CHAPTER-III

INSTRUMENTATION
3.1 Introduction

Aligned with the goals and objectives of the stated research problem, various relevant synthesis, necessary characterizations and evaluation of their thermal, morphological and electrochemical properties, were conducted. In this chapter, the materials synthesized, basic materials characterization techniques and electrochemical testing specifications are presented.

3.2 Material Synthesis

There have been some reports in the literature regarding different synthesis techniques for obtaining graphene-related nanocomposite materials. Some of the chemical methods used in this research are presented below:

3.2.1 Synthesis of Functionalized Graphene

The term “in-situ” implies “in position” and represents the status in the reaction mixture about the chemical reactions. Normally, in-situ reductions for reagents are conducted in flasks, in water/oil baths, under reflux conditions. Thus, after subsequent heat treatment, the base materials get reduced to the desired product. Such methods are usually followed to synthesize graphene based nanocomposite materials.

In this study, graphene was made to react with $\text{H}_2\text{SO}_4$: $\text{HNO}_3$ (3:1). The reacted material was further tip sonicated for about half an hour by ultrasonication. The obtained product was identified as carboxylic acid functionalized graphene, henceforth referred as F-GE-COOH. Thionyl chloride was mixed with F-GE-COOH, and at a temperature of 75 °C, left for 24 hours. By this, carboxylic acid group in F-GE-COOH was converted to formyl chloride and hence forth, shall be referred as F-GE-COCl. The mixture was cooled, centrifuged and washed. After excess reactants removed by the treatment, the treated samples were left overnight at 90 °C to dry (Liu et al. 2009; Scheuermann et al. 2009; Xu et al. 2008; Zhuang et al. 2010; Husale et al. 2010; Wang et al. 2009).

3.2.2 Synthesis of GE-chitosan Derivative

F-GE-COCl (400 mg) was mixed with chitosan (2 g) in 100 mL 2% acetic acid at 75 °C for 24 hours with continuous stirring. After the reaction terminates, the product was washed three times with 2% acetic acid to remove unreacted chitosan.

For synthesis of GE-chitosan Grafted Derivative, GE-chitosan (0.1 g) was reacted with $\text{K}_2\text{S}_2\text{O}_8$ (0.02 g) and subsequently with four different compounds: poly anthranilic acid (PAA), poly meta nitroaniline (PMNA), poly dichloroaniline (PCA), poly sulphanilic acid (PSA). Further after being centrifuged at 20,000 rpm, washed twice with water,
dried at 90 °C, the products obtained are respectively referred as F-GE-chitosan-PAA, F-GE-chitosan-PMNA, F-GE-chitosan-PCA and F-GE-chitosan-PSA. Successful attempts at using the in-situ preparation of graphene based nanocomposites are reported in chapter four of this thesis.

3.3. Materials Characterization

Characterization techniques, such as X-ray diffraction, scanning electron microscopy, transmission electron microscopy, etc. were used on the samples for phase identification, to find the textural features and determination of their composition.

3.3.1. X-ray Diffractometry

X-ray diffraction is a non-destructive analytical characterization technique for determination of phase and structure of the crystal. In this method, an X-ray beam is allowed to hit the target, and after being diffracted by the target, the beam is detected and analyzed as a function of incident and scattered angles, polarization, and wavelength (or energy). For any particular sample, there is always a unique unit cell configuration, producing particular relative intensities of the recorded diffraction peaks. Therefore, the unit cell size and geometry can be measured from the angular positions of the X-ray diffraction results. Fig. 3.1 shows an X-ray diffractometer (Siemens D5000) located at the Microstructural Analysis Unit (MAU), University of Technology Sydney (UTS) able to analyze up to 50 samples with a single loading (William 2013; Renato et al. 2015).

Fig. 3.1 X-ray diffractometer (Siemens D5000 model). (Image captured from the Science Faculty Resource Manage System, UTS)
3.3.2. Scanning Electron Microscopy and Transmission Electron Microscopy

Electron diffraction is a characterization method used to analyze material by lighting a beam of accelerated electrons to a sample to obtain an interference pattern (Fig. 3.2), usually performed through scanning electron microscope (SEM) and transmission electron microscope (TEM) to analyze crystal structure and specific morphology (Tobias et al. 2012; Bojeong et al. 2015).

SEM images a sample by scanning it in a raster scan pattern with the excited electron beam. The atoms that make up the sample produce signals while each scan to deliver knowledge about the sample's surface topography, composition, and other properties such as electrical conductivity. A Field Emission SEM (FE-SEM) is equipped with a field emission cathode in the electron gun to provide enhanced resolution and to minimize the charge issues and sample damage.

![FE-SEM facility (Zeiss Supra 55VP).](Image captured from the Science Faculty Resource Manage System, UTS)

The beam of electrons in a TEM, on the other hand, is transmitted through an ultra thin sample on a copper grid, interacting with the specimen as the electrons pass through to generate photos. TEMs are able of imaging at a very high resolution to reveal information at the nanometer scale, such as lattice planes, \(d\)-spacing, etc., so they have better resolution than SEMs. Generally, SEMs (FE-SEMs) are used for preliminary analysis while TEMs are on duty for in-depth investigations of lattice parameters and
very fine nanostructures. Fig. 3.3, as shown below, presents a commercial TEM setup (JEOL 2011 model).

![A commercial TEM setup (JEOL 2011 model).](image)

**Fig. 3.3** A commercial TEM setup (JEOL 2011 model).

### 3.3.3. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is a type of measurement to determine the weight changes of samples associated with changes in temperature. This analysis accurately detects the weight of a sample as temperature elevates, drawing a continuous line to identify weight loss processes about the chemical reactions occurring. TGA can be carried out in air or noble gases for different applications. In the case of graphene-based nanocomposite materials, TGA is often conducted in the air as a quantitative method to determine the composition of graphene and the embedded nanoparticles (Aqdas et al. 2016; Khalid et al. 2016). Fig. 3.4 shows a typical TGA instrument of TA Instruments.
3.3.4. Electrochemical Testing

The assembled test cells were electrochemically tested for a systematic study of the electrochemical properties of the active materials. The electrochemical test and measurements are typically done through cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy, discussed below. The overall electrochemical performance can be further estimated from all these results.

3.3.5. Cyclic Voltammetry

Cyclic Voltammetry (CV) is a type of potentiodynamic electrochemical measurement, recording a relationship of current vs. voltage when the potential at the working electrode is ramped linearly versus time (at a certain scan rate) to a set potential and reversed back to the original potential at the same sweep rate. CV is used to examine the electrochemical properties of an analyte in solution upon a single or a few scans. In the examining voltage range, an analyte can be reduced or oxidized on a forward scan.
as the scan proceeds, and then re-oxidized or re-reduced on the return scan, as a sign of highly reversible redox couples (Climent et al. 2015; Martin et al. 2012).

For supercapacitors and lithium rechargeable batteries, specific reactions can be known from CV measurements through redox peak potentials. The measurements also confirm the energy storage mechanism involved. CV curves can also be used to compute the specific capacitance of the active material using the relationship as shown below. The area under the current–potential curve can be estimated by integration, and then the area is divided by the sweep rate \((v, \text{ V s}^{-1})\), the mass of active material of the electrode \((m, \text{ g})\), and the potential window \(((V_a-V_b), \text{ V})\), giving a specific capacitance \((C)\) in \(\text{F g}^{-1}\):

\[
C = \frac{1}{mv(V_a-V_b)} \int_{V_a}^{V_b} I(V) \, dV
\]

In the research project reported in this thesis, all CV analyses were carried on an electrochemistry workstation. Fig. 3.5 gives an electrochemistry workstation project (CHI660D model) serving in the lab of the Department of Physics, KIIT University.

![Electrochemistry workstation (CHI660D model)](image)

**Fig. 3.5** Electrochemistry workstation (CHI660D model).

### 3.3.6. Fourier Transform Infrared Spectroscopy (FTIR)

In FTIR or Fourier Transform Infrared spectroscopy, shown in Fig 3.6, when, IR radiation passes through a sample, some of the infrared radiation gets is absorbed, while rest are transmitted. The resulting spectrum thus represents a molecular fingerprint of the sample (Painter et al., 1982) indicating molecular absorption and transmission through the sample. As no two unique molecular structures produce the same infrared spectrum, infrared spectroscopy is much useful for several types of analysis.
Particularly, the process is necessary to study orientation in polymers (Koenig, 1999; Stothers, 1963). The differing alignment of the molecules results in changes in the intensities of some of the infrared modes and therefore is an indicator of crystallinity. As each interatomic bond may vibrate in several different motions such as stretching or bending, individual bonds may absorb more than one IR frequency.

With the frequency range of IR radiation being 4000 to 400 cm⁻¹, stretching absorptions usually produce stronger peaks than bending. However, weaker bending absorptions are much useful in differentiating similar types of bonds, for example, aromatic substitution, while symmetrical vibrations do not cause absorption of IR radiation (either of the carbon-carbon bonds in ethene or ethyne absorbs IR radiation, Bose, 1965; Bible, 1967; Mathieson, 1967; Klug, H. P. and Alexander, 1954). The schematic representation of an FTIR spectroscopy is shown in Fig. 3.6.

![Fig. 3.6 A schematic representation of an FTIR spectroscopy](image)

### 3.3.7. UV-Visible Spectroscopy

UltraViolet-Visible (UV-Vis) absorption spectroscopy is the determination of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. The short-wavelength limit for simple UV-Vis spectrometers is 180 nm due to absorption of ultraviolet wavelengths below 180 nm by atmospheric gases. The absorbance, A, is related to the input and output intensities according to the Beer-Lambert Law, as shown in Equation 2.1.
The absorbance $A$ can be divided by the path length to yield the absorption co-efficient $\alpha$ which quantifies the absorbance thus using composite depth into account.

The excitation of outer electrons is due to the absorption of UV or visible radiation. Because when an atom absorbs energy, electrons are elevated from the ground state to an excited state due to which the atoms can rotate and vibrate with the corresponding vibrations and rotations should discrete energy levels. They are being packed on top of each electronic level as shown in Fig. 3.7.

$$\frac{I}{I_0} = e^{-\alpha} \quad (2.1)$$

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy (Pandey et al., 2005; Ray and Bousmina, 2005; Yang et al., 2007; Sorrentino et al., 2007; Zhao et al., 2008). Attractive polarization forces between the solvent and the absorber are responsible for lowering the energy levels of both the excited and unexcited states. The impact is striking in the excited state; with the energy difference between the excited and unexcited states is slightly decreased. This power difference causes a small red shift and influences $\pi \rightarrow \pi^*$ transitions. Finally, it is dominated by the blue group appearing from solvation of lone pairs. The effect is known as solvatochromism (Bordes et al., 2008).

**Fig. 3.7** Energy level diagrams. $E_0$ represents the ground state while $E^*$ is the excited state.