

Experimental Methods

2.1 Introduction

The characterization performed in the thesis work are summarized in Figure 2.1. Various techniques are used for the characterization of inorganic nanomaterials and their functionalized counterparts with focus on the structural and elemental modification. In the following section, a brief description about each of them is discussed.

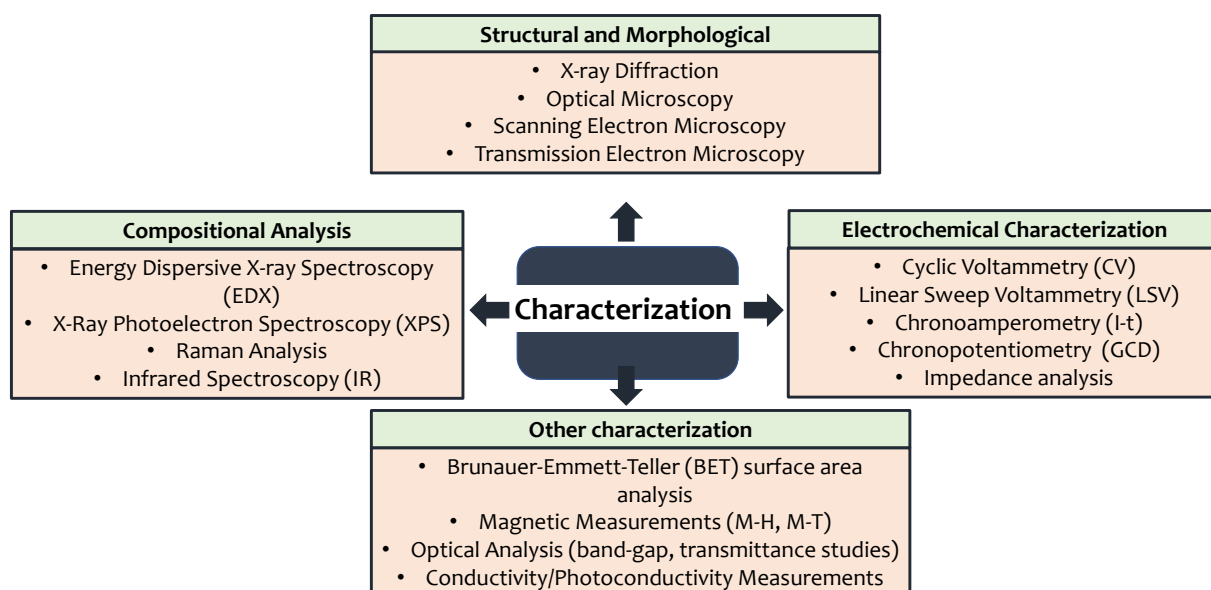


Figure 2.1: Characterization performed for analysis in the thesis.

2.2 Structural and Morphological Analysis

2.2.1 X-ray Diffraction (XRD)

Powder X-ray diffraction is widely used for the identification of unknown crystalline material, crystal structure and crystal size. X-ray diffraction occurs when the incident rays interact with the sample and produces constructive or destructive interference satisfying Bragg's law:

$$n\lambda = 2d\sin\theta \quad \dots 2.1$$

Where n is an integer, a wavelength of $K\alpha$ Cu (1.54 \AA), d is inter-planar distance. In a crystal, the typical inter-atomic spacing is around $2\text{-}3 \text{ \AA}$, so the suitable radiation for diffraction study of crystals is x-ray which matches exactly with the wavelength of source. Particularly in case of fluorination, due to similar ionic size of F^- and O^{2-} , any significant change in the crystal structure is not expected. However, F^- is known to affect the crystal growth leading to oriented crystal grown that can be analyzed using XRD.

2.2.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is the most widely used type of electron microscope for analyzing the morphology in the nanostructures. Materials are prone to etching and selective growth during fluorination process that can be analyzed using scanning electron microscopy.

2.2.3 Transmission Electron Microscopy (TEM)

For analyzing the sample at even higher magnification and resolution transmission electron microscopy (TEM) can be performed. High-resolution TEM can also provide in depth information about the trace elements presence by analyzing the interplanar distances. Further crystallinity can also be deduced by the selected area diffraction (SAED) pattern of the material.

2.2.4 Surface Area Analysis (Brunauer–Emmett–Teller)

Brunauer–Emmett–Teller (BET) analysis can be performed to analyze the surface area and pore morphology of materials using N₂ adsorption/desorption isotherm curves. For metal oxides, fluorination induced etching can increase the surface area. However, fluorination is concomitant with decrease in specific surface area and pore volumes of porous carbon materials due to the formation of functional groups. However, some cases shows a higher specific surface area and pore volume upon C-F bond formation.

2.3 Compositional Analysis

Various analytical and spectroscopic techniques can be explored for analyzing the composition of materials as discussed below.

2.3.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a surface analyzing technique and gives the composition of the material. It is used to observe the functionalization of the fluorinated material. In the XPS survey spectrum, the presence of F1s peak at ~684-686 eV suggests the successful fluorination of the sample. For fluorocarbons, the presence and percentage of covalent, semi-ionic and ionic C-F bonds in fluorocarbon can be investigated by the high resolution F1s and C1s spectrum which is further deconvoluted into different C-F bond peaks. The semi-ionic bonds are observed at approximately 287-290 eV and 685-688 eV in the C1s and F1s XPS spectra respectively. The ionic and covalent bonds peak are observed at lower and higher binding energy than the semi-ionic bond respectively in XPS spectra. In case of metal oxide fluorination, substitutional or interstitial fluorination can take place. Interstitial fluorine has a slightly higher binding energy than that of substitutional fluorine. Further, for getting an idea about the depth of fluorination, XPS depth profiling can be performed where, argon sputtering is performed on the sample and repeated XPS analysis is performed to get an idea about the nature and quantify of fluorine along the bulk.

2.3.2 Fourier-transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy is a technique used to obtain infrared spectrum of absorption or emission of a solid, liquid or gas. FTIR spectroscopy stimulates the bond vibrations upon exposure of material with infrared radiation (IR region = 4000 - 400 cm⁻¹) of electromagnetic spectrum at specific frequency. These frequencies can be detected and gives fingerprint information about the functional group present in the material under consideration. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

2.3.3 Raman spectroscopy

Raman spectroscopy also gives an idea about the bonding present due to change in the polarizability of material upon interaction with laser of specific wavelength. Raman spectroscopy is a very strong tool especially for characterization of carbon material and its

functionalization. Any carbon material having graphitic structure will exhibit a G band ($\sim 1560\text{ cm}^{-1}$) which arises due to the E_{2g} vibration mode of the sp^2 - hybridized carbon and in addition to that a D band ($\sim 1330\text{ cm}^{-1}$) is also generated due to the disordered structure or the defects present. I_D/I_G ratio is calculated to analyze the change in defect density upon fluorination of the material. With increase in the etching by fluorinating precursor, the I_D/I_G ratio is expected to increase.

2.4 Magnetic Measurements

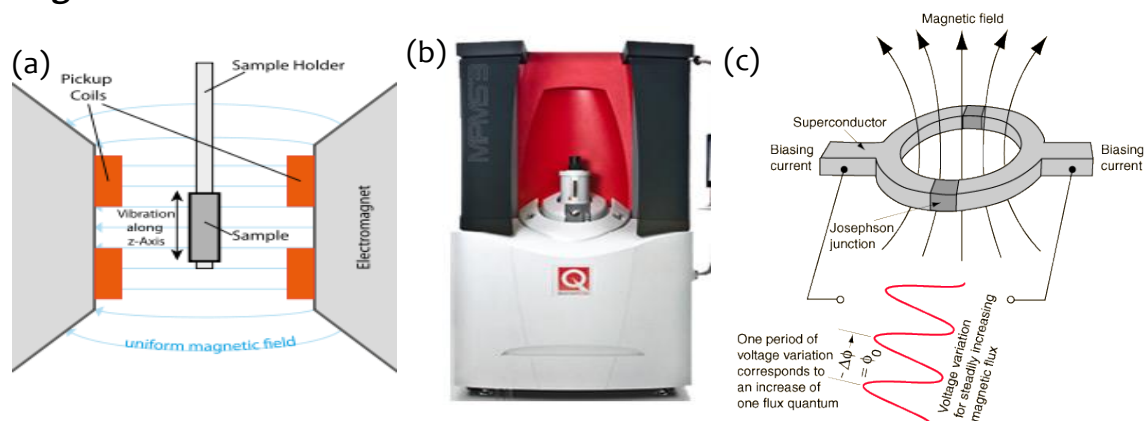


Figure 2.2: Schematic demonstrating the working principle of (a) Vibrating Sample Magnetometer (VSM), (b,c) Superconducting Quantum Interference Device (SQUID) and its corresponding photograph. Figure adapted from: <https://lot-qd.de/en/products/materials-science/magnetometers/product/mpms3-squid-magnetometer>.

The magnetic measurements can be performed by Vibrating sample magnetometer (VSM) or Superconducting Quantum Interference Device (SQUID). VSM measures the magnetization of magnetic material placed in an external magnetizing field by converting the dipole field of the sample into an AC electrical signal. In VSM, sample to be analyzed is placed inside the uniform magnetic field and then vibrated sinusoidally using vibrator. The induced voltage in the pickup coil is proportional to the sample's magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup, as shown in Figure 2.2a, the induced voltage is measured through the lock-in amplifier using the piezoelectric signal as reference for weak signals. By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material. SQUID magnetometer is used to measure the overall magnetic moment of a sample (Figure 2.2b). SQUID magnetometer is very sensitive as it is configured to detect small magnetic field. It consists of two superconductors separated by thin insulating layers to form two parallel Josephson Junction. When the sample is moved up and down, it produces an alternating magnetic flux in the pick-up coil. The magnetic signal of the sample is obtained via a superconducting pick-up coil together with a SQUID antenna. This device acts as a magnetic flux-to-voltage converter (Figure 2.2c). This voltage is the amplified and read out by the magnetometer's electronics.

2.5 Electrochemical Characterization

2.5.1 Cyclic Voltammetry (CV)

Cyclic voltammetry is a powerful and popular electrochemical technique. The curve obtained by CV is known as Cyclic Voltammograms. The X-axis represents the parameter which is imposed on the system i.e., a variable quantity, usually the applied potential (V) while Y-axis is the response that is obtained in against of parameters that is being inserted, the resulting current (I). So, a cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scans. A typical cyclic voltammogram of a redox couple is shown in Figure 2.3a.

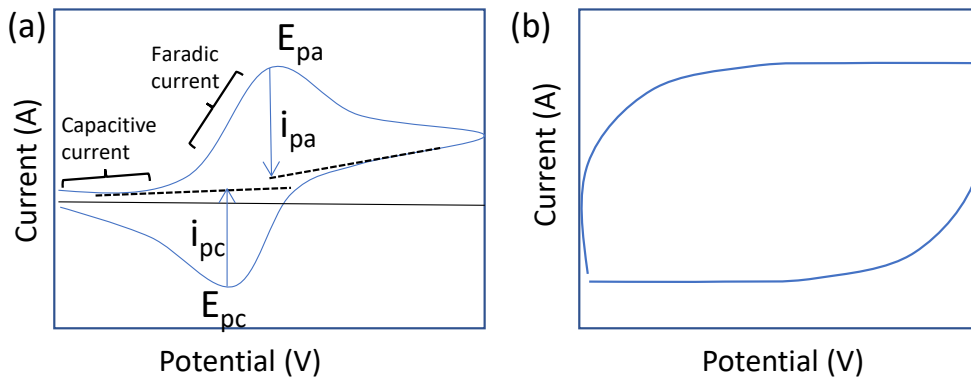


Figure 2.3: Cyclic voltammogram of (a) redox couple (b) EDLC supercapacitor

A typical voltammogram of an electric double layer capacitor (EDLC) consists of a rectangular shape and any deviation from this shape indicates the contribution of resistive behavior of device (Figure 2.3b). In case of pseudocapacitors, redox peaks are observed in the curves due to the presence of faradic reactions taking place. The specific capacitance can be calculated from the CV by the given formula:

$$C = I \times \Delta t / \Delta V \times m \quad \dots 2.2$$

Where C is the specific capacitance, I the constant discharge current, Δt the discharge time, ΔV the voltage difference in discharge and m is the mass of active material within the electrode.

2.5.2 Galvanostatic Charge-Discharge (GCD)

Galvanostatic charge/discharge is a standard technique used to test the energy storage capability and charging and discharging profile of the device. This method is also known as Chronopotentiometry. Cycle is defined as the repetitive loop of charging and discharging. In this method, the potential is measured by applying the current pulse to the working electrode against a reference electrode as a function of time. When current is applied, the potential changes abruptly due to IR (Internal Resistance) loss and then potential changes gradually as the concentration overpotential is developed across the electrodes as concentration of the electrolyte is exhausted at the electrode surface.

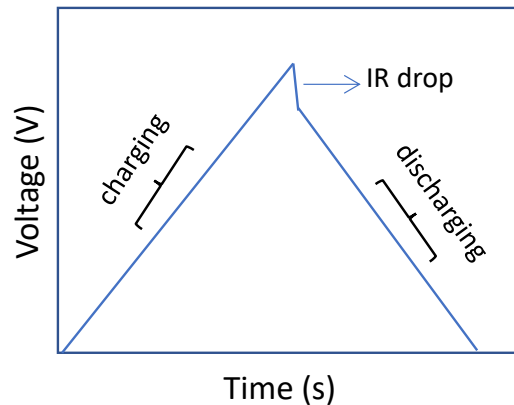


Figure 2.4: Galvanostatic charge/discharge cycles of supercapacitor.

A symmetric triangular shape is observed for an ideal EDLC showing the whole amount of charge stored while charging is dissipated during the discharging cycle (Figure 2.4). However, some asymmetry is always there and IR drops are observed. For faradic reactions, redox peaks are also observed in the GCD curves which are in consistent with the CV curves. The specific capacitance from GCD can be calculated from the following equation:

$$C = i\Delta t/m\Delta V \quad \dots 2.3$$

Where i is the current density, Δt is the discharge time, m is the mass of the active material loaded and ΔV is the potential range of the GCD cycle.

2.5.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy is also termed as AC impedance spectroscopy. It is a method of electrochemical characterization for electrochemical system. The complex impedance

plane or Nyquist plot gives the variation of real impedance with imaginary impedance and each data point corresponds to a single frequency. To measure the real and imaginary part of impedance, A.C. perturbation voltage is applied. The impedance of an ideal capacitor with a zero real component is given by following formula:

$$Z = Z' - Z'' = \frac{1}{j\omega C} = \frac{1}{j2\pi fC} \quad ..2.4$$

Where ω is the angular frequency and f is the frequency.

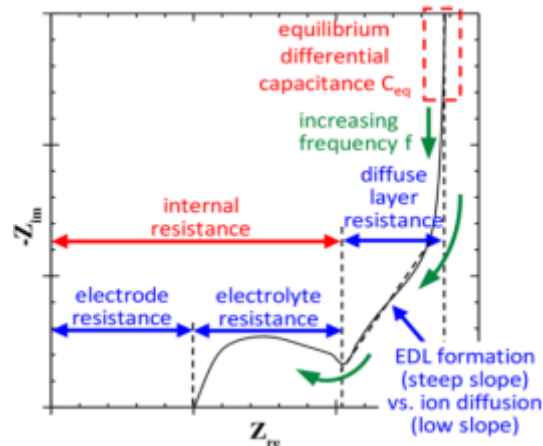


Figure 2.5: Nyquist plot of supercapacitor. Figure adapted from [Mei et al., 2018].

Ideally, Nyquist plots of EDLCs show a straight line parallel to y -axis in low frequency region with a semicircle observed at high frequencies. The slope of the line in the low frequency region represents the capacitive behavior and ionic transport. The diameter of the semi-circle at high frequency range represents the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface. The smaller the diameter, the lesser is the R_{ct} value. The beginning of the semicircle line represents the resistance (R_s) of the electrolyte in contact with the current collector and electrode. The termination of the semicircle line represents the internal resistance (R_p) of the electrode (Figure 2.5).

2.6 Fabrication of Interdigitated Electrodes

Nano patterning is a one of the miniaturization technique for fabrication of patterns, especially used for electronic devices. It generally uses photolithography methods but many techniques have been developed. The batch fabrication of microstructures requires a low-cost, high throughput surface patterning technology.

There are many techniques through which micro/nano patterning could be possible. They are,

- Photolithography – A conventional and classical method
 - Ion beam Lithography
- X-ray lithography
- Electron beam lithography
- Alternate Nano lithographic Techniques
 - Micro-contact printing
 - Nano-imprint lithography
 - Scanning Probe lithography

The lithography technique used in the thesis is photolithography. Photolithography is a process used in microfabrication to selectively remove parts of a thin film. It uses light to transfer a geometric pattern from a photomask to a light-sensitive chemical on the substrate. A series of chemical treatments then engraves the exposure pattern into the material underneath the photoresist. Photolithography is classified in to three categories i.e. Contact, Proximity and projection lithography. Projection lithography works like an overhead projector. The resolution in projection photolithography reaches up to 1 μm .

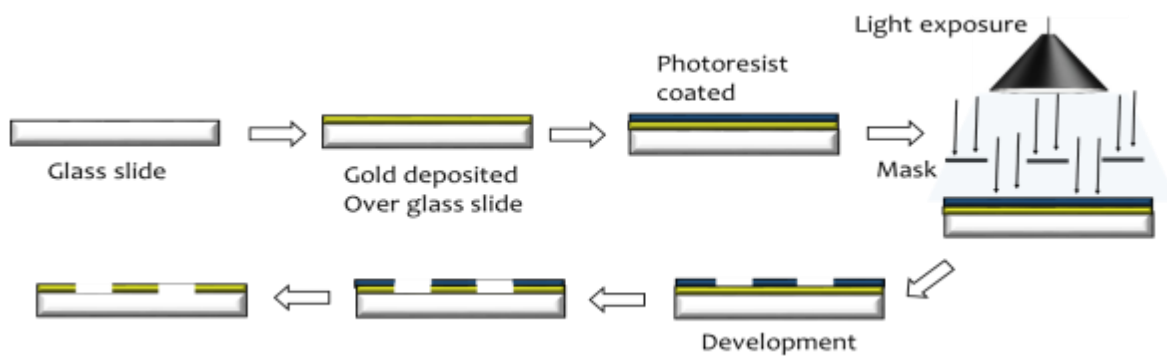


Figure 2.6: Steps involved in fabrication of electrode pattern using photolithography technique.

Interdigitated electrode (IDEs) can be fabricated by simple procedure utilizing essential lithography process. Various steps included in photolithography are shown below in the Figure 2.6. Using photolithography, interdigitated electrodes of appropriate specifications (Figure 2.7) have been fabricated as shown inset Figure 2.7.

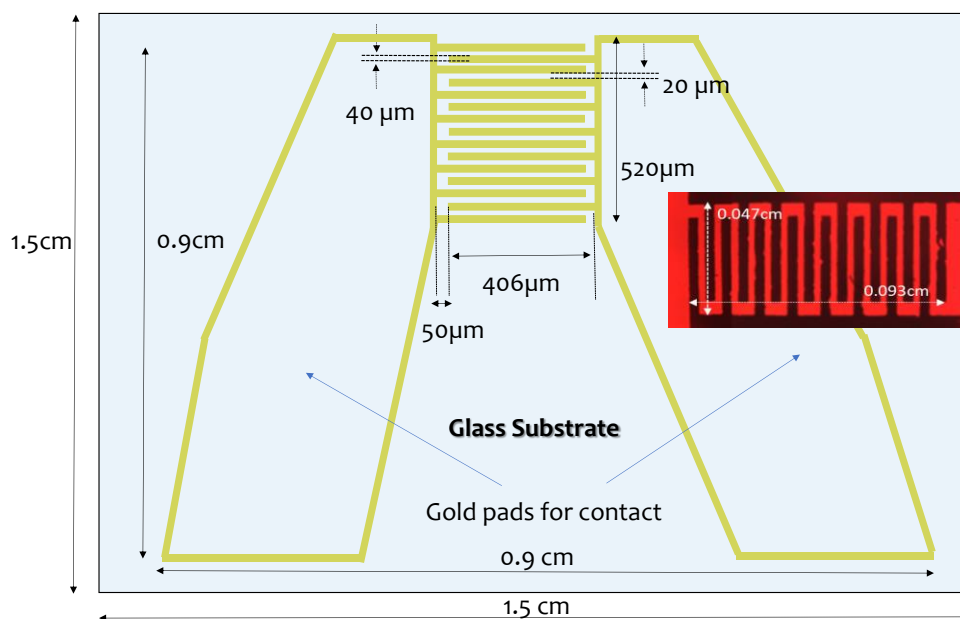


Figure 2.7: Schematic diagram of the gold electrodes. Inset shows optical image of the interdigitated gold electrodes.

2.7 Conclusions

The second chapter of the thesis summarizes the compositional and physical characterization techniques viz, SEM, TEM, XRD, BET, IR, Raman, XPS used in the thesis. The electrical/electrochemical techniques that are used for detailed characterization of supercapacitors, photoelectrochemical cells and sensors are elaborated with their basic principle. Magnetic characterization using SQUID is also discussed in detail. Further, projection photolithography technique for fabrication of interdigitated electrodes is also discussed.