CHAPTER-VII

SUMMARY AND CONCLUSIONS
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7.1: Summary

The technologies involved in the solar energy harvesting, efficiency boosting of the device and energy conservations by various means could alleviate the environmental and energy crisis manifested by global warming through greenhouse effect and fast depletion of conventional energy sources respectively. These problems could be partly remedied by the use of “Smart Windows”, with tunable optical properties, involving chromogenic materials. Smart Window encompasses a wide and developing range of technologies that cover large area glazing in buildings, automobiles, planes and airport displays. The quantitative analysis reveals that a smart window can save energy equivalent to that generated by a solar cell at its highest efficiency of 17%.

Materials that are able to change their optical properties as a response to an external stimulus are referred to as “chromogenic”. The change can be effected through irradiation by light (photochromic materials), change in temperature (thermochromic materials) and the application of an electrical field (electrochromic materials), to mention the most common alternatives.

Electrochromic materials were brought to public attention some 35 years ago in influential work on tungsten oxide. In essence, the optical absorption in the visible range changes between widely separated extreme as charge is inserted or extracted. These materials were immediately considered for application in information display.

Electrochromism is broadly defined as a reversible optical change in a material induced by an external voltage. The mechanism underlying the optical change is the insertion of small ions into the electrochromic material and the subsequent extractions of the same ions. They are of two types,

1) Cathodically coloring – those with reduced colored state (e.g. WO$_3$)
2) Anodically coloring - those with an oxidized colored state (e.g. NiO)
A good quality electrochromic material needs maximum reversibility, highest coloration efficiency, minimum switching time, low potential window and maximum stability in terms of color/bleach cycles.

Nickel oxide is a promising candidate for electrochromic devices due to its optical switching from a transparent to a brownish state on oxidation, thus it is advantageously complementary to the blue colored cathodic tungsten oxide and hence the combination of nickel (anodically coloring) and tungsten oxides (cathodically coloring) may lead to enhancement in energy conservation.

Though NiO is not a favored material for EC device due to its moderate Electro Chromic (EC) parameters, the surface morphology plays a crucial role in these regards. Thus synthesis of nano structures with different surface morphologies may give a promising way to make NiO more competent EC material.

With this view, the present work has been planned. An emphasis has been given on the preparation of NiO thin films by various simple chemical and electrochemical techniques in order to synthesize various nanostructured morphologies. Impact of the structural outcome on the optical modulation, coloration efficiency, reversibility, response times and stability is studied at length. The subject matter has been organized in seven chapters.

**Chapter-I** begins with introduction of nanostructured materials and its advantages over conventional one. Further introduction of chromogenic devices have been discussed, focused specifically on electrochromic devices and the importance and need of smart window technology is highlighted. The structure of the electrochromic devices, its performance parameters has been discussed. History of electrochromic devices, various applications, current research and development in electrochromic technology has been dealt in detail.

Nickel oxide compound, its coloration mechanism and its explanation using crystal field theory has been thoroughly discussed followed by survey of literature. At the end of the section the purpose of dissertation and plan of work has been discussed.

**Chapter II** deals with the description of the Sol-Gel dip coating, Chemical Bath deposition, electrodeposition and chemical precipitation techniques. The necessary
theoretical background and details of the characterization techniques such as X-ray Diffraction (XRD), Fourier Transformation Infrared (FT-IR) Spectroscopy, X-Ray photoelectron spectroscopy (XPS), Scanning Electron Microscopy (SEM) and UV-Vis spectroscopy is given. The electrochemical tools for the study of electrochromic properties such as cyclic voltammetry (CV) and Chronocoulometry (CC) etc. have been discussed. The colorimetric analysis based on CIE 1931 with 2°observer and in-situ transmittance measurements have been discussed in order to define the color scale and response time of the electrochromic material.

Chapter-III begins with preparation NiO films from nickel acetate precursor by sol-gel dip coating technique. The amorphous nature of the films was confirmed by X-ray diffraction measurements. X-ray photoelectron spectroscopy (XPS) measurements showed that the films exhibited presence of NiO phase. The NiO thin films prepared by sol-gel dip coating method exhibits a smooth and compact nature thereby hindering the overall electrochromic performance. The EC device made up of glass/ITO/NiO/KOH/ITO/glass show transmittance modulation of 41 %, response times of 5.9/4.5 s for coloration and bleaching, lightness difference of 29.41% and electrochromic coloration efficiency of 32 cm²/C at 630 nm.

Chapter-IV describes electrochromic performance micro porous NiO thin films as a function of film thickness (deposition time) by chemical bath deposition (CBD). Morphological investigation revealed microporous nature composed of interconnected porous network, forming well defined 3D envelopes. Such a microporous interconnecting network facilitates the control over surface area and porosity/open structure, affecting the ion insertion kinetics (ion diffusion length and time, ionic mobility, etc) leading to enhanced EC performance. The transmittance modulation or optical density differences during the coloring/bleaching process were found to increased with the film thickness. It is observed that the NiO thin films deposited for 60 min showed maximum transmittance modulation and coloration efficiency (ΔT = 46 % and CE=42 cm²/C at 630 nm) and exhibits faster response time (2.9 s for bleaching and 3.5 s for coloration).

Chapter-V deals with the synthesis, characterization and electrochromic performance of NiO thin films prepared by potentiostatic electrodeposition by using
two types of organic surfactants: (1) non-ionic: polyethylene glycol (PEG), polyvinylpyrrolidone (PVP) and (2) anionic: sodium dodecyl sulfate (SDS). An aqueous solution containing nickel sulfate precursor and potassium hydroxide was used to grow the samples. The effect of organic surfactants on its structural, compositional, morphological, wettability, optical, electrochromic and in situ transmittance response time and colorimetric analysis were studied using X-ray diffraction, FT-IR spectroscopy, XPS spectroscopy, UV-Vis spectroscopy, scanning electron microscopy, contact angle measurement, optical transmittance, cyclic voltammetry and CIE system of colorimetry. X-ray diffraction revealed the polycrystalline nature of NiO consisting of a cubic phase. A micro porous structure with pore diameter of about 150-200 nm was observed for pure NiO. The films deposited with the aid of organic surfactants exhibits various surface morphological features. PVP-mediated NiO thin film shows noodle-like morphology with well-defined surfaces whereas, an ordered pore structure composed of channels of uniform diameter was observed for PEG. A nanoporous structure with pore diameter of about 40-50 nm stem from SDS which provide larger surface area and helps to improve electrochromic performance compared with that of NiO deposits from surfactant-free solution. Wetting behavior shows, transformation from hydrophilic to superhydrophilic nature of NiO thin films deposited with organic surfactant. The surfactant-mediated NiO produce high color/bleach transmittance difference of up to 58 % at 630 nm, due to enhanced paths for electrolyte access. On oxidation of NiO/SDS, the CIELAB 1931 2° color space coordinates show the transition from colorless to the deep brown state (L*= 84.41, a*=-0.33, b* = 4.41, and L* = 43.78, a* = 7.15, b* =13.69), with lightness difference of about 40.63 %. The coloration efficiency of 54 cm²/C was observed for NiO/SDS thin films.

**Chapter-VI** describes deposition of *dandelion flower* like (DFL) nickel oxide thin films by a simple and cost effective wet chemical precipitation method. The DFL-NiO composed of interconnected nano-flakes exhibit higher surface area and porosity, affecting ion insertion kinetics, leading to enhanced EC performance. The DFL-NiO prepared at 300 °C exhibit excellent electrochromic behavior with a color/bleach transmittance difference of 63 %, phototropic contrast ratio of 4.34, fast coloration and bleaching times of 5.84 s and 4.43 s respectively and high coloration efficiency
(68 cm²/C). The chromaticity measurement showed relative high lightness difference of 51.52%. This study demonstrated that dandelion flower like morphology deposited by precipitation method has potential for excellent electrochromic devices.

7.2: Conclusions

It is observed that the nanostructured morphology of NiO thin film has a positive impact on enhancing the EC parameters required for smart window applications. Thin films of NiO can be synthesized by simple, cost effective chemical and electrochemical methods. Use of proper surfactants can be made to tailor the morphology. Nanoporous interconnecting architecture made up of NiO flakes in dandelion flowers produced by precipitation method seems to be the best morphology for increasing effective surface area and porosity so that the electrolyte soaking from all directions of the flower takes place thereby affecting the ion insertion kinetics (intercalation and deintercalation during coloration and bleaching). This leads to overall electrochromic performance boosting. Figure 7.1 represents these conclusions in nutshell.

Figure 7.1: Overall transmittance modulation and coloration efficiency evaluated for NiO thin films prepared by different methods (effect of morphology).
Summary and Conclusions

The use of chemical precipitation and electrodeposition methods for NiO thin film deposition and use of proper surfactants for tailoring variety of nano structured morphologies will open new avenues for systematic research.

**Future Scope:**

Schematic Diagram of electrochromic Device based on WO$_3$ as working electrode and NiO as counter electrode (ion storage layer) NiO:

Fabrication of complementary ECD (CECD) devices containing two electrochromic layers, one of which is anodically colored nanostructured NiO which serve as ion storage layer while the other cathodically colored WO$_3$ serve as working electrode both on an electronically conducting transparent substrate (ITO/Glass), which is separated by an electrolyte layer. Above Fig. shows the cross-section of a typical CECD with WO$_3$ as the cathodically colored layer and NiO as the anodically colored layer, together with the description of voltage application and transmission measurement. In such a dual-layer CECD, they are colored together and bleached together. The two materials can be switched simultaneously to provide higher optical contrast and coloration efficiency and at the same time a proper charge balance can be maintained in the device, which results in better device performance, such as a high optical modulation, higher open-circuit stability and long-term switching
stability, than that of single-layer ECD. The key parameters of high-performance complimentary electrochromic devices based on nanostructured WO$_3$ and NiO allows people to dynamically control the heat and light flow into a building just by applying small voltage that tinted the smart window and can block up to 98% of transmitted light and 100% of UV light all the time. With emerging smart window, substantial savings in energy consumption upto 20-30 % through reduction in electrical load by means of heating, ventilation and air condition system.