

Nanostructured based electronic device fabrication and characterization

M.Sc. Thesis

By
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**DISCIPLINE OF PHYSICS
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Nanostructured based electronic device fabrication and characterization

A THESIS

*Submitted in partial fulfillment of the
requirement for the award of the degree*

**Of
Master of Science**

By

SIMRAN LAMBORA



**DISCIPLINE OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY INDORE**

June 2018



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Nanostructured based electronic device fabrication and characterization** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2016 to June 2018 under the supervision of Dr. Rajesh Kumar, Associated Professor, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

**Signature of the student with date
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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the Supervisor of
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(Dr. RAJESH KUMAR)

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SIMRAN LAMBORA has successfully given his/her M.Sc. Oral Examination held on **19 June, 2018**.

Signature of Supervisor of MSc thesis
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Simran Lambora
Master of Physics
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DEDICATION

Dedicated to my parents

Abstract

Fabrication and operation of two electrochromic materials in core-shell form is presented here. Nickel oxide and polyaniline have been used for fabricating their hybrid nanostructures to improve electrochromic behavior. Nickel oxide nanopetals deposited on fluorine doped tin oxide substrate was used as backbone to grow polyaniline using two step methodology consisting of hydrothermal method followed by electropolymerization method. The hybrid core-shell nanoarrays show improved coloration efficiency, color contrast, switching speed. To measure electrochromic behavior, in-situ UV-Vis spectroscopic technique and cyclic voltammetry have been done.

Keywords: electrochromism, nanostructures, UV-Vis spectroscopy, cyclic voltammetry.

LIST OF PUBLICATIONS

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NOMENCLATURE

λ	Wavelength
ν	Frequency
η	Coloration Efficiency
E	Energy
Q	Charge

ACRONYMS

NSs	Nanostructures
NPs	Nanoparticles
NiO	Nickel Oxide
PANI	Polyaniline
EC	Electrochromic
ECD	Electrochromic Device
CP	Conducting Polymer
FTO	Fluorine doped tin oxide
XRD	X-ray diffraction
AFM	Atomic force microscope
CV	Cyclic voltammetry
OD	Optical Modulation

Chapter 1 Introduction

1.1 Background

Hybrid core/shell nanostructures have been a hotspot in the field of nanomaterial science.[1,2] Various materials such as metal/metal oxides, metal/metal, semiconductor/semiconductor, metal oxide/conducting polymer, oxide/oxide, have been explored as core/shell NSs. Hybrid organic-inorganic materials represent an interface between two worlds of chemistry.[3] The interest in these materials has increased in recent few years due to their multiple advantages such as flexibility, ease of processing and high performance. These advantages make them highly promising for devices such as the electrochromic devices. As the name suggest, the electrochromic device is a device which changes color as a result of an electrical bias. This phenomenon of changing color is known as electrochromism. Recently, conducting polymers are in increasing demand with interesting optical properties due to its multiple redox states which accompanied rich colors. But there are some bottlenecks also with CP such as slow transport of counter ions into the EC layer to balance charge and due to this rate of interconversion between redox states is limited.[4] But this discrepancy can be circumvented by integrating CP into self-supported core/shell nanoarrays. By doing this, surface area increases and diffusion distance for ion/electron transport gets smaller leading to fast kinetics with fast switching speed.[5] Hybrid NSs of metal oxide/conducting polymer will be discussed in this thesis. Core-shell nanostructures show improved electrochromic properties like stability, color contrast ratio, optical modulation, cyclic reversibility, efficiency, etc. and can be used in many applications.[3]

This thesis is focused on understanding electrochromism and electrochromic devices.

1.2 Electrochromism

Electrochromism is the phenomena of reversible change in optical properties (color) of a material when external voltage is applied.[6] The electrochromic behavior can be observed in reflection/transmission/absorption mode depending on the material and substrate. The electrochromic devices are mainly used in anti-glare glasses of automobiles, transmissive type smart energy efficient windows.[6,7] The main reason for occurring this phenomenon is reversible change in redox states acquired by material and these materials are known as electrochromic materials. Electrochromism occurs due to reversible change between two redox states of a chemical species with different optical spectrum.

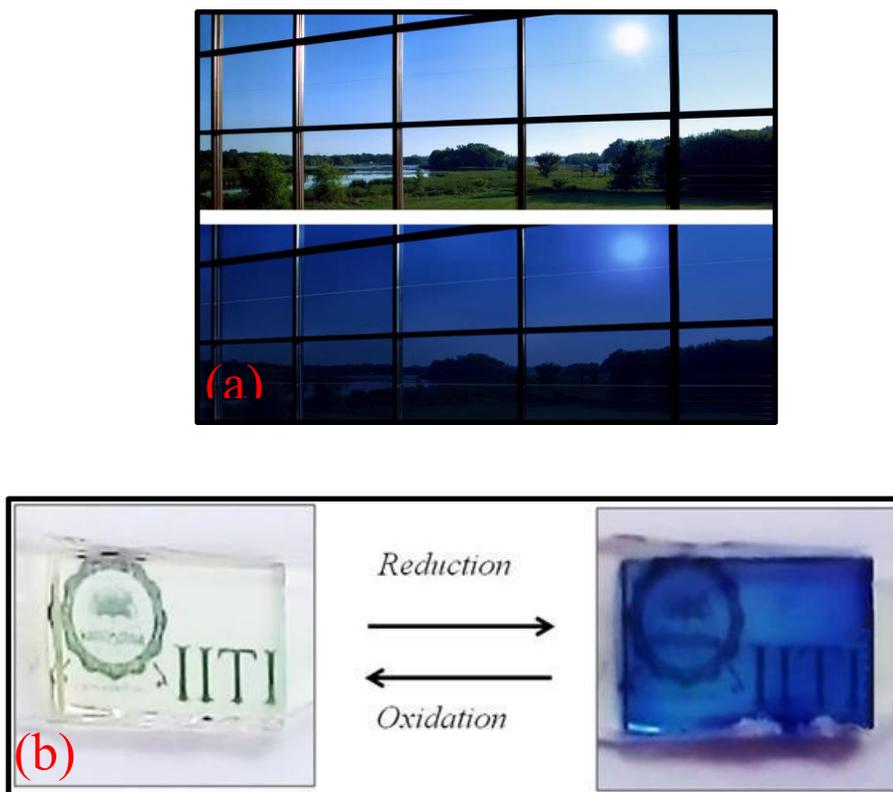


Figure 1.1: (a) Electrochromic window & (b) Electrochromic display made using viologen derivatives.[8]

Electrochromism is mainly observed in transition metals because these materials consist of multiple redox states. Conducting polymers are special class of conjugated polymers and also exhibit many redox states and show good electrochromism.[9,10] Both organic and inorganic materials show electrochromism but there are some merits and demerits also. Color can appear in EC displays in transmissive mode or reflective mode when viewed in external light. Unlike the usual electronic displays, transmission or reflection makes it possible to fabricate EC display as paper like display with appropriate engineering.[5,11,12] Material understanding and device composition are the two important factors which are needed to be established for making good quality ECDs.

1.2.1 Electrochromic materials

The material used in EC device should possess some properties like high coloration efficiency, good stability, fast switching speed, high optical contrast, etc.[5] Inorganic and organic both type of elements show electrochromism, so these materials can be divided in two classes:

1.2.1.1 Inorganic EC compounds

Transition metal and their oxides show good electrochromism and are being used since long. These materials exhibit many redox states and good stability.[13–15] The first material demonstrating electrochromism was tungsten oxide WO_3 . [16] These EC materials are deposited mostly in form of thin film by many techniques like hydrothermal method, sputtering, sol-gel method, template technique etc.[3] Metal oxides are currently used in smart windows. Improvement in properties of these materials like durability, color contrast, switching time, and cost is still need to be done. Materials which change color upon reduction are referred as cathodically EC and which change color upon oxidation is referred as anodically EC

materials. Nickel oxide is fabricated during project work which is discussed later. Nickel oxide shows good switching speed and color contrast comparatively other transition metal oxides.

1.2.1.2 Organic EC compounds

Viologen shows good electrochromism as has been already published in various research papers.[8,14,17] Conducting polymers are new in this class, which also shows this behavior. Conjugated polymers of aniline, thiophene, pyrrols, furan etc are electrochromic active because by electrochemical doping, alteration in π – conjugated electronic structure induces some change in band gap and optical contrast.[6,18] These polymers can be easily synthesized by electrochemical polymerization. Aniline, thiophene, and pyrrols derivatives are of particular interest because of their facile synthesis, suitable bandgaps and low redox potentials.[10] Aniline is environment friendly material with low cost and easy availability. Polyaniline is synthesized over NiO film which is described in chapter 2.

1.2.2 Device Geometry Paradigms

Along with other necessary constituents, EC material needs to be fabricated in device form to achieve predefined performance. An ECD is composed of two redox couples which are present between two electrodes to ensure the operation of the device. During the operation, one species gets reduced while the other one gets oxidized to complete the whole process. An ECD must switch between colored and bleached state reversibly. The fundamental geometry of an ECD is shown in the figure 1.2. For electrochromism, two conditions are mandatory: first one is that both redox couples must be transparent and the second one is that atleast one of these redox couples should be electrochromic active. More active species among two redox materials is called as primary and always kept

nearer to the working electrode, while on the other hand, redox supporting agent is present which can be electrochromic active or any other ion storage material. An electrolyte separator is sandwiched between these two redox materials which is an ionic conductor and works as a mediator to transport ions from one electrode to other. At the same time, the electrolyte must have zero electronic conduction to avoid short circuit in the device. All these above mentioned layers are sandwiched between two transparent conducting electrodes. The switching speed (coloration/transparent) of the device depends upon the nature of constituents present within the device.

ECD can be of two types:

- Single layer ECD: Only one type of electrochromic material is present.
- Double layer ECD: Both redox layers are electrochromic active.

Single layer EC devices have less number of redox states compared to double EC devices. Transmittance of single layer ECD is higher in its neutral state while in case of double layer ECD; color tuning capability during operation is good.

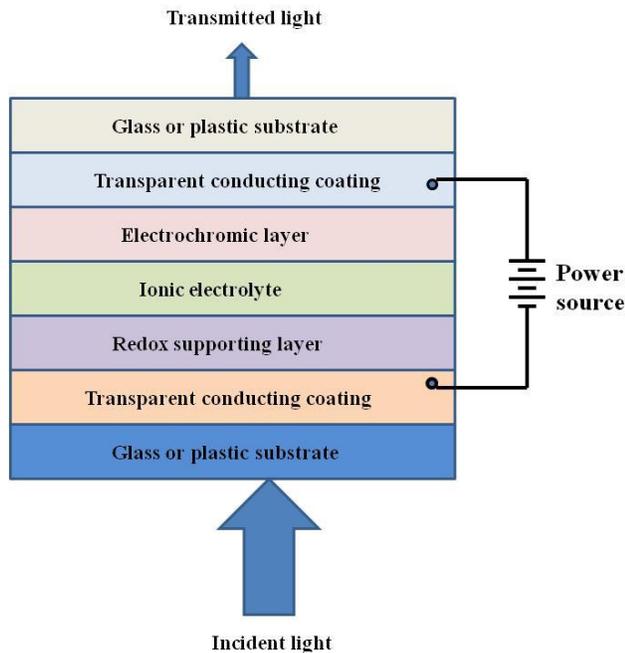


Figure 1.2: Layered geometry of a typical electrochromic display.

Other components of the EC device includes are following as:

Transparent conducting electrode (TCE): Generally, these are glass/quartz substrate coated with either indium doped tin oxide (ITO) or fluorine doped tin oxide (FTO).

Electrochromic active layer: This layer is made up of electrochromic active material which responds during the operation.

Ionic conductor electrolyte: Electrolytic layer is sandwiched between electrochromic material layer and redox supporting material. This layer should be good ionic conductor in nature but electric insulator to avoid short circuiting in device.

Redox supporting layer: Generally, this layer is used as a supportive material to complete the redox reaction for electrochromism. This material can also show electrochromism.

1.2.3 Color perceived

In case of metal nanoparticles, prominent spectroscopic features overserved due to surface Plasmon resonance and because of this sharp and intense absorption band in visible range rises. The origin of this absorption is free electron oscillation in the conduction band of metals.[19] In electrochromism, the color reaches to our eyes is the result of the light after gets reflected/transmitted by the material along with nonlinear sensitivity of different wavelength.

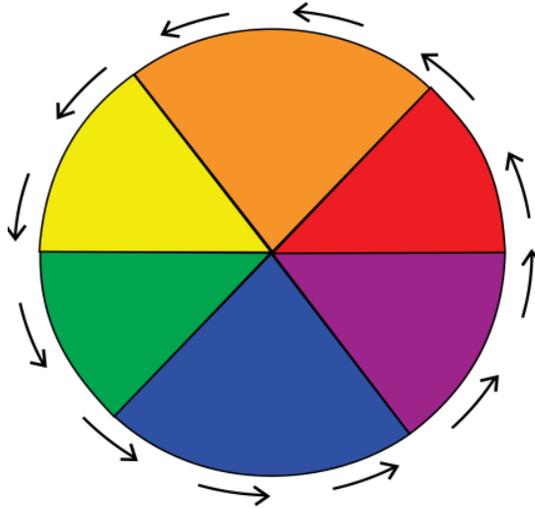


Figure 1.3: Color wheel to check various color combinations.

We can understand from figure 1.3 that the complementary color system easily allows one to relate the maximum absorbed color. From an example, we can understand this in a better way. The film which shows green color transmission mode has minimum absorption in green wavelength spectrum (560 – 600 nm) . To perceive green color, absorption in red region(650 – 700 nm) and blue region(350 – 450 nm) will be high. Thus, for green color red and blue colors are the complementary colors. Accordingly, blue color is yielded by absorption of red and green color and so on.[20] During the operation, if any color is perceived we can explain that in the same manner as discussed above. Color like yellow, cyan and magenta can also be seen which are obtained as a result of the combinations of red, green and blue colors as shown in the figure 1.4a. From figure 1.4b, it can be visualize that initially, when the device is in OFF state, white light comes out after reflecting from ‘IITI’ but in the ON state of the device, the substrate absorbs yellow color which is the combination of red and green color and so, ‘IITI’ looks blue in color. No change in color is observed if non-reflective surface (like black paper) is used in the experiment.

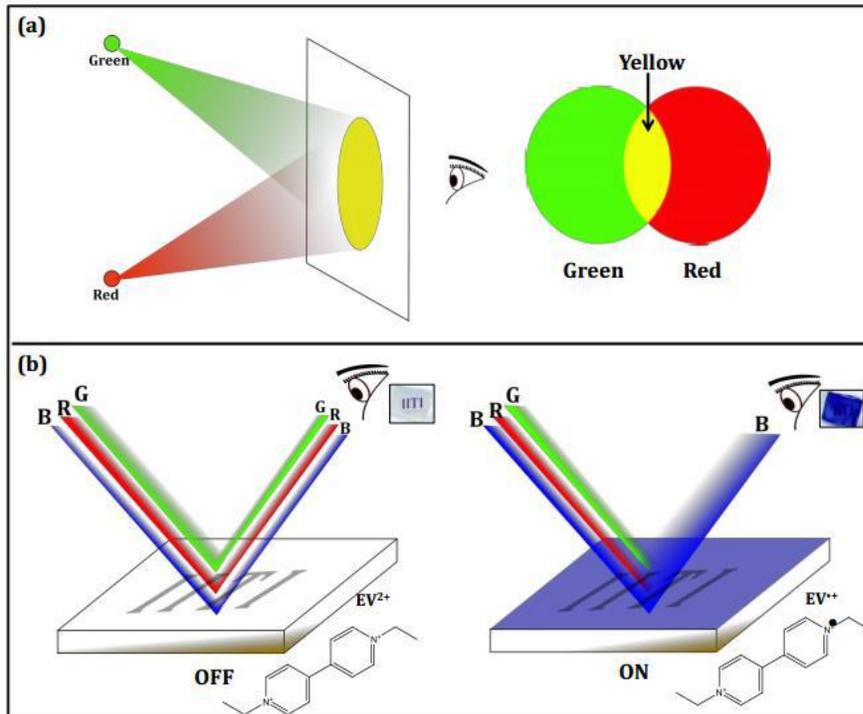


Figure 1.4: (a) Shows color combination (b) Schematic presentation of blue color perceivance of the fabricated electrochromic display with the actual images given in inset of the figure.

1.2.4 Various parameters for Electrochromism

1.2.4.1 Contrast ratio (CR):

Contrast ratio is defined to quantify the color change in ECDs. CR can be referred to either a specific wavelength or to white light. For reflective devices, CR is given by the expression:

$$CR = \frac{R_0}{R_x}$$

where R_0 and R_x is the intensity of light reflected from bleached and opaque state respectively.

In case of transmissive devices, CR is given by:

$$CR = \frac{T_0}{T_x}$$

where T_0 and T_x is the intensity of the transmitted light from bleached and opaque states respectively.

1.2.4.2 Optical density (OD):

The optical density expresses the optical transmittance of material at a given wavelength and is expressed as

$$OD = \log_{10} \left(\frac{1}{T} \right)$$

where T is the transmittance.

1.2.4.3 Coloration efficiency(η):

Coloration efficiency is defined as the change in optical properties like transmittance and absorbance by a certain amount of injected charge per unit area(unit cm^2 / C). This is also known as electrochromic efficiency and is used for the comparison of the efficient electrochromic layers. The expression for coloration efficiency is given by:

$$\eta = \frac{\Delta OD}{Q(\text{cm}^2/\text{C})}$$

where ΔOD represent the change in optical density and Q is the charge required during the device operation.

1.2.4.5 Switching time:

Switching time is the time taken by the device to change one state to another i.e. from colored to transparent or bleached. The switching speed

of ECDs depends upon ionic conductivity of the electrolyte, ion diffusion between the layers, and accessibility of the electro active sites for ions, applied field intensity, film thickness and conductivity of the transparent electrode.[21]

1.2.4.6 Cyclic reversibility:

EC device is able to switch between colored and transparent states so many times. Cyclic reversibility can be defined as number of cycles an ECD turns ON and OFF. Cycling counts of EC device provides the information about the life of the fabricated device.

1.2.4.7 Stability of device

Electrochromic material plays an important role in ECD's stability. Multiple redox switching of the material reduce device performance. Environmental condition and applied field also important for consistent performance. Therefore, redox stability and good environment are required for EC device's good performance.[22]

Chapter 2 Experimental details

2.1 Microscopic Techniques

2.1.1 Scanning electron Microscope (SEM)

A scanning electron microscope is a powerful tool to obtain morphological, topographical, compositional information of the sample by providing three dimensional highly magnified pictures. The principle of SEM is same as light microscope but probes are different. In SEM, highly energetic electrons are used as a probe. The interaction of incident electrons and atoms of specimen leads in emission of many signals like secondary electron (SE), back scattered electron (BSE), characteristic X-rays, auger electrons, etc. These signals contain information about the samples structure, atomic number, texture, chemical composition etc. SEs are the loosely bound electrons of the specimen atoms which are dislodged when primary electron beam strikes the samples surface and transfer its energy to the surface atoms. These electrons provide information related to surface texture and roughness. Because of low energy around 3-5 eV, these electrons give highly resolved topographical information. When collision between primary electrons and the specimen atomic nucleus take place, it causes electron to bounce back. These BSEs contain information about atomic number of sample, i.e. larger the BSEs produced, higher the atomic number will be. Characteristic X-rays and auger electrons give the chemical information.

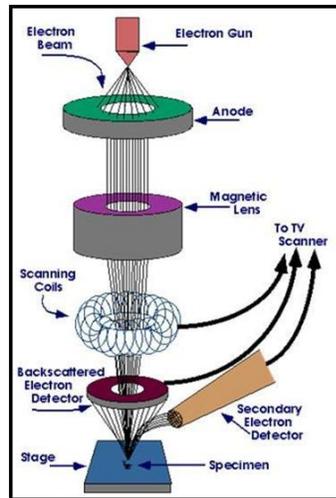


Figure 2.1: Schematic illustration of scanning electron microscope.[23]

Working:

As probe is electron here, so an electron gun is used to generate an electron beam. Cathode of tungsten with a sharp tip is used for producing a narrow beam of electrons. Anodic coil is used to accelerate the electrons because of repulsive force between anode and electrons. The diameter of the electron beam must be very small for producing high resolution images. Electromagnetic lenses are used to focus the electrons at a small spot by varying the current. If the current is low, then diameter of the beam will be small and resolution will also be high. To avoid the contamination, ultra high vacuum is required. For the current to flow through the sample, it is necessary that sample surface should be conductive. Metal coating of the specimen surface is done before to put in the equipment. When electrons come in contact with sample, secondary electrons ejected out from sample surface and gives information about size, shape, texture, etc. The electron beam is scanned across the surface and signals are detected with the help of several detectors. Different type of information is provided by different detectors.

2.1.2 Atomic Force Microscope (AFM)

For studying nanostructures, atomic force microscopy is one of the most versatile and powerful microscopic technique. This technique is versatile because it provides three dimensional topographical images as well as various types of surface measurements and it is important because it can produce images at angstrom scale resolution with height information with minimum preparation of sample. AFM is one kind of scanning probe microscopes.

Working

AFM operate by measuring force between probe and the sample. The probe is a sharp tip, 3-6 μm tall pyramid with 15-40 nm end radius, attached with a cantilever, scans over the sample surface. As the tip approaches the surface, the close range attractive forces between the tip and surface cause the cantilever to deflect towards the surface. However, as the cantilever is brought closer to the surface such that the tip touches the surface, repulsive forces increase and cause the cantilever to deflect away from the surface.

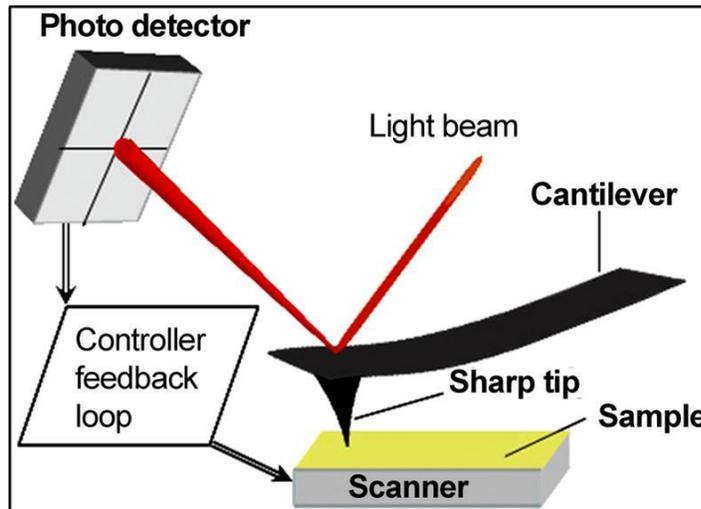


Figure 2.2: Schematic illustration of atomic force microscope.[24]

These cantilever deflections are detected by using a laser beam. Any cantilever will cause a slight change in the reflected beam direction when the incident beam is reflected off the flat top of cantilever. These changes are tracked by using position-sensitive photo diode (PSPD). Thus, if the AFM tip passes over the raised surface part, the resulting cantilever deflections are recorded by PSPD. By scanning the cantilever over the interested region, AFM produces the topographical images of the sample.

2.2 Spectroscopic techniques

2.2.1 Raman Spectroscopy

Spectroscopy is the study of interaction of electromagnetic radiation with matter. Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Photons of laser light are incident on the sample, absorbed by the sample and then reemitted. Raman effect is the shift in the frequency of the incident photon and the reemitted photon. Raman shifted photons can be

either higher or lower energy depending on the vibrational state of molecule. This spectroscopic technique is used to get information about crystal structure and molecular vibrations. Raman bands arise from a change in polarizability of the molecule. When light incident on the sample, almost light is scattered by the material elastically and there is no change in energy. This type of scattering is known as Rayleigh scattering. A very small percentage of scattering take place inelastically and thus scattered light has different energy from incident light. This scattering is either stokes or anti-stokes according to their energy.

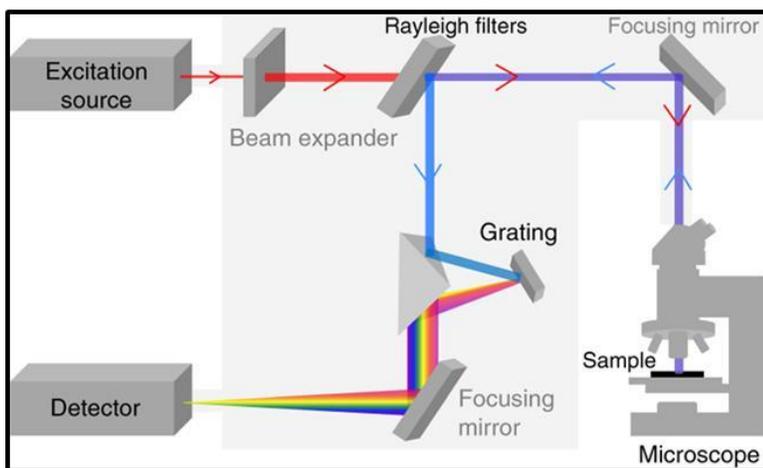


Figure 2.3: Schematic diagram of Raman spectrometer. (Taylor, 2003)

Working

The incident light incident on the molecule and distorts the electron cloud to form a virtual state. This virtual state is unstable and the photon is scattered immediately. In Rayleigh scattering, the electron in the ground is excited and falls to the original ground level. Raman scattering can be classified as two types:

- i. Stokes Raman scattering

In this process, an electron is excited from the ground level and falls to a vibrational level. It involves energy absorption by the molecule thus Stokes scattered light has less energy than incident light.

ii. Anti-Stokes Raman scattering

In this process, an electron is excited from the vibrational level and it falls to ground level. It involves energy transfer to the scattered photon thus anti-Stokes scattered light has more energy than incident energy.

Charge-Coupled devices (CCD) is used to detect the Raman scattered light.

2.2.2 UV-Vis spectroscopy

UV-Vis spectroscopy is the absorption/reflectance spectroscopy in ultraviolet and visible region of electromagnetic spectrum. As light is a sort of energy, absorption of light by molecules causes increment in energy of these molecules and as a result the absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. The total potential energy of a molecule is the sum of vibrational, rotational and electronic energies. The electronic energy is larger than vibrational and rotational energies. Because of highly energetic UV-Vis light, when photon of this light falls on sample, electronic transitions occur in the molecules. From this technique, we can get the information about band gap of a material, thin film thickness etc. Because

of low cost, versatility, speed and accuracy, UV-Vis spectrometer is a very popular instrument.

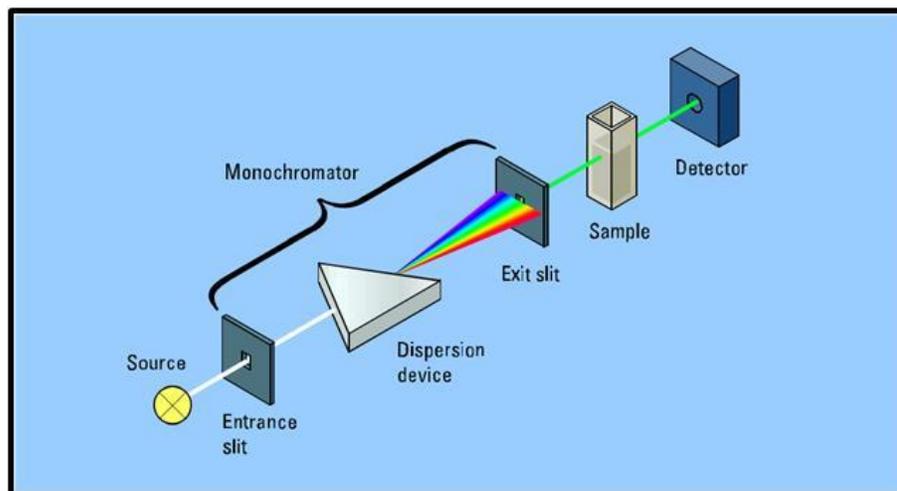


Figure 2.4: Schematics illustration of UV-Vis spectroscopy.[25]

Working

Ultraviolet absorption spectra arise from transition of electron within a molecule from a lower level to a higher level. The electrons undergo transition when the molecule absorbs ultraviolet radiation. UV-Vis spectrophotometer is used in determination of concentration of the absorber. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species. When the beam from the source is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of the medium is proportional to the intensity of the light.

2.2.3 X-ray Diffraction (XRD)

X-ray diffraction technique is mainly used for phase identification of a crystalline material and structural properties like lattice parameter, strain etc. XRD is based on constructive interference of monochromatic x-rays and crystalline sample. The constructive interference is produced by the incident rays with sample if Bragg's law $2d \sin \theta = n\lambda$ is satisfied. According to this law, the wavelength of incident x-rays must be comparable to the interatomic spacing of the crystalline sample. In this equation, n is the order of diffraction, λ is the wavelength of incident x-rays, d is the interatomic distance between planes of atoms and θ is the scattering angle.

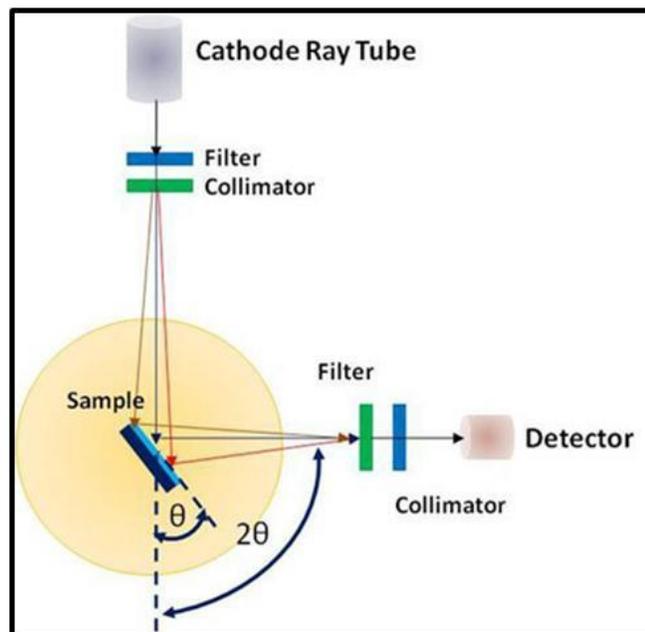


Figure 2.5: Schematic illustration of x-ray diffraction.[26]

Working

X-ray diffractometer consist of three main components: an X-ray tube, a sample holder and an X-ray detector. X-rays are generated in a cathode

ray tube by heating a filament to produce electron and then accelerate the electrons towards the target by applying voltage followed by bombarding these electrons towards the target. Characteristic X-rays are produced when these electrons dislodge the inner core shell electrons of the target material. These X-rays are the filtered to produce monochromatic radiation, collimated to focus, and directed towards sample. The diffraction occurs when interaction between incident ray and sample satisfy Bragg's law. These diffracted rays are then detected, processed and counted. All possible diffraction directions of the lattice can be attained by scanning the sample through a range of 2θ angles. The conversion of obtained diffraction peaks to d-spacing allows identification of minerals.

2.3 Electrochemistry

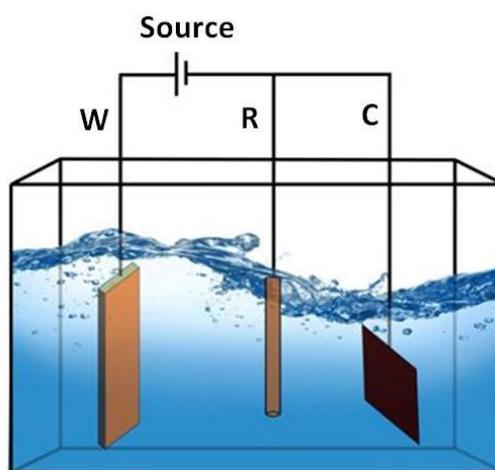


Figure 2.6: Schematic illustration of electrochemical cell.

Electrochemistry is the branch of chemistry which examines the phenomena resulting from combined electrical and chemical effects. Electrochemical reactions take place in an electrochemical cell which consist two conductive electrodes (anode and cathode). The anode is the electrode at which oxidation occurs while reduction take place at cathode.

Electrolyte, which contains freely moving ions, is present in between these electrodes. Along with these two mentioned electrodes one more electrode which is commonly known as reference electrode is also present in the cell and use to check potential on the working electrode.[27]

2.3.1 Cyclic Voltammetry

Cyclic voltammetry is an electrochemical technique which is performed by cycling the potential of a working electrode and measuring the resulting current. The potential of the working electrode is measured against a reference electrode which maintains a constant potential and the resulting applied potential produces an excitation signal. Plot between current and potential is known as cyclic voltammogram and it is obtained by measuring current at working electrode during the potential scans. The potential scans show both reduction and oxidation in one cycle. Reduction process occurs when potential scans from lower value to extreme point which is called switching potential while oxidation take place when potential scan is reversed. The resulting current during reduction is known as cathodic current and during oxidation, anodic current is obtained.[28]

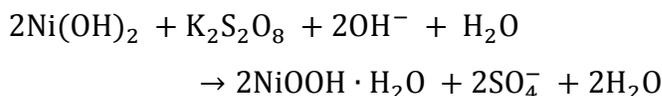
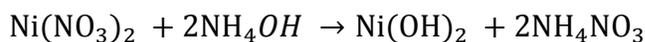
2.4 Synthesis techniques

Hybrid nanostructures of NiO/ PANI are fabricated using hydrothermal method followed by electrochemical polymerization.

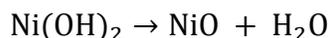
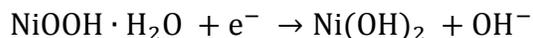
2.4.1 Synthesis of NiO Nanopetals

Hydrothermal method was used to prepare nickel oxide nanostructures. In this synthesis, nickel nitrate, potassium persulfate, and aqueous ammonia were used as precursors. The solution was obtained by dissolving nickel

nitrate $\text{Ni}(\text{NO}_3)_2$ (0.26 g), $\text{K}_2\text{S}_2\text{O}_8$ (0.042 g) and aqueous NH_4OH (1.10 ml) in DI water (30 ml) under stirring for 10 min at room temperature. The FTO glass was put vertically in the 150 ml Teflon lined steel autoclave. The prepared precursor solution was added in the vessel and kept it in an electric oven for 5 hours at 150°C . FTO glass deposited with $\text{Ni}(\text{OH})_2$ is carried out from the vessel and washed with deionized water. After drying it in air, the glass electrode was annealed for 3 hours at 250°C . Finally, uniformly well aligned NiO nanopetals coated on FTO glass were obtained. This process can be illustrated by using the following reactions:[29–31]



During annealing:



2.4.2 Synthesis of NiO nanopetals/PANI nanohemispheres core/shell

NiO NPs deposited on FTO glass substrate as described in the previous section is used as working electrode in the electrochemical polymerization of aniline. A three electrode electrochemical system is used in this process in which one is working electrode on which process takes place, second is reference electrode which is used to maintain potential on the working electrode, and the third electrode is counter electrode which is used for current flow. In the cell, Pt wire and Hg/HgCl are used as counter and reference electrode respectively. Electrolytic solution was prepared by

dissolving aniline (0.182 ml), perchloric acid (1.0 ml) in 20 ml DI water with stirring for 10 min. Before applying 0.01 mA constant current for 1 hour 10 minute for the polymerization galvanostatically of aniline, five 10 seconds pulses of 0.10 mA current was applied to prepare the hemispherical shaped nanostructures. After the polymerization process, the working electrode is taken out from the electrochemical cell and washed with ultrapure DI water then dried under atmospheric condition.[4] As a result we got hybrid nanostructure of NiO/PANI core/shell nanoarrays.

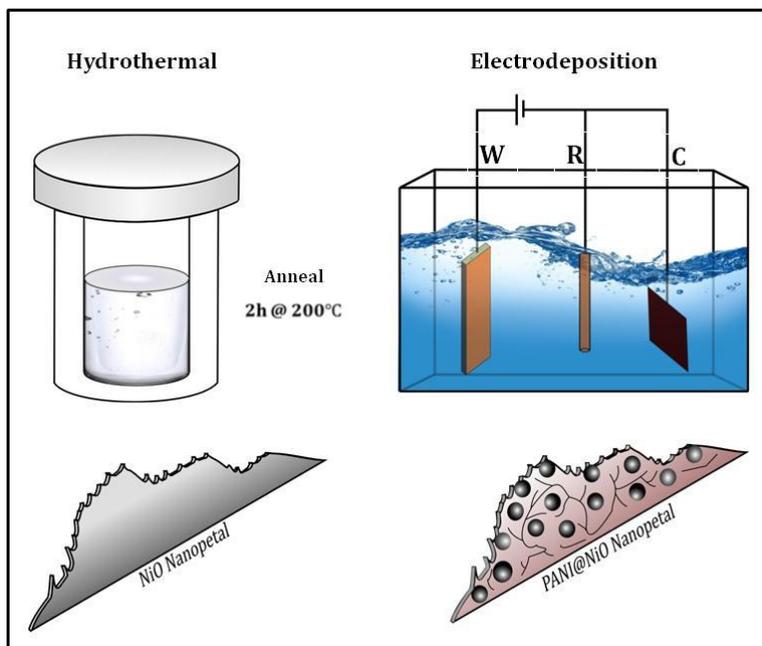


Figure 2.9: Schematic presentation of two step synthesis process of EC electrode preparation by hydrothermal method followed by electrodeposition.

Chapter 3 Results and Discussion

3.1 XRD Analysis:

The crystal structure of the prepared nanostructures of NiO and NiO/PANI core/shell hybrid structure on the FTO glass were examined by XRD. The X-ray diffraction patterns were recorded in Rigaku Smart Lab, Automated Multipurpose X-rays diffractometer with Cu K_{α} radiation ($\lambda = 0.154$ nm) from 20° to 80° .

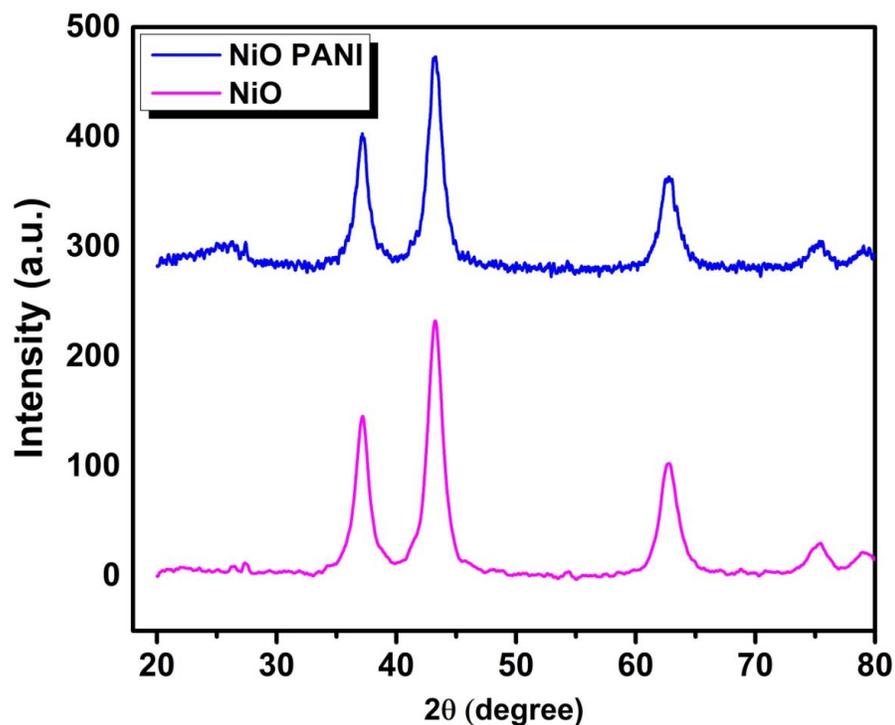


Figure 3.1: X-ray diffraction pattern of NiO@PANI and only NiO nanostructures.

Figure 3.1 shows XRD pattern showing diffraction peaks of nickel oxide nanoparticles and PANI@NiO nanostructures. First peak obtained is at 37° but the maximum intensity is at 43° and after that intensity is decreasing which is at 63° , 76° , and 79° respectively. The peak positions and their relative intensities are in good agreement with the face centered cubic (FCC) structure of NiO-NPs revealing the crystalline nature of the NPs. PANI has amorphous nature and it can be observed in NiO-PANI core-shell spectra around 23° where a broad hump is present extra than in only NiO spectra.[32]

3.2 SEM Analysis:

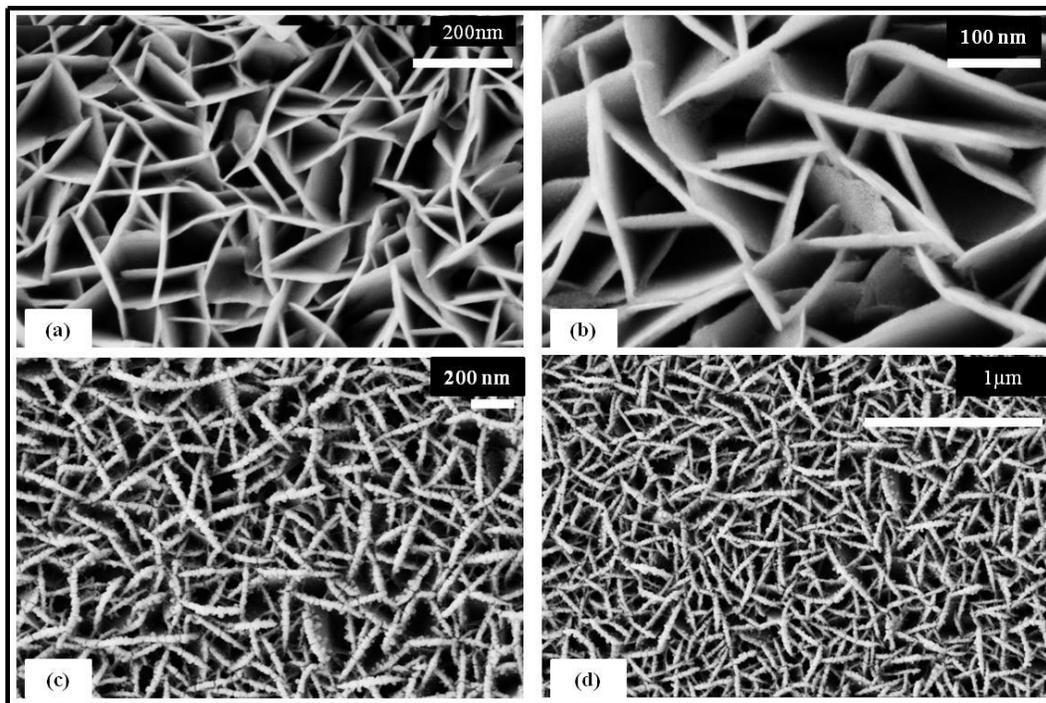


Figure 3.2: (a), (b) Shows SEM images of NiO NSs and (c), (d) shows SEM images of hybrid NiO-PANI core-shell nanostructures.

Morphological and topographical information is obtained by using scanning electron microscopy. From SEM images as shown in figure 3.2(a), (b) we can see the petal like of nickel oxide nanoparticles at different magnifications. From figure 3.2(c), (d) dot shaped PANI deposited on these nanopetals is observed. The nanostructures fabricated on flat transparent substrate are dense and uniform which is an essential condition for good electrochromism. The hemispherical shape of PANI nanoparticles deposited on NiO nanopetals is obtained because of heteronuclear growth of PANI on NiO film. So, shape of the grown nanostructured is confirmed by SEM characterization.[32]

3.3 EDX Spectrum

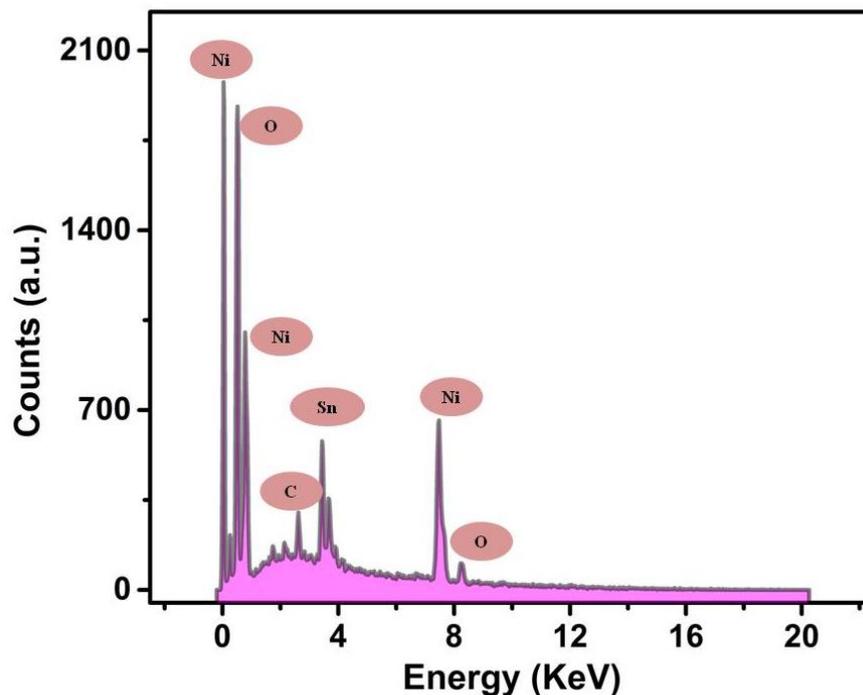


Figure 3.3: EDX spectrum confirms the presence of the Ni, C, O in fabricated NSs.

From electron dispersive x-ray spectroscopy, we can know about the elements present in the sample. Here, EDX spectrum shows the peaks corresponding to Ni, O, C elements which confirms the presence of these elements in the prepared NiO-PANI core-shell nanostructures.[32]

3.4 Raman Analysis

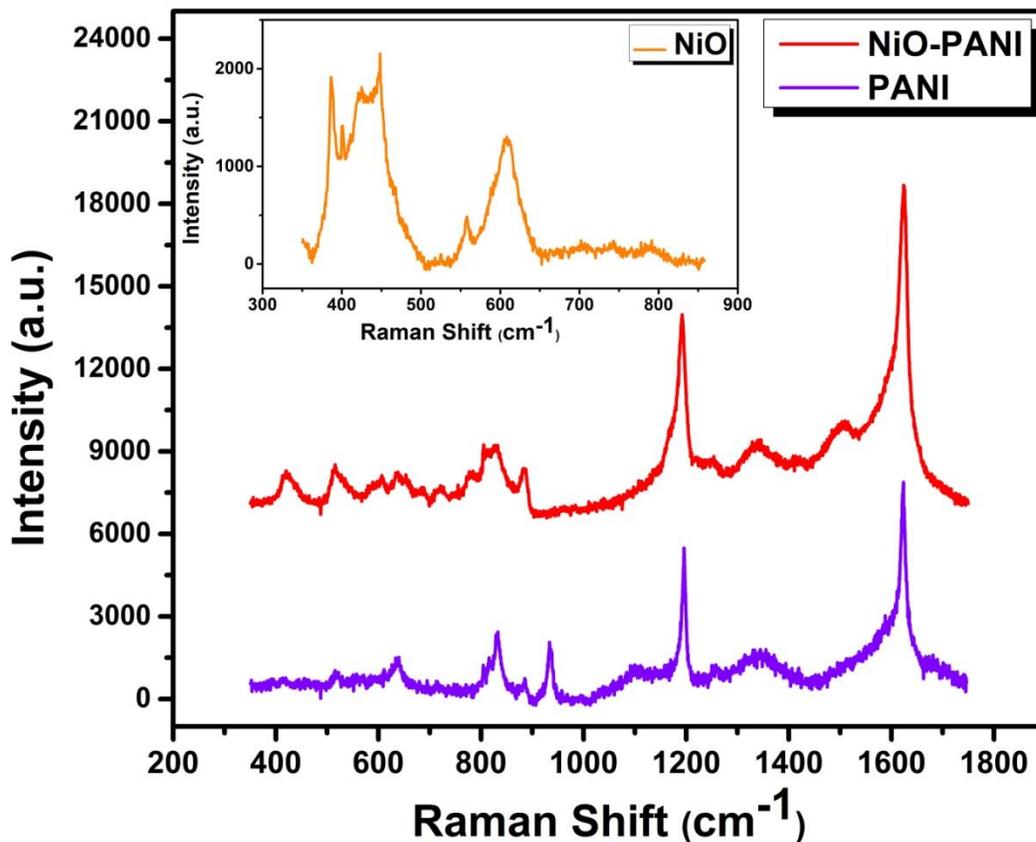


Figure 3.4: Raman spectra of Ni, PANI and NiO-PANI core-shell NSs.

Figure 3.4 shows Raman spectra from PANI deposited NiO nanopetals and NiO along with PANI. Two Raman peaks (yellow curve) observed at 470

cm^{-1} and 514 cm^{-1} are corresponding to Ni-O bending and stretching modes respectively. In Raman spectrum of PANI (blue curve), there are so many peaks are obtained as a result of benzene ring distortion, C-C stretching and C-N vibration. At 1623 cm^{-1} the peak is due to C-C stretching and at 1529 cm^{-1} peak is because of C-N vibration. Peaks at 827 cm^{-1} and 415 cm^{-1} give the information about C-H bending whereas other peaks at 1396, 1340, 1262, 1195 and 514 cm^{-1} appear due to benzene ring distortion. Both NiO and PANI peaks are present in hybrid nanostructures and confirm the presence of both materials.[32]

3.5 Electrochromism in NiO/PANI core-shell

3.5.1 Cyclic Voltammetry

Cyclic voltammetry is a very good tool to measure electrochemical properties of a sample. For cyclic voltammetry, three electrode system is used in which one electrode is working, second one is counter and the third electrode is reference electrode. The above mentioned electrodes have been studied by carrying out cyclic voltammetry in typical three-electrode system at a scan rate of 50 mV/s where fabricated electrode was used as the working electrode & SCE and Pt wire as the reference and the counter electrodes respectively. From cyclic voltammetry, we obtain information about oxidation/reduction states and so color variation also. Aniline show many redox states accompanied by rich colors while nickel shows two redox states only. Figure 3.5 shows CV plot obtained during electro-polymerization of aniline when NiO deposited FTO electrode used

as working electrode in the electrochemical cell. During the forward scan, A_1 , A_2 and A_3 are anodic peaks and represent oxidation state of aniline and nickel oxide which are as follows Leucoemeraldine salt (LS), Emeraldine salt (ES) and pernigraniline (PG) and Ni^{+2} . [4] In the reverse scan, C_1 , C_2 and C_3 are cathodic peaks and represent reduction states.

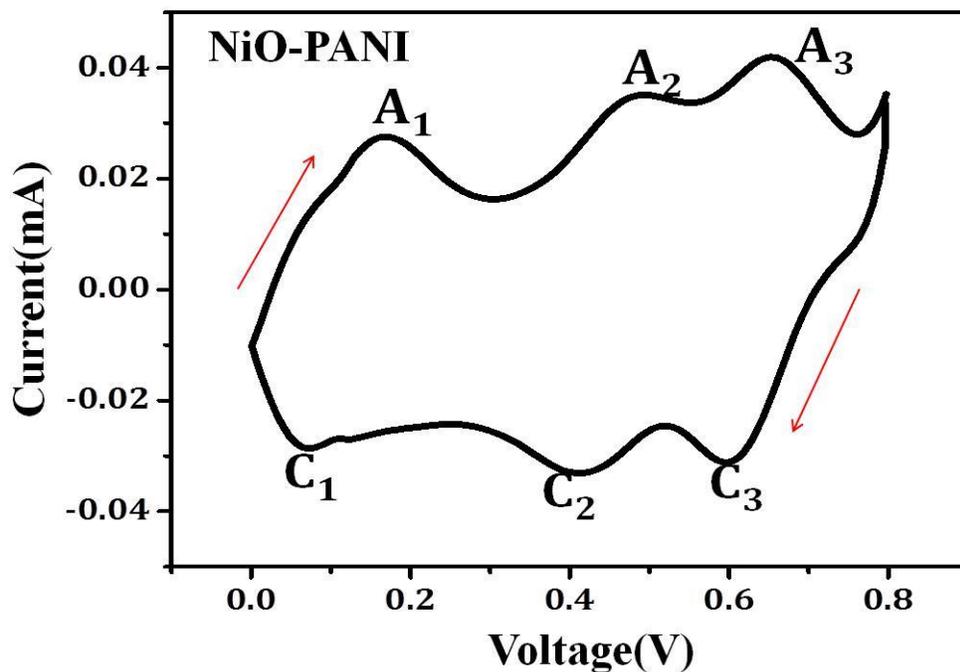
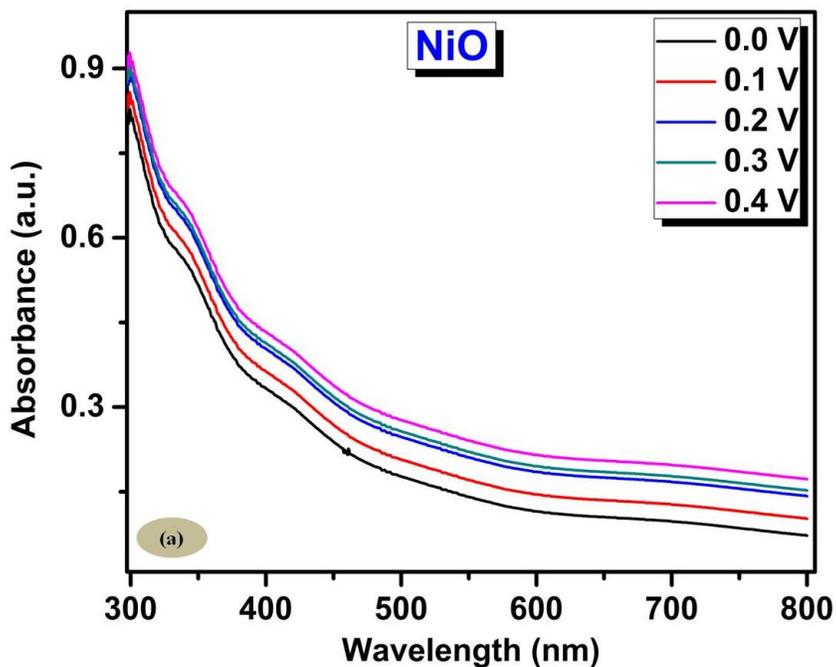


Figure 3.5: CV plot of NiO-PANI nanostructure during polymerization of aniline.

3.5.2 In-Situ UV-Vis Spectroscopy

In-situ UV-Vis spectroscopy was done to check the bias induced color switching of the fabricated hybrid nanostructures. By applying external voltage, absorbance increases because of redox process of the species. For doing this measurement, two electrode system was used as working

electrode and counter electrode. The electrolyte solution consists of 1 M KOH with NiO-PANI deposited FTO substrate and Pt wire which are used as working and counter electrodes respectively. Figure 3.6(a) shows the potential dependent absorption spectra of bare NiO-NPs electrode placed in the electrochemical cell. An overall increase in the absorption of all wavelengths in the whole spectrum in the range (300-800 nm) can be seen which signify variation in the appearance of the electrode from being transparent to becoming opaque rather than giving an appearance of a particular color. Figure 3.6(b), shows the absorption spectra of PANI and 3.6(c) shows absorption spectra of PANI on NiO nanopetals.



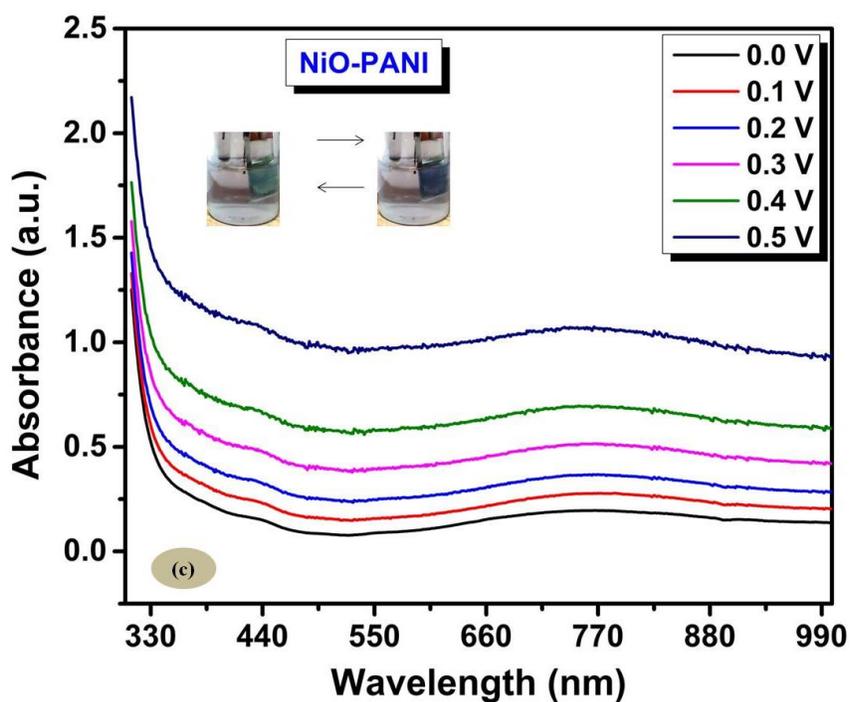
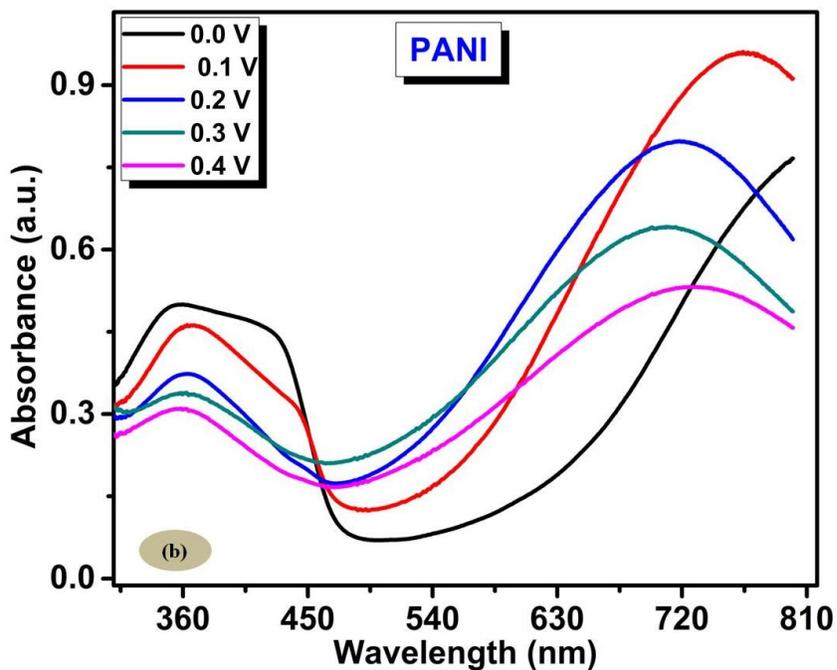
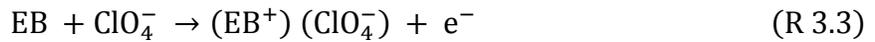
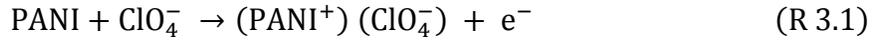


Figure 3.6: Absorption spectra of (a) NiO-NPs (b) PANI and (c) NiO/PANI core/shell nanoarrays..

In PANI there are some intermediate redox states. Initially in its reduced state LE show light yellow color, intermediate oxidized state show light green color and finally gets converted into completely opaque state which is shown in figure 3.6(c). During electro-polymerization aniline exhibits various redox states which are following as: $LB \rightarrow ES \rightarrow EB \rightarrow PS$



Where reactions R 3.1 and R 3.3 correspond to the peaks A_1 and A_2 and R 3.2 show the protonation of the Emeraldine salt into base. The absorption spectra of PANI deposited on bare FTO electrode with different biasing given in the figure 3.6(b) show two peaks, one at 360 nm (low absorbance) and another at 790 nm (high absorbance) in zero bias condition. With increasing applied bias from zero to 0.4 V, the higher absorbance peak show blue shift with enhancing absorbance value. On the other hand, the low absorbance peak did not show any significant change in its position however a bias induced decrease in the absorbance was seen clearly from the figure 3.6(b). The bias induced diminishing of the low intensity peak signifies the change of color from light yellow to sky blue because of change in redox state. Though an appreciable color switching is observed, the color contrast in PANI is poor with no color tuning. Figure 3.6(c) shows the electrochromic behavior of the hybrid fabricated electrode consisting of PANI nanohemispheres on NiO nanopetals with applied bias by keeping the electrode in an electrochemical cell. It can be observed from the UV-Vis spectra (figure 3.6c) that the bias induced changes in absorption spectra are much higher in hybrid form rather than their individual forms (figure 3.6a & 3.6b) in the same potential range.

Chapter 4 Conclusions and Future scope

4.1 Conclusion

In summary, we have successfully synthesized PANI@NiO nanostructures by hydrothermal method followed by electro-polymerization technique. These hybrid nanostructures show power efficient electrochromic properties as compared to their individual ones in an electrochromic cell. A very poor contrast in colored and bleach both states is obtained when only PANI or NiO is used as the active electrode but it can be improved by hybrid nanostructures of these materials i.e., PANI@NiO. The main reason behind this improvement in contrast is increase in surface area of the hybrid nanostructures which leads to the easy electron transportation through the inorganic/organic nano interface and results in increasing ion diffusion. The beauty of NiO/PANI core-shell electrochromic behavior is in its switching between transparent to opaque states rather than colored state.

4.2 Future scope

Present work deals with the synthesis of PANI@NiO nanostructures to verify their electrochromic behavior. But there are some bottlenecks also and because of that people are searching for a very good electrochromic material.

- Switching speed of materials into bleached and opaque states is still an issue.
- Power consumption is also one of the biggest challenges which need to be reduced in future devices.

- Fabrication of device in larger scale needs to be carried out for commercialization.
- Because of higher surface area of nanostructures, these materials can show good energy storage and can be used in supercapacitors, batteries etc.
- Thermal and electrochemical stability of the polymer electrolyte stability will reflect product safety, recyclability and shelf-life.

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