compositional information about the sample was analysed by EDX using JEOL model JED-2300.

**2.3.10. N$_2$ adsorption – desorption Isotherm**

In heterogeneous catalysis, the reaction occurs at the surface. To predict the catalyst properties, surface area determination is very important. Brunauer-Emmett-Teller method is the widely used procedure for the determination of the surface area of solid materials and involves the use of BET equation. This method is based on the physical adsorption of gases on solid surfaces which leads to multilayer adsorption. The BET equation can be represented as
Materials and Methods

\[ \frac{P}{V} (P_0-P) = \frac{1}{V_mC} + \frac{(C-1)}{V_mC} \frac{P}{P_0} \]

- **V** - Volume of gas adsorbed at equilibrium pressure \( P \)
- **\( P_0 \)** - Standard vapour pressure of the adsorbate at liquid nitrogen temperature
- **C** - Isothermal constant.

By plotting \( \frac{P}{V} (P_0-P) \) Vs \( \frac{P}{P_0} \) and determining \( V_m \) from slope of the resultant straight line in the partial pressure range of 0.05 to 0.35, the specific surface area can be calculated using the relation

\[ A = \frac{V_m N_0 A_M}{W \times 22414} \]

- **\( N_0 \)** - Avogadro number
- **\( A_M \)** - the molecular cross sectional area of the adsorbate (0.162 nm\(^2\) for \( N_2 \))
- **\( W \)** - Weight of the sample (g)

The method is based on the adsorption of \( N_2 \) at liquid \( N_2 \) temperature.

Several computational procedures are available for derivation of pore size distribution of mesoporous samples from physisorption isotherms. Most popular among them is the Barrett-Joyner-Halenda (BJH) model. First, the volumes desorbed from the sample at different partial pressures are converted to liquid volumes (multiplying by 0.00156). The next step is to use Kelvin equation to calculate the value of the volume of the liquid in the capillary. The Kelvin equation shows that the smaller the pore radius, the lower the vapour pressure, \( P \), in the pore

\[ \frac{P}{P_o} = \exp \left( -\frac{2\gamma r}{r_k RT} \right) \]

Pore volume is a property that has been utilized extensively in characterizing a molecular sieve material due to its ability to adsorb selected...
molecules. It is always determined using several probe molecules such as n-hexane, water, nitrogen etc. The probe molecules of various sizes also have been used to gain information on the size of the pore openings, using gravimetric adsorption methods.

Advantage with nitrogen as adsorbate lies in that the value of $C$, on almost all surfaces is sufficiently small to prevent localized absorption and at the same time large enough to prevent the adsorption layer from behaving as a two dimensional gas. Here we determine the volume of $N_2$ gas adsorbed by a known weight of sample at liquid $N_2$ temperature. Since the area occupied by single adsorbed molecular nitrogen can be estimated, the total surface area can be calculated by multiplying the area of one molecule by the number of molecules required for forming the monolayer. Adsorption varies directly with pressure and inversely with temperature. Here the temperature is held constant and the amount of nitrogen adsorbed at liquid nitrogen temperature is measured at different relative pressures. Linearity of the plot is limited to relative pressures in the range 0.1 to 0.3.

In the present investigation simultaneous determination of surface area, pore size distribution and total pore volume of the samples were achieved in a Micromeritics Tristar 3000 surface area and porosity analyser. Prior to the analysis the samples were degassed at 90°C for half an hour and then at 250°C for overnight.

2.3.11. Cyclic Voltametry

The common characteristic of all voltammetric techniques is that they involve the application of a potential ($E$) to an electrode and the monitoring of the resulting current ($i$) flowing through the electrochemical cell. In many
Materials and Methods

cases the applied potential is varied or the current is monitored over a period of time \(t\). Thus, all voltammetric techniques can be described as some function of \(E, i, \) and \(t\). They are considered active techniques (as opposed to passive techniques such as potentiometry) because the applied potential forces a change in the concentration of an electroactive species at the electrode surface by electrochemically reducing or oxidizing it. Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. Cyclic voltammetry (CV) has become an important and widely used electroanalytical technique in many areas of chemistry. It offers a rapid location of redox potentials of the electroactive species. It is rarely used for quantitative determinations, but it is widely used for the study of redox processes, for understanding reaction intermediates, and for obtaining stability of reaction products. This technique is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that point the scan would be reversed and run in the positive direction. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be performed. A three-electrode arrangement is used. The method uses a reference electrode, working electrode, and counter electrode which in combination are sometimes referred to as a three-electrode setup. Electrolyte is usually added to the test solution to ensure sufficient conductivity. The combination of the solvent, electrolyte and specific working
electrode material determines the range of the potential. Common materials for working electrodes include glassy carbon, platinum, and gold. These electrodes are generally encased in a rod of inert insulator with a disk exposed at one end. The main virtue of voltammetric techniques is their good accuracy, excellent precision (<1%), sensitivity, and wide dynamic range. In cyclic voltammetry, the electrode potential ramps linearly versus time. This ramping is known as the experiment's scan rate (V/s). The potential is applied between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. This data are then plotted as current \(i\) vs. potential \(E\).

**General Uses**

- Quantitative determination of organic and inorganic compounds in aqueous and nonaqueous solutions.
- Measurement of kinetic rates and constants
- Determination of adsorption processes on surfaces
- Determination of electron transfer and reaction mechanisms
- Determination of thermodynamic properties of solvated species
- Fundamental studies of oxidation and reduction processes in various media
- Determination of complexation and coordination values

**Common Applications**

- Quantitative determination of pharmaceutical compounds
- Determination of metal ion concentrations in water to sub–parts-per-billion levels
Materials and Methods

- Determination of redox potentials
- Detection of eluted analytes in high-performance liquid chromatography (HPLC) and flow injection analysis
- Determination of number of electrons in redox reactions
- Kinetic studies of reactions

Limitations

- Substance must be oxidizable or reducible in the range were the solvent and electrode are electrochemically inert.
- Provides very little or no information on species identity.
- Sample must be dissolved
- Accuracy varies with technique from 1 to 10%.
- Detection limit varies with technique from parts per thousand to parts per trillion.

Electrochemical measurements were made on BAS Epsilon Electrochemical analyzer (Bioanalytical system USA) interfaced to a PC.

2.3.12. Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a contactless, non-destructive method to probe the electronic structure of materials. The energy levels in a semiconductor quantum well structure are investigated using the technique of photoluminescence (PL). If a light particle (photon) has energy...
greater than the band gap energy, then it can be absorbed and thereby raise an
electron from the valence band up to the conduction band across the forbidden
energy gap. In this process of photoexcitation, the electron generally has
excess energy which it loses before coming to rest at the lowest energy in the
conduction band. At this point the electron eventually falls back down to the
valence band. As it falls down, the energy it loses is converted back into a
luminescent photon which is emitted from the material. Thus the energy of the
emitted photon is a direct measure of the band gap energy, \( E_g \). The process of
photon excitation followed by photon emission is called photoluminescence.
The period between absorption and emission is typically extremely short, in
the order of 10 nanoseconds. Under special circumstances, however, this
period can be extended into minutes or hours.

The intensity and spectral content of the emitted photoluminescence is a
direct measure of various important material properties, including:

1) **Band gap Determination.** The spectral distribution of PL from a
semiconductor can be analyzed to non-destructively determine the
electronic band gap. This provides a means to quantify the elemental
composition of compound semiconductor and is vitally important
material parameter influencing solar cell device efficiency.

2) **Impurity Levels and Defect Detection:** The PL spectrum at low sample
temperatures often reveals spectral peaks associated with impurities
contained within the host material. The high sensitivity of this technique
provides the potential to identify extremely low concentrations of
intentional and unintentional impurities that can strongly affect material
quality and device performance.
3) **Recombination Mechanisms:** The quantity of PL emitted from a material is directly related to the relative amount of radiative and nonradiative recombination rates. Nonradiative rates are typically associated with impurities and thus, this technique can qualitatively monitor changes in material quality as a function of growth and processing conditions.

4) **Material Quality:** In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination.

Photoluminescence measurements were carried using Jobin Yvon Fluoromax-3 spectrometer equipped with 150W Xe lamp.

### 2.3.13. Electron spin resonance spectroscopy (ESR)

ESR is sometimes also referred to as EPR (electron paramagnetic resonance) or EMR (electron magnetic resonance). Electron spin resonance (ESR) or electron paramagnetic resonance spectroscopy (EPR) is a sophisticated spectroscopic technique that detects free radicals or inorganic complexes in chemical and biological systems. Generally, these radicals are unstable, but when they are first reacted with spin-trapping reagents, they can be trapped and stabilized. On the other hand, with use of a spin-labelling reagent, the molecules without radicals can also be measured with ESR/EPR. EPR detects unpaired electrons of materials contained in a homogeneous magnetic field.
field using microwave radiation to establish a resonance condition that can be detected by suitable microwave detectors. It is often called electron spin resonance (ESR) since many systems with unpaired electrons are free radicals. EPR is a technique used in chemistry and physics, in materials science (e.g. to characterize polymers, magnetic and conducting materials, crystalline defects, etc.) and increasingly in biology and medicine. EPR can also be used for magnetic resonance imaging where it has the special advantage of only detecting unpaired electrons contained, usually, in a specific spin-labelled drug. It uses magnetic fields corresponding to a microwave frequency range between 1GHz and 500GHz to study paramagnetic materials and molecules. EPR can be used to obtain structural information of molecules together with details about their electron density distributions. In principle, EPR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant or doing the reverse. In practice, it is usually the frequency that is kept fixed. A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency. By increasing an external magnetic field, the gap between the $m_s = +1/2$ and $m_s = -1/2$ energy states is widened until it matches the energy of the microwaves. At this point the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, due to the Maxwell-Boltzmann distribution, there is a net absorption of energy, and it is this absorption that is monitored and converted into a spectrum. Since the source of an EPR spectrum is a change in an electron's spin state, it might be thought that all EPR spectra for a single electron spin would consist of one line. However, the interaction of an unpaired electron, by way of its magnetic moment, with nearby nuclear spins, results in additional allowed energy states and, in turn, multi-lined spectra. In
such cases, the spacing between the EPR spectral lines indicates the degree of interaction between the unpaired electron and the perturbing nuclei.

Applications

EPR spectroscopy is used in various branches of science, such as biology, chemistry and physics, for the detection and identification of free radicals and paramagnetic centers such as F centers.

EPR measurements were made on a VARIAN, USA E-112 ESR Spectrometer with X-band microwave frequency (9.5 GHz) with sensitivity of $5 \times 10^{10} \Delta H$ spins.

2.3.14. Conductivity Studies

The electrical conductivity was measured at room temperature using a standard Four Point Probe technique. The probes were placed on the surface of the pellet. The thickness of the pellets was measured using a micrometer. The calculation of conductivity is as stated below,

$$\sigma = \frac{I \ln 2}{V \pi t}$$

where $\sigma =$conductivity, $I =$current in Ampere, $V =$ voltage in Volts and $t =$ thickness of the pellet in cm.

Conductivity measurements are taken in Keithley 2400 Source meter, 2001 Multimeter, a 4-point probe set up.

2.4. Application studies

2.4.1. Photocatalysis

The photocatalytic experiments were carried out in an Oriel Arc lamp designed to produce uniform illumination. The diameter of the collimated beam is around 1 inch (2.54 cm) and the work plane is 2.6 inches (6.65 cm).
from the lower end of the beam tuning assembly. The uniform illuminator contains a fan cooled lamp housing that provides a stable and temperature controlled environment for the lamp. The light source of the photoreactor system used is a 150 W Xe ozone free lamp with an average life of 1500 hrs. The filter used for the study is 420-630 nm dichoric mirrors (cold mirror) with an irradiance of 96 mW/cm² in order to get visible light irradiation.

The photocatalytic degradation of some water pollutants such as dyes, pharmaceutical residues, endocrine disruptors, phenolic compounds such as phenol and nitrophenol were performed under visible light irradiation. The percentage degradation of dyes and 4-nitrophenol were studied using the equation, \((C_0 - C)/C_0 \times 100\), where \(C_0\) and \(C\) represent the initial and final concentration of the samples. Degradation of the endocrine disruptor Bisphenol-A, the antibiotic Sulfamethoxazole and phenol were analysed using HPLC (Dionex Ultimate 3000) with photodiode array UV detector and a 5µm Thermo Hypersil ODS-2 C-18 reverse phase column (150*4.6mm). The degradation products were analysed using LC-MS.

The antibacterial studies were also performed under visible light irradiation. The bacteria selected for the present study was salmonella typhi, the Typhoid causing bacteria. The antibacterial activity was measured using colony counting method.

2.4.2. Thermal diffusivity Measurement

The thermal diffusivity measurements of the polyaniline modified samples were performed using thermal lens spectroscopy. The excitation source is a continuous wave (cw), 532 nm diode pumped solid state laser, (DPSS) with a maximum power of 150 mW. A 2mW He–Ne used as the probe.
Materials and Methods

is arranged to be collinear with the pump, using a dichroic beam splitter. The thermal lens signal was collected using an optical fiber, positioned at the center of the probe beam spot and connected to a photodetector–DSO system. A filter for 532 nm was used before the detector to remove the residual pump.

2.4.3. Nonlinear optical studies

The 3rd order nonlinearity of the polyaniline modified samples was analysed using Z-scan technique. A Q-switched Nd: YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source. The Z-scan system is calibrated using CS₂ as a standard. The transmitted beam energy, reference beam energy and their ratio are measured simultaneously by an energy ratio meter (Rj7620, Laser Probe Corp.) having two identical pyroelectric detector heads (Rjp735). The effect of fluctuations of laser power is eliminated by dividing the transmitted power by the power obtained at the reference detector; both being measured using identical photo detectors.

2.4.4. Light amplification in dye doped nanocomposites

The Lasing studies of the same systems were also performed and in the experimental setup, the laser dye containing aqueous dispersion of polyaniline samples were placed in cuvettes length of 3cm, and width of 0.5 cm. The pumping source of random lasing is a frequency doubled Q-switched Nd: YAG laser (Spectra Physics, 532 nm, 10 Hz). A set of calibrated neutral density filters was used for varying the pump energy. The pump power was measured by using ‘COHERENT Labmater Power meter’ and it is varied from 14 to 170 mW. The laser emission was recorded using a collecting fiber coupled to a monochromator-CCD system (Spectra Pro) with a resolution of 0.03 nm. A high-speed photodetector and an oscilloscope (Tektronix) were used to measure the temporal intensity profile of the emitted laser pulse.
References


[23]. Electrical Conductive Adhesives with Nanotechnologies By Yi (Grace) Li, Daniel Lu, C.P. Wong; Springer New York Dordrecht Heidelberg London.


[27]. http://portal.tugraz.at/portal/page/portal/felmi/research/Scanning%20Electron%20Microscopy/Principles%20of%20SEM.


---MORE---