CHAPTER 2

EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

2.1 EXPERIMENTAL TECHNIQUES

Preparation of polymer fibers with diameters ranging from few micron to few nanometer scale has significant interest due to its potential impact in many applications such as nano-electronics and optical sensors. These applications require the fabrication of one (1D), two (2D) and three-dimensional (3D) network of nanofibers. The individual components are created and assembled together into larger structures. The processing techniques has been used to prepare nanofibers such as

- Drawing
- Template synthesis
- Phase separation
- Self-assembly
- Electrospinning
- Sol-Gel method
- Hydrothermal method
- Solvothermal method
Thus, the electrospinning process seems to be the only method for mass production of one-by-one continuous nanofibers from various polymers (Huang et al 2003).

2.1.1 Drawing

It’s based on dry spinning process and widely used for the preparation of one-by-one long single fibers. In this process, a micropipette with a diameter of few micrometers was dipped into the droplet near the contact line using a micromanipulator. The micropipette was then withdrawn from the liquid and moved at a speed of approximately $1 \times 10^{-4}$ m/s, resulting in a nanofibers being pulled and then deposited on the surface. This process was repeated for several times to form a nanofiber which is then solidified by rapid evaporation of the solvent. This method offers increased flexibility in the control of key parameters of drawing such as drawing speed, and the drawn upon surface topography, thus enabling repeatability and control on the dimensions of the fabricated fibers (Nain et al 2006).

2.1.2 Template Synthesis

In this technique, the nanofiber created by passing of polymer solution through the pores of nano-scale diameter under the application of water pressure on one side, causes extrusion of the polymer, which gave nanofiber upon coming into contact with a solidifying solution. The diameter was determined by the pores size of the membrane. The template synthesis involves the use of nanoporous membrane as a template to make nanofibers of solid or hollow shape. The most important feature of this method may lie in that nanometer tubules and fibrils of various raw materials such as electronically conducting polymers, metals, semiconductors, and carbons can be fabricated.
2.1.3 Phase Separation Method

The phase separation consists of dissolution, gelation, and extraction using a different solvent, freezing, and drying resulting in nanoscale porous foam. The process takes relatively long period of time to transfer the solid polymer in to the nano-porous foam. At low gelation temperature, nano-scale fiber network is formed, whereas, high gelation temperature led to the formation of platelet-like structure (Wang et al 2006).

2.1.4 Self-Assembly

Self–assembly refers to the build-up of nano scale fibers using smaller molecules. In this technique, a small molecule is arranged in a concentric manner so that they can form bond among the concentrically arranged small molecules which, upon extension in the planes normal to gives the longitudinal axis of a nano fiber. The main mechanism for a generic self-assembly is the inter molecular forces that bring the smaller unit together. A hydrophobic core of alkyl residues and a hydrophilic exterior lined by peptide residues was found in obtained fiber. It is observed that the nano fibers produced in this technique has diameter range 5-8 nm and several microns in length. The self-assembly is a process in which individual, pre-existing components organize themselves into desired patterns and functions. However, similarly to the phase separation and the self-assembly is time-consuming in processing continuous polymer nanofibers. Thus, the electrospinning process seems to be the only method which can be further developed for mass production of one-by-one continuous nanofibers from various polymers. Although there are a number of techniques used for the synthesis of nanofiber but electrospinning represents an attractive technique to fabricate polymeric biomaterial into nanofibers.
Electrospinning is one of the most commonly utilized method for the production of nanofiber. It has wide advantage over the previously available fiber formation techniques because here electrostatic force is used instead of conventionally used mechanical force for the formation of fibers (Wang et al 2006). Goksu Cinar et al designed and synthesized oppositely charged short amyloid-inspired peptide sequences: Ac-EFFAAE-Am (AIP-1) and Ac-KFFAAK-Am (AIP-2; Figure 1a,b) that self assemble into amyloid like nanofibers upon mixing at pH 7 in water. Cinar et al (2012) and Zhang et al (2005) reported Designer self-assembling peptide nanofiber scaffolds for 3D tissue cell cultures.

2.1.5 Sol-Gel Method

The sol-gel method is a versatile process used in making various ceramic materials. In a typical sol-gel process, a colloidal suspension (sol) is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. Thin films can be produced on a substrate by spin-coating or dip-coating. A wet gel will form when the sol is cast into a mold, and the wet gel is converted into a dense ceramic with further drying and heat treatment.

2.1.6 Hydrothermal Method

Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of water, reaching the pressure of vapor saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced. It is
widely used for the synthesis of small particles. Many reports have been used
the hydrothermal method to prepare TiO$_2$ nanofibers (Dewangan et al 2011,
Okumura et al 2011). Hydrothermal synthesis has been applied to synthesize
crystalline oxides with a high surface area and unique morphology.

2.1.7 Solvothermal Method

The solvothermal method is similar to the hydrothermal method
except that the solvent used here is nonaqueous. However, the temperature
can be elevated much higher than that in hydrothermal method, since a variety
of organic solvents with high boiling points can be chosen. The solvothermal
method normally has better control than hydrothermal methods of the size and
shape distributions and the crystallinity. The solvothermal method has been
found to be a versatile method for the synthesis of a variety of nanoparticles
and nanostructured materials. The solvent plays an important role in
determining the crystal morphology. Solvents with different physical and
chemical properties can influence the solubility, reactivity, and diffusion
behavior of the reactants; in particular, the polarity and coordinating ability of
the solvent can influence the morphology and the crystallization behavior of
the final products

2.1.8 Electrosponing Method

Electrosponing is a versatile process which has been recognized as
one of the most efficient technique and cost-effective method for the mass
production of 1-dimensional (1-D) nanostructures of oxides, non-oxides and
polymer nanofibers (NFs) (Teo & Ramakrishna 2006) with diameters ranging
from a few nanometers to a few microns. The basic principle of this technique
is based on generating the direct movement of charged molecules by applying
high voltage to supply the ejection of a liquid jet through spinneret from
polymer solution droplet (Li & Xia 2004). In electrosponing, an electric field
draws a polymer melt or polymer solution from the tip of a capillary to a collector. A voltage is applied to the polymer, which causes a jet of the solution to be drawn towards a ground collector, while the liquid jet is drawn to the collector, rapid evaporation of solvent serves to solidify the fiber (Huang et al 2003).

A typical experimental setup of the electrospinning process (Figure 2.1) consists of a syringe-like apparatus that contains the polymer solution. The narrow end of the syringe is connected to a capillary, e.g. glass or Teflon. A platinum electrode dipped in the polymer solution is connected to a high voltage DC supply. When the high voltage DC supply is turned on, the electrode imparts an electrical charge to the polymer solution. Near the critical point, where the electric field strength is about to overcome the surface tension of the fluid, the free surface of the suspended drop ejected from the tip and then deposited on to the collector. Typical operating conditions are: internal diameter of the capillary-end is usually 0.7 – 1mm, flow rates of 3-10 ml/h are commonly employed at a potential drop of 5 – 20 KV and distance of 10 – 30 cm between the capillary-end and target. The solvent evaporates during the trajectory before reaching the collector and the jet finally solidifies forming fibers from hundreds of micrometers down to as small as tens of nanometers. Some advantages and disadvantages of various nanofibers processing techniques were listed in Table 2.1.

![Figure 2.1 Schematic of Electrospinning technique](image-url)
Table 2.1 Advantages and disadvantages of various nanofiber processing techniques

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drawing</td>
<td>Minimum equipment requirement</td>
<td>Discontinuous process</td>
</tr>
<tr>
<td>Template Synthesis</td>
<td>Synthesis Fibers of different diameters can be easily achieved by using different templates.</td>
<td>Micron length fibers are produced</td>
</tr>
<tr>
<td>Phase Separation</td>
<td>Minimum equipment requirement. Process can directly fabricate a nanofiber matrix. Batch-to-batch consistency is achieved easily. Mechanical properties of the matrix can be tailored by adjusting polymer concentration.</td>
<td>Limited to specific Polymers</td>
</tr>
<tr>
<td>Self-Assembly</td>
<td>Good for obtaining smaller nanofibers</td>
<td>Complex process</td>
</tr>
<tr>
<td>Electrospinning</td>
<td>Cost effective. Long, continuous nanofibers can be produced</td>
<td>Jet instability</td>
</tr>
</tbody>
</table>

2.1.8.1 Parameters

Nanofibers properties can dramatically vary because there are many variables that may influence the process such as:

- Solution properties: Polymer molecular weight, viscosity, elasticity, conductivity, surface tension, dielectric effect of solvent, and polymer concentration.
• Processing conditions: Voltage, solution feed rate, type of collector, nozzle orifice diameter and distance from nozzle to collector, collection time.

• Ambient conditions: Temperature, relative humidity, type of atmosphere and pressure.

Many parameters for the process affect the fiber diameter, such as gap distance between needle and collector, polymer flow rate, and the applied voltage. One of the most effective parameters for controlling the fiber diameter is the concentration of polymer in the solution.

The important features of electrospinning are

• Suitable solvent should be available for dissolving the polymer and the ceramic precursors.

• The vapor pressure of the solvent was evaporates quickly which enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range.

• The viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette.

• The power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustaining the jet from the pipette.

• The gap between the pipette and grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form.
The electrospinning process involves the understanding of electrostatics, fluid rheology and polymer solution properties such as rate of solvent evaporation, surface tension and solution conductivity. These fundamental properties are constantly interacting and influencing each other during the electrospinning process. By modifying the standard electrospinning set up, the structure and morphology of the electrospun nanofibers can be changed. The change of the geometry of core/shell for the bi-components nanofibers or hollowed structures can be obtained different solutions and calcination or dissolving the core polymer with a solvent (Sawicka & Gouma 2006). Also by controlling the spinning parameters and the rapid evaporation of solvent at room temperature, such as with dichloromethane (boiling point 40°C, vapor pressure 475 mbar at 20°C), porous nanofibers can be produced (Bognizke et al 2001).

![Diagrams showing influence of various parameters on fiber diameter](image)

**Figure 2.2 Influence of various parameter on the fiber diameter**

Most common problems which may be to appear in the electro spun nanofibers are different fiber diameters, the formation of beads formation and
the presence of pores. Different fiber diameters may be obtained during the electrospinning process when the jet is split into multiples jets and that the liquid jet is traveling from the needle to the collector. However, there are several parameters which affect the fiber diameter such as polymer properties (viscosity, type of solvent, etc), applied electrical voltage, distance from the needle to the collector and the feeding rate, as shown in Figure 2.2. In the case of beads, the polymer concentration is one of the most important parameters that may affect; higher polymer concentration result in fewer beads. Moreover, the voltage applied also causes effects (Huang et al 2003). More recently, as a result of increasing demand for specialised nanostructured composite materials, a more complex variant of this process such as co-axial electrospinning, Emulsion electrospinning, Melt electrospinning has been developed.

2.1.8.2 Coaxial electrospinning

Recently, to synthesize tubular or core-shell (cable-like) structures, the electro-hydrodynamic (EHD) spinning has been extended to generate electrified coaxial jets (Barrero et al 2006) emerging from the tip of electrified conical menisci of two co-flowing liquids, in a process so-called coaxial electrospinning or co-electrospinning (Li & Xia 2004). In this co-electrospinning, two immiscible liquids are injected through two capillary needles located coaxially one inside the other. One of the liquids flows through the inner needle (i.e. inner liquid) and the other liquid flows through the annular gap between the outer and the inner needle (i.e. outer liquid).

2.1.8.3 Emulsion electrospining

Emulsion electrospining is similar to the normal solution electrospining, except that the solution is replaced with water-in-oil (W/O) emulsion. Emulsion electrospining has originally been used to incorporate a
water soluble drug into a hydrophobic or an amphiphilic polymer. A water-
soluble polymer is substituted for the water soluble drug. Sanders et al (2003) 
electrospun water-in-oil emulsions, where the water drops contained 
dissolved solutes (e.g., salt, protein, sugar), and the continuous organic phase 
was poly (ethylene-co-vinyl acetate) dissolved in dichloromethane. The 
resulting fibers were about 20 mm in diameter, much larger than typical for 
electrospinning and contained droplets of the aqueous phase. Water-in-oil 
(W/O) emulsion system consists of two immiscible phases, which is designed 
to uniformly disperse aqueous CNC suspensions into hydrophobic PLA 
solutions.

2.1.8.4 Melt electrospining

Melt-electrospinning has inherent advantages, such as cleaner 
processing with environmental safety, and higher productivity (with lower 
production cost) due to the absence of solvent. In order to fabricate thinner 
fibers via melt-electrospining, the viscosity of a polymer melt should be 
reduced by adjusting the processing parameters or polymer parameters. 
Important parameters reported for melt electrospining are the molecular 
weight, tacticity, melting point of the polymer, electric field strength, distance 
from the nozzle, mass flow rate, and process temperatures (electrospining 
temperature, heating chamber temperature).

2.2 CHARACTERIZATION

2.2.1 Power X-ray Diffraction Analysis

X-ray diffraction is one of the potential methods to characterize the 
crystalline materials such as phase identification, determination of crystal 
structures, size of the particle, and texturing. It 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 toward the sample. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg’s Law ($n \lambda = 2d \sin \theta$) where $\lambda$ is the incident wavelength, which is generally CuKα1 (1.54056 Å) or CuKα2 (1.5444 Å), and $d$ is the spacing between the arrays of atoms. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. 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-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns. Particle size can also be determined from the X-ray diffraction patterns. The size can be calculated from the broadening of the peaks based on Scherrer formula,

$$d = \frac{K \lambda}{\beta \cos \theta} \quad (2.1)$$

where,  
$d$ is the mean particle size,  
$K$ is a constant and the value is 0.89,  
$\lambda$ is the wavelength of X-ray,  
$\beta$ is the full width half maximum and $\theta$ is the scattering angle.

In the present study, X-ray diffraction of all samples were analyzed with a Rigaku Rintz Ultima + model diffractometer with X-ray radiation of wavelength 1.54056 Å. Simplified schematic diagram of a X-ray diffractometer is shown in Figure 2.3.
Figure 2.3 Schematic diagram of a X-ray diffractometer

2.2.2 Raman Spectroscopy

When light is incident on a sample, most of the light is elastically scattered in random directions (the total kinetic energy before collision $K_1$ = the total kinetic energy after collision $K_2$); this phenomenon is known as Rayleigh scattering. The small remaining (or missing) fraction of the light is inelastically scattered; the phenomenon is known as Raman scattering. The resulting energy levels in the illuminated sample may be higher or lower than the energy level of the initial state of the electrons. Roughly speaking the inelastically scattered light has a wavelength higher or lower than the one of the incident light. The difference in energy is due to rotational and vibrational transitions in the material target. This shift in photon energy corresponds to the energy of phonons that have been created or annihilated.

When the photon loses energy into the creation of a phonon, it is said to be Stokes scattered, and when it gains energy from the annihilation of a phonon it is said to be anti-Stokes scattered. Figure 2.4 illustrates the processes involved in both Rayleigh and Raman scattering.
Different Raman signals may be observed if there is more than one vibration or rotational degrees of freedom in the sample. To be active in the Raman spectrum, a vibration must produce an oscillating polarizability $\alpha$. The phenomenon is different in infrared spectroscopy where a vibration must produce an oscillating dipole.

![Raman and Raman Signals Diagram]

**Figure 2.4  Processes involved in Rayleigh and Raman scattering and the production of Stokes and anti-Stokes lines**

This small signal can be detected by extremely sophisticated spectrometers and used to probe into the properties of the material such as phase state, degree of crystallinity, and crystal size among others.

### 2.2.3 Fourier Transform Infrared spectroscopy

Infrared spectroscopy is a non-destructive technique used for materials analysis. Infrared absorption spectroscopy is the study of interaction of infrared radiation with matter as a function of photon frequency. Fourier Transform Infrared Spectroscopy (FT-IR) provides specific information about
the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. The IR region is commonly divided into three smaller areas: near-IR (400-10 cm\(^{-1}\)), mid-IR (4000-400 cm\(^{-1}\)), and far-IR (14000-4000 cm\(^{-1}\)). Infrared photons have enough energy to cause groups of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiation only at certain wavelengths and frequencies. An FT-IR is typically based on the Michelson’s Interferometer experimental setup.

Figure 2.5 shows the schematic diagram of the FT-IR spectrometer. FT-IR Instrument contains a source, interferometer and a detector. The solution is put into a sample tube. The light passes through a beam splitter, which sends the light in two directions at right angles. One beam goes to a stationary mirror then back to the beam splitter. The other goes to a moving mirror. The motion of the mirror makes the total path length variable versus that taken by the stationary-mirror beam. When the two meet up again at the beam splitter, they recombine, but the difference in path lengths creates constructive and destructive interference. The recombine beam passes through the sample. The sample absorbs all the different wavelengths characteristic of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector now reports variation in energy versus time for all wavelengths simultaneously. A laser beam is superimposed to provide a reference for the instrument operation. Energy versus Time is an odd way to record a spectrum, until recognize the relationship between time and frequency. A mathematical function called a Fourier transform allowed to convert intensity versus time spectrum into intensity versus frequency spectrum.
2.2.4 Photoluminescence Spectroscopy

If a light particle (photon) having an energy greater than the band gap energy, is incident on a material, then it can be absorbed and thereby raise an electron from the valence band up to the conduction band across the forbidden energy gap (Figure 2.6).
In this process of photo-excitation, 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. Depending on the lifetime of higher energy state, the emission spectrum termed as fluorescence or phosphorescence. To measure photoluminescence spectrum, two essential equipments are necessary. One is spectrometer with photo-electro-transfer device; the other one is the light-excitation source. Various light sources such as lasers or lamps can be used as excitation source in the PL measurement system. If a lamp source is used, it is first passed through a monochromator and then made to fall on the sample. Light emission from the sample is first diffracted by the diffraction grating which is then sent to the photomultiplier through the exit slit and finally recorded by the computer.

### 2.2.5 Transmission Electron Microscope

In a Transmission Electron Microscope (TEM), a beam of focused high energy electrons is transmitted through a thin sample to reveal information about its morphology, crystallography, particle size distribution, and its elemental composition. It is capable of providing atomic-resolution lattice images, as well as giving chemical information at a spatial resolution of 1 nm or better. The unique physical and chemical properties of nanomaterials not only depend on their composition, but also on their structures, TEM provides a means for characterizing and understanding such structures. TEM is unique as it can be used to focus on single nanoparticles in a sample, and directly identify and quantify its chemical and electronic
structure. Perhaps the most important application of TEM is the atomic resolution real-space imaging of nanoparticles.

![Diagram of a Transmission Electron Microscope](image)

**Figure 2.7 Schematic diagram of Transmission Electron Microscope**

The schematic diagram of a TEM is shown in Figure 2.7. The electron beam generated by the gun is demagnetized through the first condenser lens; the second condenser lens converges the probe at the specimen and controls the spot size. Just below the second condenser lens is a condenser aperture that can be used to change the electron current and therefore the intensity of the beam as well as change the angle of beam convergence changes, which modifies the coherence of the beam.
The specimen sits below the condenser lens and above the objective lens. The specimen position and the objective lens are the heart of the TEM, whereas the combination of the objective lens, the intermediate lens and the projection lens determine the overall magnification of the microscope.

2.2.6 Scanning Electron Microscope

In Scanning electron Microscopy (SEM) well aligned beams of electrons are used for imaging. A beam of electrons is produced at the top of the microscope by heating a metallic filament known as electron gun, which follows a vertical path through the electromagnetic lenses set in the column of the microscope as presented in the block diagram of SEM in Figure 2.8. As a result, the beam is focused and directed down towards the sample. As the beam hits the sample, electrons (back scattered or secondary) are ejected from the sample. Detectors gather these electrons and convert them to a signal that is sent to a viewing screen producing an image. Additional field-emission cathode in the electron gun of a scanning electron microscope (which is called FESEM) provides further narrower probing beams at low as well as high electron energy, resulting in improved spatial resolution with the highest magnification possible and also reduces the possibility of charging the sample and damage for the application to a minimum. Sometimes an arrangement is attached to the instrument for energy dispersive X-ray analysis (EDS). EDS identifies the elemental composition of the material imaged in the SEM for all elements with atomic number greater than boron. This depends on the generation of the x-ray fluorescence from the atoms which are struck by the scanning beam. The x-ray photon is a characteristic of the element from which it is produced. These photons are collected and analyzed to get the signature of its mother element.
2.2.7 X-ray Photoelectron Spectroscopy (XPS)

Photoelectron spectroscopy (PES) is a widely used technique to investigate the electronic state and composition of a sample. It is a semi-quantitative method for obtaining composition and chemical state information. Because it is a surface-sensitive technique and the photoelectrons generally have low kinetic energies, XPS experiments must be conducted in an ultra-high vacuum (UHV) environment ($10^{-9} - 10^{-10}$ Torr) with soft X-rays of known energy (1–2 keV). This results in the photoemission of electrons from atoms in the sample, the kinetic energies of which are measured by the spectrometer. These energies identify the elements present in the sample surface and can provide information on their chemical states. The phenomenon is based on the photoelectric effect outlined by Einstein in 1905 where the concept of the photon was used to describe the ejection of electrons from a surface when photons impinge upon it. Schematic of the photoemission process depicted in Figure.
Figure 2.9 Schematic of Photoemission process

A specimen is irradiated by X-ray of a fixed wavelength (hv) and photoelectrons are consequently excited from the specimen (Figure 2.9). Conservation of energy states that,

$$K.E. = h\nu - B.E. - \varphi_{\text{spectrometer}}$$  \hspace{1cm} (2.1)

where K.E. is the kinetic energy of the photoelectron, B.E. is the binding energy associated with the excited electron in a particular orbital and \( \varphi \) spectrometer is the spectrometer (i.e. detector) work function. Each element’s orbitals is unique and is dependent on bonding environment, it can act as ‘fingerprints’ for identifying elements and chemical compounds.

Limitations

Despite the many benefits to XPS, nothing is foolproof, nor is anything without limitations. The smallest analytical area XPS can measure is \( \sim 10 \mu m \). Samples for XPS must be compatible with the ultra high vacuum environment. Because XPS is a surface technique, there is a limited amount of organic information XPS can provide. XPS is limited to measurements of
elements having atomic numbers of 3 or greater, making it unable to detect hydrogen or helium. XPS spectra also take a long time to obtain. The use of a monochromator can also reduce the time per experiment.

**Advantages**

XPS has a greater range of potential application than UPS since it can probe down to core electrons. XPS is good for identifying all but two elements, identifying the chemical state on surfaces, and is good with quantitative analysis. XPS is capable of detecting the difference in chemical state between samples. XPS is also able to differentiate between oxidations states of molecules.

**2.2.8 Specific Surface Area (BET Theory)**

Physical adsorption at the gas/solid interface is routinely measured in the laboratory. The most common example is found in measuring nitrogen adsorption isotherms of porous materials at 77 K between 0-100 kPa, which corresponds to the full range of $P/P_0$ for nitrogen ($P_0$ is the saturation pressure). The wide and cheap availability of nitrogen as a gas and liquid (used for cooling to 77 K) combined with its practicality as a probe molecule in determining surface area and pore size characteristics has established N$_2$ adsorption as a ubiquitous characterization tool and commercial instruments specifically for this purpose are widespread.

**BET theory**

The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces)
between the adsorbate gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure. Nitrogen adsorption/desorption using the Brunauer-Emmett-Teller method (BET, Quantachrome autosorb iQ2) automated gas sorption analyzer was shown in Figure 2.10.

![Figure 2.10 Nitrogen adsorption/desorption using Brunauer-Emmett-Teller method (BET, Quantachrome autosorb iQ2) automated gas sorption analyzer](image)

Weak van der walls interaction of molecules with a pore surface leads to the physical adsorption. The Brunauer,Emmett and teller (BET) theory of physical adsorption is normally used for analysis of adsorption data to compute surface area.

**Advantages**

BET method leads to a surface area parameter which allows to compare, classify and evaluate different samples and to take into account pores (micro-, meso- and macro pores), roughnesses and particle shapes by
measurement. These analyses require relatively low manpower. BET surface area gets also calculated out of a complete adsorption and desorption isotherm to be used as complementary parameter for the determination of pore volume and pore size distribution.