Chapter 2

Synthesis and experimental methods

This chapter describes the synthesis and experimental techniques used to obtain the data discussed in this dissertation. The first part narrates the synthesis procedures of carbon nanostructures both as separate material as well as in functional form, namely chemical vapour deposition, modified Hummer’s method, hydrothermal solution process and thin film deposition. Subsequently, we discuss instrumental parameters and conditions employed for the data acquisition relative to the techniques for spectroscopic (photoemission, pump & probe and Raman) and microstructure studies (scanning electron and transmission electron microscopy). We also describe X-ray diffraction (XRD) employed to obtain structural information, UV-Vis spectroscopy used to determine the optical band gap and electrical setups for establishing sheet resistance.
2.1 Synthesis techniques

2.1.1 Chemical vapour deposition

Significant research efforts have been devoted to the development of high-yield synthesis of carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene and graphene oxide (GO), as well as of hybrid nanostructures where these carbon structures constitute one of the building blocks. Common techniques for the synthesis of these carbon nanostructures are arc discharge\(^1\), laser ablation\(^2\) and chemical vapour deposition (CVD).\(^3\) CVD, initially designed in the 1960s and 1970s, is a proven versatile technique frequently used in the semiconductor industry because it allows for high purity controlled growth and cost-effective operations. This technique is also commonly used in optoelectronics applications, optical coatings, and coatings of wear resistant parts.\(^4\) Generally, in the process a substrate is maintained at high temperature and exposed to the volatile precursor/s. The precursor/s is/are usually carried by an inert gas, which flows over the substrate. Relatively high temperatures are required for the reaction and/or cracking of the precursors and hence for the formation of the desired solid phase, which is finally deposited onto the substrate.

In this PhD project CVD was employed for the growth of carbon fibres (CFs) and CNTs. For the growth of carbon nanostructures, the CVD process comprises of decomposition of hydrocarbons (e.g. methane, benzene, acetylene, naphthalene, etc.) catalysed by metals or their mixtures (e.g., Co, Ni, Fe, Pt and Pd) deposited on the substrates (such as Si, SiO\(_2\), Mg, Al\(_2\)O\(_3\), etc.).\(^5\)\(^6\) The gas precursor is often used simultaneously with hydrogen or argon to prevent amorphous carbon growth in the catalyst free regions. It is critical to avoid the co-deposition of amorphous carbon to obtain high quality CNTs and CNFs.

The synthesis of CNTs and CNFs is a two-step process. In first step the catalyst is prepared by deposition on the substrate, followed by either chemical etching or thermal annealing. Thermal annealing results in catalyst island formation on the substrate; the precursors diffuse on the surface and the nanostructures nucleate at these islands.\(^7\)\(^-\)\(^10\) The main parameters,
which control the growth of CNTs and CNFs in CVD, are the reaction environment, the catalyst, the growth temperature and the carbon source. In general, the growth temperature for the synthesis of CNTs and CNFs with CVD ranges from 400°C to 900°C. The sequence of steps involved during CVD growth are illustrated in figure 2.1. The flow of precursor/s in a CVD reactor/chamber is generally assumed to be laminar, therefore the velocity of the gaseous species at the walls of the reactor will be zero and the region close to the walls where the gas velocity strongly varies is called the boundary layer. The bulk precursor gases can diffuse through the boundary layer and decompose at the surface of the substrate to form the desired product. The consumption rate of the reactants at the surface of the substrate is controlled by surface reaction rates. The dissociation of precursor/s is usually fast as the substrate is placed at an elevated temperature and by-products diffuse out through the boundary layer.

methods, is promising for scaling-up the synthesis of carbon nanostructures and enabling controlled growth on various surfaces. Although the crystallinity of CNTs and CNFs grown by arc-discharge and laser evaporation methods is better,

![Figure 2.1: Various steps involved during CVD growth: (1) diffusion of hydrocarbons through the boundary layer, (2) adsorption of precursors on substrate covered with catalyst, (3) reaction takes place, (4) desorption of adsorbed species, and (5) by-products through the boundary layer.](image)
CVD provides several other advantages such as high yield, patterned, robust and direct growth with controlled orientation with desired chirality on the substrates suitable for devices. These features make the CVD process preferable over other synthesis techniques.

Previously, CVD methods have been successfully utilized to control the chirality (semiconducting & metallic), diameter and orientation of CNTs.\textsuperscript{[11-14]} We employed the CVD method for the synthesis of CNFs on InAs nanowires and for the growth of single walled carbon nanotubes (SWCNTs). These experiments were performed in the Analytical Division of the TASC-IOM-CNR laboratory, Trieste Italy and at the Department of Engineering at the Cambridge University, United Kingdom.

**Pre-treatment of InAs substrates:** For the synthesis of CNFs-InAs hybrid nanostructures, InAs nanowires grown vertically on the InAs substrate (prepared by Lucia Sorba and her team at the Istituto Nanoscienze-CNR in Pisa, Italy) were used as a template. The de-gassing of the InAs substrates was performed in H\textsubscript{2} atmosphere to pre-treat and clean the surface. The samples were annealed using a silicon heater and the temperature was measured by using an infrared pyrometer.

**Growth conditions for CNFs-InAs hybrid nanostructures:** The CVD growth was performed with and without a catalyst (iron). When we used the catalyst, iron deposition was done at room temperature, followed by annealing to the chosen growth temperature. Fe catalyst films were deposited \textit{in situ}, at room temperature by electron bombardment (Fe target from Aldrich, 99.9% purity) at a growth rate of \(~0.35\ \text{Å/min.}\) The C\textsubscript{2}H\textsubscript{2} and H\textsubscript{2} (SIAD, grade 5) as precursor gasses in different flux ranges. The pressure in the growth chamber during the CVD process was in the range of 1 to 5×10\textsuperscript{-4} mbar.

**Substrates used for growth of SWCNTs:** Two types of substrates were used for the synthesis of SWCNTs, (a) thin films of 150 nm thermally grown SiO\textsubscript{2} support layer on polished n-type Si(100) substrates\textsuperscript{[15]}, on 10 nm thick Al\textsubscript{2}O\textsubscript{3}
support layers grown via magnetron sputtering\textsuperscript{[16]}, (b) The thin films of 30 nm TiN grown via atomic layered deposition (ALD) on Si substrates\textsuperscript{[17]}

**Growth conditions for SWCNTs:** Aligned and unaligned SWCNTs bundles were synthesized in an ultrahigh vacuum system (base pressure $<1\times10^{-10}$ mbar). In this setup it was possible to control the chemical state of the catalyst (before and after growth) via X-ray photoelectron spectroscopy and to monitor precisely all the CVD parameters (\textit{i.e.} precursor gas purity, pressure and pressure gradient, sample temperature, gas fluxes, \textit{etc.}).

**2.1.2 Graphene oxide synthesis/reduction of graphene oxide**

Many methods are reported to produce graphene such as mechanical exfoliation or chemical vapour deposition\textsuperscript{[18, 19]}, however these methods are not ideal candidates for large-scale production. We have used the modified Hummer’s method\textsuperscript{[20, 21]}, through which graphene oxide/reduced graphene sheets are produced in bulk form to incorporate them into other materials and thereby exploit them for various applications. The flow chart of the different steps in the preparation of graphene by the modified Hummer’s method is given in figure 2.2. The as-synthesized reduced graphene oxide
(rGO) and graphene oxide (GO) were used to produce the rGO-ZnO and GO-TiO$_2$ hybrids discussed in Chapters 6 and 7 of this thesis.

### 2.1.3 Hydrothermal solution processing

The hydrothermal solution process is another excellent approach to synthesize the hybrid carbon nanostructures. It allows to fabricate the hybrid building blocks in a single-step soft solution process with low energy consumption. The hydrothermal technique has several other benefits like cost effectiveness, simplicity, higher and uniform dispersion of reactants and processing of complex materials. Most significant is the suitable tailoring of the chemical environment to control the reaction conditions for having the desired shape, size and orientation of hybrid nanostructures. We used a hydrothermal solution process for the synthesis of rGO-ZnO hybrid nanostructures and for the titanium dioxide nanoparticles.

*Synthesis of rGO-ZnO hybrid nanostructures*
The rGO-ZnO hybrid nanostructures were synthesised by a hydrothermal solution process.

Synthesis of TiO$_2$ nanoparticles

The TiO$_2$ nanoparticles were synthesized by a hydrothermal technique using a Teflon-lined autoclave (see figure 2.4). The various steps involved in the synthesis process are sketched in figure 2.5.
2.1.4 Preparation of GO-TiO$\textsubscript{2}$ composite films

The indium tin oxide (ITO) coated glass substrates, with a sheet resistance of 15-25 $\Omega$/sq (Sigma Aldrich) were cut into 2 cm x 1 cm pieces. These substrates were cleaned with a detergent mixture of distilled water, acetone and isopropyl alcohol (IPA) for 15 min each. The washed substrates were dried in a hot and dry air flux. The GO and TiO$\textsubscript{2}$ nanoparticles suspensions were prepared in isopropanol and ethanol respectively, in separate glass beakers. The as-prepared suspensions were mixed together and sonicated to get a homogenous composite solution. The composite solution was released drop wise onto the conducting ITO substrate with the help of syringe and spin coated at 3000 rpm for 40 s. The as-prepared films were annealed at 150 °C for 1 h.
2.2 Characterization techniques

2.2.1 Photoelectron spectroscopy (Chapters 3, 6, 7)

The origin of photoelectron spectroscopy can be traced back based to photoelectric effect process for which A. Einstein received the Nobel Prize in 1921\textsuperscript{[22]} and theory of photons as quanta of energy was deduced in later developments. In the middle of 1960’s Kai Siegbahn and co-workers developed the photoelectron spectroscopy technique at the University of Uppsala, Sweden, which led to the Nobel Prize for him in 1981. \textsuperscript{[23 24]} Photoelectron spectroscopy or Electron spectroscopy for chemical analysis (ESCA) as it is sometimes called, can be successfully employed for all types of samples: solids, liquids and gasses.

Photoelectron spectroscopy is a photon-in electron-out experiment performed in ultra-high vacuum chamber equipped with electron energy analyser as shown in figure 2.6. A photon beam (light source) obtained from conventional laboratory source or synchrotron radiation is impinged on specimen. An electron is emitted after absorbing a photon, carrying a certain amount of kinetic energy. A schematic picture for single electron transition is depicted in figure 2.6. The fundamental equation used for energy conversation in photoemission theory is as follows\textsuperscript{[25]}

\[ h\nu = E_B^{\text{E}_{\text{vac}}} + E_{\text{kin}} = E_B^{\text{E}_{\text{F}}} + \Phi_{\text{spectra}} + E_{\text{kin}} \]  

(2.1)

where \( h \) is the Planck’s constant; \( \nu \) is the frequency of the photon; \( E_B^{\text{E}_{\text{vac}}} \) is the binding energy referenced to the vacuum level of the specimen of a given electron; \( E_{\text{kin}} \) is the kinetic energy of the outgoing electron just when leaving the specimen; \( E_B^{\text{E}_{\text{F}}} \) is the binding energy referenced to the Fermi level; \( \Phi_{\text{spectra}} \) is the spectrometer work function and \( E_{\text{kin}} \) is the kinetic energy of the photoelectron as measured in the spectrometer.

The interaction of X-rays with sample generates photoelectrons with a large distribution of kinetic energies and emission angles. These photoelectrons are received over a narrow or broad acceptance angle. The electrostatic analysers are employed for measuring the distribution of kinetic energies of
Figure 2.6: Principle of a typical photoelectron spectrometer with a conventional Laboratory X-Ray source.  

Figure 2.7: Schematic view of the photoemission process in the single particle picture. Electrons (here in a metal) with binding energy $E_B$ can be excited above the vacuum level $E_{\text{vac}}$ by photons with energy $h\nu$.  

the electrons, yielding a spectrum. The incident X-ray photons penetration depth is fairly large for a given specimen.

Nevertheless, for conventional laboratory sources (emitting Mg or Al K$\alpha$ radiation), the mean free path of the emitted photoelectrons is very small because of scattering and typically amounts to a few nm. Therefore, only
the electrons emitted from the first few atomic layers of specimen can escape without scattering, hence photoelectron spectroscopy is a surface sensitive technique.

The widths of photoemission peaks in an XPS spectrum are determined by the core hole lifetime, the resolution of the instrument, and satellite characteristics. The core hole produced in an atom is highly unstable, and its lifetime is of the order of \( \sim 10^{-15} \) s for light elements. The lifetime, \( \tau \), is associated with the uncertainty in the energy of the core hole, \( \Gamma \), through the Heisenberg uncertainty principle, \( \Gamma \tau = \hbar = 10^{-16} \) eV \( \cdot \) s. The line shape due to the core hole lifetime is Lorentzian. The photoemission peak width is also affected by the energy dispersion of the incident X-rays as well as the resolution of the analyser, which have a Gaussian line shape.

The photoemission core level peak intensities are directly proportional to the number of atoms of given kind weighted by their excitation probabilities and by the transmission function of the analyser. The most common way used to analyze the core level intensities is a so-called three step model, (1) excitation of electrons from the atoms by absorbing the incident photons, leaving the holes filled by the radiative or non-radiative processes, (2) transport of the photoemitted electrons from depth \( \xi \) to the surface of the specimen, which includes elastic and inelastic scattering phenomena, (3) escape of photoelectron from the surface into the vacuum and detection by analyzer. Consider a particular level \( n_{lj} \) of an atom Q at position \( x, y, z \), the core level intensity can be written as

\[
I_{Qn_{lj}} = A \int \int \int l_{\Phi}(x,y,z) \rho_{Q}(x,y,z) \frac{d\sigma_{Qn_{lj}}}{d\Omega} x \exp[-\xi/(\lambda_{e}\sin\theta)] x \Omega_{(\Phi,y,z)} \, dx \, dy \, dz \quad (2.2)
\]

where \( A \) is a constant of the experimental geometry, \( l_{\Phi}(x,y,z) \) is the intensity of the incident photon beam, \( \rho_{Q}(x,y,z) \) is the atomic density of atomic type Q, \( \frac{d\sigma_{Qn_{lj}}}{d\Omega} \) is the differential photoelectric cross-section of a specific level \( n_{lj} \) of involved atom Q and \( \Omega_{(\Phi,y,z)} \) is the solid angle and position on the surface of the specimen.
Core level chemical shifts are another important aspect of photoemission studies. Core levels are usually assumed as not influenced at all by chemical bonding, and in reality, they do not mix at quantum level with the valence bands responsible for inter atomic or molecular bonding. K. Siegbahn et al. pointed out that core-level binding energies are greatly sensitive to any change in valence-level charge distributions.\[28\] In a generalized picture, if an atom is less electronegative in comparison to its neighbour, its core electron will experience a different Columbic attraction, which results in a change in core level binding energies (initial state effect). In addition to the initial state effect, there is also the final state effect: the outgoing electron is attracted by the core hole left behind and this attraction depends on the screening of the core hole by the electron cloud. The better the screening, the higher will be the kinetic energy of the photoelectron and therefore the lower the binding energy.

Multiplet splitting is also a very significant characteristic of core level photoelectron spectra, which originates from atoms of the given specimen of which the valence levels are partially filled. The simplest explanation of atomic multiplet splitting is given by Russell-Saunders or LS couplings picture. When an electron of given spin and angular momentum is emitted from the core level, the new (N-1) system of core sub-shell comprised of hole together with partially filled valance electrons couple in various final states of spin and orbital angular momentum quantum number of different energies, thereby yielding more than one binding energy states for the single core level.\[26\] Hedman et al first time confirmed that core level binding energies of N1s and O1s are split into two components for paramagnetic molecules of O2 and N2 because the spin exchange interaction of the 1s core level electron left behind after photoemission with the total spin of valence electron.\[29\]

Quantification of photoemission spectrum: If we re-write \(I_{Qnjl}\) defined in (2.2) as follows:

\[
I_{Qnjl} = C_Q \cdot \lambda_e f(h\nu) \cdot \sigma_{Qnjl} \cdot K_{E_{kin}}
\]  

(2.3)
where $C_Q$ is the concentration of atoms of type Q in the probed volume; $f(h\nu)$ the photon flux given in photons/cm$^2$•s; $\lambda_e$ the electron mean free path which depends on the kinetic energy of the photoelectrons, $\sigma_{Qnlj}$ the orbital cross section and $K_{E_{kin}}$ the instrumental efficiency of detecting photoelectrons with the kinetic energy $E_{kin}$, we can define a sensitivity factor, which will be a characteristic of a certain photoemission line measured with the spectrometer used: $S_Q = \sigma_{Qnlj} \cdot K_{E_{kin}}$ and calculate the relative atomic percentage was calculated from photoemission spectra as follows:[30,31]

$$C_Q \text{ [at\%]} = \frac{I_{Qnlj} / (S_Q \cdot \lambda_e^Q)}{\sum_i \left( I_{inlj} / (S_i \cdot \lambda_e^i) \right)} \quad (2.4)$$

where i refers to all the atomic species present in the probed volume; since the kinetic energy of the photoelectrons of different species vary, so do the sensitivity factors and the electron mean free path.

**Light sources used in photoemission experiments**

For the photoemission experiments, an X-ray source with high flux is required. For a conventional laboratory, X-rays are generated by bombarding metallic anodes (usually Al or Mg) with a high-energy electron beam. In general, more than one sharp X-ray line will be emitted from the target (anode) material; energy width associated to each line varies depending upon the anode material. Most often one therefore uses a monochromator, usually composed of one or more crystals, which diffract the X-rays under a certain angle (Bragg condition), and are placed in a way that only the desired photons arrive at the sample.

Another most important light source for high-resolution photoemission experiments is synchrotron radiation. The synchrotron yields an extended band of intense radiations (infrared to hard X-rays), which are strongly collimated and polarized. Synchrotron radiation can supply a variable source of high intensity, and well-focused X-rays for photoemission studies when employed with an appropriate monochromator.
Photoelectron spectroscopy has been extensively used in the projects discussed in this thesis to investigate the electronic structures and chemical composition of the surfaces. The photoemission experiments on CNFs-InAs hybrid nanostructures were performed at the Analytical Division of the TASC-IOM-CNR laboratory (Trieste, Italy), where the analysis chamber is equipped with a conventional non-monochromatized Mg Kα X-ray source and a 120° hemispherical electron energy analyser. The in-situ X-ray photoelectron spectroscopy analysis, including catalyst deposition, was performed in an ultra-high vacuum system (base pressure <1x10⁻¹⁰mbar). The synthesis chamber is directly connected with the analysis chamber. The XPS spectra were obtained before and after all CVD steps in normal emission geometry, using an energy resolution of ~1 eV and normalized to the photon flux and counts per second. The C1s binding energy positioned at 284.8 eV was used as reference for the XPS data. The XPS peaks were analysed by performing a non-linear mean square fit of the data, reproducing the photoemission intensity using Doniach-Sunjic lineshapes superimposed to a Shirley background.

To understand the effect of temperature on interfacial properties of rGO-ZnO hybrid nanostructures, a high resolution photon source is needed. Therefore, synchrotron radiation-based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) setup was used to perform the core level photoemission measurements as a function of temperature at the bending magnet beam line 9:3:2 of the Advanced Light Source of Lawrence Berkeley National Laboratory, USA. The details of the AP-XPS equipment are discussed elsewhere. [32] The specimen was placed on a sample holder equipped with a boron nitride heater plate and a thermocouple (k-type) was placed on the top of the sample for accurate measurement of temperatures. XPS data was acquired at a photon beam energy of 750 eV, the energy resolution of the beam line was about $E/\Delta E = 3000$. A small piece of Au foil was placed on part of the sample for energy reference. The data was acquired with SES software and data analysis was performed with IGOR Pro applying XPS fit procedures. The curve fitting of the spectra was done using a Gaussian-Lorentzian lineshape in 70-30% ratio after the Shirley background correction.
The XPS data collected on GO-TiO$_2$ composites was recorded at Nanoscience and Technology Department, National Centre for Physics, Quaid-i-Azam University Islamabad, Pakistan. Thin films of GO-TiO$_2$ were deposited on indium tin oxide (ITO) substrates by spin coating for performing the XPS measurements. The XPS data was collected under UHV conditions ($3 \times 10^{-10}$ mbar), using a Scienta-Omicron system equipped with a micro-focused monochromatic Al K$_\alpha$ (1486.7eV) source having a spot size of 700 μm. The source was operated at 15 KeV with constant analyser energy (CAE) 100 eV for survey scan and 20 eV for the high resolution scans. To avoid charging effects, charge neutralization was applied using a low energy-electron flood gun. The data acquisition was done with the Matrix software and analysis was performed with IGOR Pro along with XPS fitting procedures. The curve fitting of the high-resolution spectra was done using a Gaussian-Lorentzian 70-30% ratio lineshape after Shirley background correction.

### 2.2.2 Pump-probe spectroscopy (Chapter 4, 5)

Pump probe is a technique in which ultrafast electron dynamics at femtosecond time scale are investigated. In these experiments an ultrashort laser pulse is separated into a pump and a probe beam. The pump beam excites the samples and generates a non-equilibrium state, while a probe beam is utilized to observe the pump beam-induced variations in the optical properties such as reflectivity or transmission of the sample. The pump and probe beams approach to the sample with a relative time delay. After passing through the sample, the changes in the optical constants are measured as a function of time.

For the work presented in this dissertation we performed the time resolved reflectivity experiments on aligned and unaligned SWCNTs bundles to understand the excited carrier dynamics at femtosecond timescale. Two different pump probe setups (high and low fluency) were used to investigate the transient reflectivity dependence behaviour in a broader range of exciting pulse fluence. The high fluence allows change in the fluency from 10-100 mJ/cm$^2$ at 1 KHz repetition rate, while the low fluence
setup allows to vary the fluency from 0.1 - 0.8 mJ/cm² with a higher repetition rate. The low fluence setup permits to study the regime for the transient reflectivity measurements at different energies. The brief details of the high and low fluency setups used for the experiments are introduced here below.

**High fluence setup**

In this arrangement the light source was an amplified Titanium-Sapphire laser system. The laser system was composed of four main components namely a coherent Verdi 5 laser (the pump laser for the femtosecond laser oscillator), a coherent Mira 500 laser (femtosecond mode-locked Ti: Sapphire laser oscillator), coherent evolution (the pulsed pump laser for the regenerative amplifier) and a BM α-line, the regenerative amplifier. The wavelength of the output pulses was centred around 795 nm (1.56 eV) with a full width at half maximum (FWHM) of 150 fs and an energy of 600 µJ/pulse. The mean output power was around 0.6 W with repetition rate of 1 KHz and a pulse peak power of 4×10⁹ W.

**Low fluence setup**

This experimental setup consisted of a cavity damped Ti: Sapphire mode-locked laser oscillator. The wavelength of the output pulses was 790 nm (1.5 eV) (790 nm with a FWHM of 120 fs). The output energy was 50 nJ/pulse for recurrence rate varying between 54.3 MHz to single shot. In this arrangement there were two operational modes. In the first mode, conventional one-colour transient reflectivity measurements were performed in the slow and fast transient response. The available pump fluences are low, between 0.1 and 0.8 mJ/cm². However, in the case of fast transient response, the higher repetition rate of this setup allowed for a standard lock-in acquisition and much more delay time, resulting in better resolution. For the second mode of operation, the super-continuum probe beam was used for transient reflectivity measurements. The wavelength of this super-continuum probe ranged from 620 to 1240 nm (1.00 - 2.00 eV) with a pulse duration of 120 fs.
2.2.3 Raman spectroscopy (Chapters 3-6)

Among optical techniques, Raman spectroscopy is very appropriate for the characterization of solid materials owing to the fact that it is a fast and nondestructive method and requires little sample preparation time.\textsuperscript{[33]} We employed micro-Raman spectroscopy to characterize carbon-based hybrid nanostructures as well as to figure out the chirality and diameter of SWCNTs. The Raman spectroscopy data presented in this thesis was collected by using three different Raman microscopes: a Thermo Scientific DXR, a Renishaw 1000 micro-Raman and a Labram Dilor Raman H10, equipped with charge-coupled devices (CCD). Renishaw Ramascope Raman spectrometer was equipped with an Olympus microscope and with a cooled CCD camera as photo detector, and operated at 532 nm excitation from Ag-ion laser. The spot size for Raman measurements was $7.8 \times 103 \ \mu m^2$. Spectra were recorded typically with 1–5 exposures of 2–4 s duration at 22 Wcm$^{-2}$. The Thermo Scientific DXR and the Labram Dilor spectrometer operated at 514.5 nm excitation and a spot size of about 1 $\mu m^2$. We used a Si wafer and highly oriented pyrolytic graphite (HOPG) for calibration of the Raman signal.

Raman spectroscopy is the study of light matter interaction in which light (photons) of a single wavelength is aimed onto the sample and the reflected light is collected with a spectrometer with the help of a CCD detector and analyzed. The selection of light sources is highly significant as one can decide to work with frequencies that correspond to electronic excitations of the sample (resonant Raman) or not, and the observed Raman scattering will be different in these cases. Coherent light sources like lasers are preferred because they deliver a high flux and a collimated monochromatic beam. The light (laser) causes absorption or scattering, in other words elastic and inelastic phenomena take place. The elastic scattering phenomena is named Rayleigh scattering, whereas the inelastic process is termed as Raman scattering. The Raman spectra are plotted by measuring the intensity of the scattered light as a function of frequency shift from the excitation frequency. By combining this information with that on the lattice
structure of the concerned material, the Raman lines can be assigned to certain vibrational modes or phonons.

This technique has been widely employed for characterization of carbonaceous materials such as graphite $^{[34]}$, SWCNTs $^{[35]}$, MWCNTs $^{[36-38]}$, CNFs $^{[39]}$, graphene $^{[40,41]}$, fullerene $^{[42]}$ and carbon thin films. $^{[43,44]}$ The two dominant Raman features, namely the radial breathing mode (RBM) at low frequencies and the tangential multifeature mode (G band) at higher frequencies, are very suitable for the characterization of SWCNTs. The RBM occur with frequencies between 120 and 350 cm$^{-1}$ for SWCNTs for the diameter range $0.7\text{nm}<\delta<2\text{nm}$. We used the relation $\omega_{\text{RBM}}=\left(A/\delta\right)+B$, where $\omega_{\text{RBM}}$ is the observed frequency of RBM mode, $A = 234 \text{ cm}^{-1}$ and $B = 10 \text{ cm}^{-1}$ to calculate the diameter, $\delta$, of the SWCNTs. $^{[45]}$ The G-band frequency was used for differentiation between metallic and semiconducting SWCNTs by an evident difference in their Raman lineshape; in fact the G band broadens and becomes asymmetric for metallic SWCNTs, whereas it has a Lorentzian line shape for semiconducting tubes, and this broadening is related to the availability of free electrons in nanotubes with metallic character. $^{[46,47]}$

2.2.4 Scanning electron microscopy (Chapters 3-7)

Since the spatial resolution of electron microscopes can be much higher than that of light microscopes, electron microscopes are the tools of choice to investigate very small specimens to extract the information regarding morphology, topography, and crystallography. The main components of a scanning electron microscope (SEM) are the electron gun, electrostatic lenses, the sample chamber and the detectors. An electron gun (thermionic or field emission) positioned on the top of the device emits a beam of highly concentrated electrons, which after passing through a series of lenses, is focussed on the specimen under investigation. A number of interactions occur when electrons arrive at the surface of the sample, and as a result primary backscattered electrons, secondary electrons, Auger electrons, and characteristic X-rays are produced. The primary backscattered and secondary electrons are collected by detectors to form the image of the specimen via CCD cameras. The secondary electrons with energies lower
than 50 eV are best suited to gain information on the topography of specimens with features of few nm. The collection of X-rays contributes information about the elemental composition of the sample. The SEM images displayed in this dissertation were obtained by using three scanning electron microscopes, a Zeiss supra 40 (electron energy range 10 keV, lateral resolution: 1 nm), a MIRA3 TESCAN (lateral resolution: 1.2 nm at 30 kV, 2.5 nm at 3 kV) and a FEI Nova NanoSEM 450 (electron energy range 1 KeV to 30 KeV, lateral resolution: 1nm). These SEM images were recorded with magnifications ranging from 1.0 Kx to 25.0 Kx.

2.2.5 Energy dispersive X-ray spectroscopy (Chapters 6, 7)

Energy dispersive X-ray spectroscopy (EDS) is an analytical tool used for chemical or elemental analysis of samples. The working principle of this technique consists in stimulating the emission of X-rays from the surface. In a typical EDS setup, a high energy beam of electrons impinges on the surface of the sample to excite the electrons from the inner shells of the atoms and hence creating core holes. These core holes are filled by electrons from upper shells resulting in the emission of characteristic X-rays, which are collected by a special EDS detector to extract the elemental information. The EDS data described in this thesis was obtained using general purpose high resolution field emission SEMs, namely a ZEISS SUPRA 40 and a FEI Nova NanoSEM 450. EDS measurements were carried out for elemental analysis of as-synthesized carbon-based hybrid nanostructures.

2.2.6 Transmission electron microscopy (Chapter 6)

The transmission electron microscopy (TEM) analysis was carried out to investigate the interface of rGO and ZnO NWs (wrapping). The TEM images shown in this thesis were recorded with a JEOL 8100 microscope running at 200 kV accelerating voltage. The sample was prepared by scratching the rGO-ZnO NWs from the surface of Ni foam. These rGO-ZnO NWs were dispersed in ethanol (Sigma Aldrich, 99 %) and ultra-sonicated for ~30 minutes. After this a drop of suspension was deposited on the Cu-grid and
vacuum dried before being introduced into the TEM. In TEM, the electrons behave like a wave front when accelerated at a very high speed (relativistic speed), which is scattered when it passes through a thin sample. These scattered electrons are focused with electromagnetic lenses to get the image or diffraction pattern.

2.2.7 X-ray diffraction (Chapter 7)

X-ray diffraction (XRD) was employed for the structural and phase analysis of pure GO, TiO$_2$ and GO-TiO$_2$ nanocomposite materials. XRD analysis was carried out with a Bruker D8 Advance X-ray powder diffractometer at the Nanoscience and Technology Department, Quaid-i-Azam University, Islamabad. The diffractometer was operated with a Cu K$_\alpha$ radiation source ($\lambda$ = 1.54056 Å), generated at 40 kV and 40 mA and the data acquired at a scan rate of 1.2/min in a 2θ range of 5° to 70°. X’pert high score and chekcell software were used for the assignments of the peak positions and for calculating the average crystallite size. The interlayer distance between two GO sheets was determined by using the Bragg’s equation, i.e. $\lambda=2dsin(\theta)$ where $\lambda$ is the wavelength of the X-ray beam ($\lambda$ = 0.154 nm) and $d$ is the distance between GO layers.

2.2.8 UV/visible spectroscopy (Chapter 7)

Ultraviolet–visible spectroscopy (UV-Vis) is an important analytical tool widely utilized in physics, chemistry and life sciences for studying the optical properties of materials. We have used the Perkin-Elmer Lambda 950 photospectrometer, equipped with an integrating sphere of 150 mm diameter, for retrieving the band gap and optical properties of GO-TiO$_2$ nanocomposite materials. The operating range Lambda 950 spectrometer is 175–3300 nm with a resolution of ~0.05 nm. To eliminate the background signal, this spectrometer is equipped with a double beam (Deuterium and Tungsten lamps) and a double monochromator. A photomultiplier tube (PMT) and a PbS detector cover the full range of UV/Vis (175 nm to 860.8 nm) and NIR (860.8 nm to 3300 nm), respectively. We collected the transmittance spectra from ITO/xGO–TiO$_2$ (x = 0 wt%, 2 wt%, 4 wt%, 8 wt%,
and 12 wt%) nanocomposite thin films. The optical bandgap of the samples was calculated based on Beer’s law by plotting the \((ahv)^2\) vs \(hv\).[41]

2.2.9 Electronic transport measurements (Chapter 7)

The electron transport measurements on GO, TiO\(_2\) and GO-TiO\(_2\) nanocomposite thin films were carried out by using a four probe Keithley (nano-source meter) system. For this, compact xGO-TiO\(_2\) (x = 0 wt%, 2 wt%, 4 wt%, 8 wt%, and 12 wt%) nanocomposite thin films were deposited on ITO substrates and contacts made by using conductive silver paste (Sigma Aldrich). From these electrical measurements the characteristic current-voltage curves were obtained.

References