Lighting and Sensing Applications of Nanostructured ZnO, CuO and Their Composites

Ahmed Eltahir Elsharif Zainelabdin
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Dedicated to:

My family and to the soul of my Mother
Abstract

Low dimensional nanostructures of zinc oxide (ZnO), cupric oxide (CuO), and their composite nanostructures possess remarkable physical and chemical properties. Fundamental understanding and manipulation of these unique properties are crucial for all potential applications. Integration of nanostructured ZnO and CuO and their hybrid composites may play a significant role in the existing technology while paving the way for new exciting areas. Solution based low temperature synthesis of ZnO and CuO nanostructures have attracted extensive research efforts during the last decade. These efforts resulted in a plenteous number of nanostructures ranging from quantum dots into very complex three dimensional nanomaterials. Among the various low temperature synthesis methods the hydrothermal technique became one of the most popular approaches. The use of hydrothermal approach enabled the synthesis of diversity of nanomaterials on conventional and nonconventional substrates such as metals, glass, plastic and paper etc.

The primary objectives of this thesis are to study and understand the characteristics of nanostructured ZnO, CuO, and their hybrid composites synthesized at low temperature. Likewise, the hybrid composites were successfully utilized to fabricate light emitting diodes and sensors. This thesis is organized into three major parts. In the beginning the synthesis and characterization of nanostructured ZnO, CuO, and their composite nanostructures are elaborated. Efforts have been made to understand the selective assembly of hierarchical CuO nanostructures on ZnO nanorods and to correlate it to the observed unique properties of the CuO/ZnO composite nanostructures. In the second part of the thesis fabrication, characterization, and device application of ZnO/p-polymer hybrid light emitting diode (HyLEDs) on flexible substrates are presented. In particular single and blended p-type light emissive polymers were controllably developed for potential greener and cheaper white light emitters. It was found that the HyLEDs exhibited rectifying diode characteristics together with white light emission covering the entire visible range. In the third part, pH
and relative humidity sensing applications of CuO nanoflowers, and CuO/ZnO nanocorals, respectively, are described. A pH sensor based on CuO nanoflowers demonstrated good sensitivity and reproducibility over a wide range of pH. By taking the advantages of the selective growth of CuO nanostructures on ZnO nanorods and their naturally formed p-n heterojunction the realization of high sensitivity humidity sensor was achieved. The humidity sensor fabricated from the CuO/ZnO nanocorals displayed the highest sensitivity factor reported so far for its constituent materials; along with reasonably fast dynamic responses. A brief outlook into future challenges and opportunities are also presented in the last part of the thesis.
Acknowledgement

Now, I am approaching the end of a long journey toward obtaining my PhD. I have not traveled this far without the help and encouragement of many people including my family, my friends, colleagues and my well-wishers. At the end of my PhD journey, I owe all those people my gratitude and appreciations. It is really a pleasant task to express my thanks to all those who contributed in various ways to the success of my PhD study and made it a memorable experience for me.

At this stage of accomplishment, first and foremost, I must acknowledge and thank The Almighty Allah for blessing, protecting, and guiding me throughout this journey and all my life. I could never have achieved this without the faith I have in Allah.

I express my profound sense of reverence to my supervisor Prof. Magnus Willander, for his endless guidance, support, motivation, and patient help during the course of my PhD. Under his guidance and encouragement I successfully surpassed many difficulties and learned a lot. He has given enough freedom during my research to encourage me becoming an independent thinker. He is a great supervisor.

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One person who has always been happy to help us, it is our research administrator Ann-Christin Norén. She kindly took care of all administrative work. Thank you Ann-Christin for all your support, I would like to thank Lars Gustavsson for his readiness in finding and solving all problems in our cleanroom. I am also very grateful for the endless support of the Linköping University administration during my PhD studies.
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I owe loving thanks to my wife Sana for her unwavering understanding and support during these hard years in Sweden. She was always there lifting me uphill this phase of life. Without your patience and encouragement nothing of this would have been achievable. Thanks for being beside me. I appreciate my beloved son Mohamed, who has made our life full of joy with his innocent acts and refreshing me with his lovely smiles and kisses. I love you Mohamed.

Norrköping, October 2012
List of Publications

Papers included in this dissertation


“Deposition of well-Aligned ZnO nanorods at 50 °C on metal, semiconducting polymer, and copper oxides substrates and their structural and optical properties”.


“CuO/ZnO Nanocorals synthesis via hydrothermal technique: growth mechanism and their application as Humidity Sensor”.


“Optical and current transport properties of CuO/ZnO nanocorals p-n heterostructure hydrothermally synthesized at low temperatures”.


“Effect of the Polymer Emission on the Electroluminescence Characteristics of ZnO Nanorods/p-Polymer Hybrid Light Emitting Diode”.


“Influence of the polymer concentration on the electroluminescence of ZnO nanorods/polymer hybrid light emitting diode”.


“CuO nanoflowers as an electrochemical pH sensor and effect of pH on the growth”.


“Synthesis and characterization of CuO/ZnO composite nanostructures: precursor’s effects, and their optical properties”.

Submitted.

Related papers not included in this thesis

“Low-temperature chemical growth of ZnO nanorods with enhanced UV emission on plastic substrates”.

“Stable white light electroluminescence from highly flexible polymer/ZnO nanorods hybrid heterojunction grown at 50 °C”.

“ZnO nanorods–polymer hybrid white light emitting diode grown on a disposable paper substrate”.

“Different interfaces to crystalline ZnO nanorods and their applications”.
   “Luminescence from zinc oxide nanostructures and polymers and their hybrid devices”.

   “Intrinsic white light emission from zinc oxide nanorods heterojunctions on large area substrates”.

   “Zinc oxide nanorods/polymer hybrid heterojunctions for white light emitting diodes”.

   “Influence of pH, precursor concentration, growth time, and temperature on the morphology of ZnO nanostructures grown by the hydrothermal method”.

   “Recent progress on growth and device development of ZnO and CuO nanostructures and graphene nanosheets”.

    “Metal Oxide Nanostructures and White Light Emission”.
    Proc. of SPIE (2012), 8263, 82630N.

    “Zinc oxide and copper oxide nanostructures: fundamentals and applications”.
List of publications

   “Scale-up synthesis of ZnO nanorods for printing inexpensive ZnO/Polymer white light emitting diode”.

   “ZnO-organic hybrid white light emitting diodes grown on flexible plastic using low temperature aqueous chemical method”.

   “CuO nanopetals based electrochemical sensor for selective Ag+ measurements”.

    “Efficient catalytic effect of two-dimensional petals and three-dimensional flowers like CuO nanostructures on the degradation of organic dyes”.

    “Nanowires assembled CuO interpenetrated-leaf architecture by (10\text{1}) twinning”.
    Submitted.

Author contribution to the papers included in this thesis

Contribution to papers I, II, III, VII
Design and carry out the experiments except for the TEM and PL measurements, analyzing the data and writing the first version of the manuscripts.

Contribution to paper V
Equally contribute to designing, measuring, analyzing, and writing the first version of the manuscript.

Contribution to papers IV, and VI
Part of the experimental work and involved in the editing of the manuscripts.
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<th>Description</th>
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<tbody>
<tr>
<td>STM</td>
<td>Scanning tunneling microscope</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
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<tr>
<td>C$_{60}$</td>
<td>Fullerene</td>
</tr>
<tr>
<td>1D</td>
<td>One dimension</td>
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<tr>
<td>2D</td>
<td>Two dimensions</td>
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<td>Three dimensions</td>
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<td>Nanostructures</td>
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<td>Silver</td>
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<td>Gold</td>
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<td>TiO$_2$</td>
<td>Titanium oxide</td>
</tr>
<tr>
<td>CeO$_2$</td>
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<td>ZnO</td>
<td>Zinc oxide</td>
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<td>CuO</td>
<td>Cupric oxide</td>
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<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>Cuprous oxide</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>pH</td>
<td>Power of hydrogen, Potential hydrogen</td>
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<td>LED</td>
<td>Light emitting diode</td>
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<td>HyLED</td>
<td>Hybrid light emitting diode</td>
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<tr>
<td>NFs</td>
<td>Nanoflowers</td>
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<tr>
<td>NPs</td>
<td>Nanopetals</td>
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<td>Nanowires</td>
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<tr>
<td>NCs</td>
<td>Nanocorals</td>
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<tr>
<td>CB</td>
<td>Conduction band</td>
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<td>VB</td>
<td>Valence band</td>
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<td>V$_O$</td>
<td>Oxygen vacancies</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>EL</td>
<td>Electroluminescence</td>
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<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>V$_{Zn}$</td>
<td>Zn vacancy</td>
</tr>
<tr>
<td>Zn$_i$</td>
<td>Interstitial Zn</td>
</tr>
<tr>
<td>E$_g$</td>
<td>Band gap</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbitals</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbitals</td>
</tr>
<tr>
<td>PFO</td>
<td>Poly(9,9-dioctylfluorene)</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4 ethylenedioxythiophene)/poly(styrenesulfonate)</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>rpm</td>
<td>Rounds per minute</td>
</tr>
<tr>
<td>HMT</td>
<td>Hexamethylenetetramine</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl ion</td>
</tr>
<tr>
<td>CNH</td>
<td>Copper nitrate trihydrate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscope</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>XRD</td>
<td>X-rays diffraction</td>
</tr>
<tr>
<td>NBE</td>
<td>Near band emission</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density-voltage</td>
</tr>
<tr>
<td>DLE</td>
<td>Deep level emission</td>
</tr>
<tr>
<td>$I_R$</td>
<td>Reverse saturation current</td>
</tr>
<tr>
<td>hrs</td>
<td>Hour</td>
</tr>
<tr>
<td>$S_f$</td>
<td>Sensitivity factor</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
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Chapter 1

1. Introduction

1.1 Nanotechnology Challenges and Opportunities

Nanotechnology is a rapidly growing technology with huge potential to develop new materials with exceptional properties and to create new and improved products for various applications. Numerous nano-based products are already entered into the marketplaces; these products include electronics, personal care, sporting goods, and automotive parts. Nanotechnology enable-products are expected to represent a huge market in the near future with chemicals industry, pharm and healthcare being the fastest and the major nanotechnology sectors. However, there are many concerns about the impact of nanomaterials on both the human health and environment [1]. Understanding and identifying the potential risks that may be associated with the usage of nanomaterials is an important step if these materials are to be dominating our future industries.

Although the term “nanotechnology” was first coined by the Japanese scientist Norio Taniguchi in 1974 to describe precision processes in semiconductor engineering [2], but the idea of creating, manipulating, and controlling materials on small scale was introduced by Richard Feynman in his famous talk “There’s Plenty of Room at the Bottom” in 1959 [3]. Later, in 80s the concepts of nanotechnology had become popular owing to the invention of new nano-characterization tools such as scanning tunneling microscope (STM), atomic force microscope (AFM), etc. which enabled the study and manipulation of nanomaterials. The discovery of the fullerene (C_{60}~1 nm) in 1985 [4], and the rediscovery of carbon nanotubes by Iijima in 1991 [5] were one of the turning points for many scientist and technologist around the world. Since small additions of carbon nanomaterials can significantly enhance the structural and electrical properties of the composite materials. Therefore, the research and development in nanotechnology fields are greatly influenced by the fabrication of new nanomaterials with improved
properties. These nanomaterials have to meet our increased demands for renewable clean energy, advanced drug delivery systems, bio-monitoring devices, green lighting technologies, and ultra-fast computing architectures, to name a few.

1.2 Nanomaterials as Driving Force for Nanotechnology

It becomes widely recognized that nanotechnology as a broad range of technologies that exploited to determine, manipulate, or integrate materials with at least one dimension between 1 and 100 nm (1 nm = 10⁻⁹ m). Such materials retain properties that different from their bulk counterparts. At the nano-scale range, a nanomaterial with particle sizes may exhibit different physical and chemical properties owing to the specific particle size. For example, quantum dots which are assembly of atoms with size of about 5-10 nm that emit different colors by only altering the dot size. As the material size shrinks, the surface area to volume ratio significantly increases to the level that the material properties are determined by the surface properties. This large surface area/volume ratio offers unique properties that have extensive applications in various industrial sectors, including medical, electronics, and chemical sectors. Varieties of new and stimulating nanomaterials have been synthesized in the last two decades, which include quantum dots and nanoparticles [6-10] as examples of zero dimension nano-entities. Likewise, nanotubes, and nano-wires/rods are examples of one dimension (1D) nanomaterials, while graphene (a single sheet of carbon atoms) is classified as a two dimension (2D) nanomaterial [11-16]. In the case of three dimensional (3D) nanomaterials there is huge number of reported structures, such as nanodandelion [17-19], nanoflowers [20-22], and hyperbranches nanostructures (NSs) [23, 24]. Likewise, combing the unique properties of two or more nanomaterials to benefit from their individual properties has led to nanocomposites that have further enhanced characteristics [25-27]. These characteristics can either represents standalone efficient nano-products or integrated with the existing technology for cheaper prices. Here, I give few examples of nanomaterials that have great potential in various important areas. Due to their high electrical conductivity carbon nanotubes have potential for the
manufacturing of low cost solar cells [28], electronics [29-31], and anti-static composite materials [32]. Metallic silver (Ag) and gold (Au) nanoparticles have been found to be very efficient as an anti-bacterial agents [33, 34] and effective catalysts for several chemical reactions under room temperature [35, 36]. While metal oxides such as titanium dioxide (TiO$_2$) nanoparticles having a large band gap which proven to be an excellent candidate for photocatalysis, UV protection, photovoltaics, and sensing [37-40]. For the photocatalysis as an example, TiO$_2$ nanomaterials have been used to cover exterior walls of buildings to offer self-cleaning surfaces, as this nanomaterial exhibits superhydrophilicity under solar irradiation [41-43]. Another example is cerium oxide (CeO$_2$) which can be applied as a diesel fuel combustion catalyst [44, 45], which reduces fuel consumption, carbon monoxide emission and other exhausts. The last example is semiconductor quantum dots which as mentioned above can emit different color depending on their particle size, this property enable them to be used in applications such as biolabeling [46], chemical sensing [47] light display [48] , etc. Thus, the research and development of nanomaterials represents the driving force for many nanotechnology sectors however, for this new technology to revolutionize the way we live today tremendous efforts are required to fully understand the basic properties, applications and functionalities of these nanomaterials. Additionally the assessment of their impact on human and environment has to be fully understood. In the next section an introductory description of the great diversity of applications that metal oxides nanomaterials can offer will be mentioned with especial emphasis on ZnO and CuO as they are the main two nanomaterials studied in this thesis.

1.3 Metal Oxide Nanomaterials for Diversity of Applications

In the current interdisciplinary age of nanotechnology metal oxide semiconductor nanomaterials have gained substantial interest due to their promising applications in a diversity of technological areas, such as electronics, optoelectronics, bio/chemical sensors, coating systems, and catalysis. These technologies require novel materials which motivated the development of controlled synthesis and functionality of oxides
nanomaterials, which in turn have attracted many research groups and funding for fundamental research on nanomaterials. It was soon recognized that the properties of metal oxide nanomaterials are significantly different from their counterpart bulk materials. This difference is due to the relatively large surface area. For example, owing to the large fraction of surface atoms of these oxides as compared to the bulk implies that oxides nanomaterials can exhibit enhanced sensitivity and catalytic activity. Here, I will present some of the most promising oxides nanomaterials which have stimulated a lot of interest in recent years for various technological applications. One of the most studied metal oxide nanomaterials for potential applications is TiO$_2$ due to its wide band gap and photocatalytic activity as well as sensitivity. As mentioned before TiO$_2$ nanoparticles have been applied as self-cleaning and anti-fogging coatings for exterior walls and windows of buildings using the concept of superhydrophilicity [41, 43]. Furthermore, UV irradiation of a tiles covered with TiO$_2$:Cu have shown to function well for self-sterilization applications [43]. Also, TiO$_2$ nanowires have been proposed as possible candidate for advanced batteries with better storage and fast charging/discharging capabilities [49]. In this regard TiO$_2$ nanowires can be used as an anode material which can store enough Li$^+$ to form Li$_{0.91}$TiO$_2$ [43, 49, 50]. Another example of an oxide nanomaterial that has received vast attention is zinc oxide (ZnO) which is one of the most promising metal oxides due to its attractive physical and chemical properties. ZnO has a unique ability to demonstrate both semiconducting and piezoelectric characteristics simultaneously, which can have numerous applications in energy harvesting domains for small devices such as cell phones [51]. The synthesis of ZnO nanomaterials has resulted in plentiful number of NSs such as nanowires, nanotubes as examples of 1D nanomaterials [52, 53], nanosheets, nanowalls and nanoplates as a 2D structures [54-57]. The 3D ZnO NSs include nanoflowers and other complex structures such as nanotetrapods [57, 58]. All these nanofeatures of ZnO have developed increasing attention in broad spreading research areas for applications in electronics, optoelectronics, and sensing. Material characteristics such as wide bandgap, large surface area to volume ratio, intrinsic n-type conductivity, and large number of
native point defects as will be discussed in the next chapter, render ZnO nanomaterials to be exciting material for diverse technological applications. These applications include transparent conductors as a low-cost replacement of ITO in applications such as displays and photovoltaics panels. ZnO has been explored for fabrication of inexpensive disposable electronics such as multisource energy converter [59], and light emitting diodes (LED) [60]. Also, ZnO nanomaterials have found resurgent attention in areas such as bio/chemical sensing owing to its relatively large surface/volume ratio as well as its high ionicity, biocompatibility, and non-toxicity combined with the conductive nature of ZnO which enable enhanced analytical and sensitivity performance [61]. One of the most urgent challenges is the realization of repeatable and stable p-type conductivity of ZnO which is very critical for electronics and photonics applications. Final example of oxides nanomaterials which will be presented in this thesis is copper oxide. Copper has two known stable oxides, cuprous (Cu₂O) and cupric (CuO) oxides. The physical properties of these two copper oxides are different since they have different crystal structures, optical and electronic properties. Studies on cupric oxide nanomaterials have grown substantially in recent years due to its direct bandgap and intrinsic p-type behavior together with low cost fabrication and good electrochemical properties. These interesting properties made CuO among the best materials for electrical, optical, catalytic, and sensing applications to name a few [62-66]. Due to the high ionicity of the Cu-O bonds in CuO, this material found considerable attention for applications in catalysis, gas sensors, and solar cells. CuO nanomaterials and bulk were used in the preparation of a number of organic-inorganic composites that possess excellent characteristics such as high electrical and thermal conductivities, mechanical strength and high temperature stability [67].

1.4 Research Outline

The main focus of this thesis is devoted to the development of synthetic methods of oxide nanomaterials and to assess their potentials for lighting applications, relative humidity (RH) sensing, and pH sensing applications. These studies have been carried
out using two metal oxides NSs and their composites together with polymer thin films. The general objectives and outcomes of this thesis work can be summarized as follows:

- To develop a controlled low temperature synthesis method that can be used to fabricate ZnO and CuO nanomaterials with excellent structural and physical properties.

- To investigate the unique structural, optical, and electronic characteristics of these nanomaterials and their composites. Various characterization techniques were applied in this work to gain deep understanding of the morphological characteristics, crystallinity, light absorption and emission, and electrical properties. All these investigations resulted in large control and functionality of the devices that have been fabricated in this work for lighting and sensing applications.

- The realization of ZnO/polymer LEDs for large area lighting applications was one of the major objectives of this thesis. This has been successfully accomplished by integrating ZnO nanorods synthesized at low temperature with organic polymers on flexible substrates. By using this strategy the lack of reliable p-type ZnO necessary for homojunction LEDs can be avoided, while applying simple solution-processable techniques. Also, the use of columnar ZnO nanorods can enhance the light extraction efficiency from such devices.

- To study the influence of nutrient solution pH on the CuO nanomaterials and to further uses CuO nanoflowers (NFs) for pH sensing application. It has been found that CuO NFs sensor possesses linear response over a wide range of pH values, with relatively fast response time and good reproducibility.

- To study and develop a novel CuO/ZnO nanocomposite p-n heterojunction for potential applications as RH sensors.
In these studies a two-step low temperature synthesis procedures were established to grow nanocorals (NCs) like CuO/ZnO heterostructures. The heterojunction of CuO/ZnO NCs exhibited a rectifying diode behavior which was successfully used for RH sensing application. The main advantages of these composite nanomaterials are the natural p-n characteristics, the broad light absorption, the high sensitivity to humidity changes, and the fast dynamic response. The combination of all characteristics offered by CuO/ZnO nanocomposites can enable the fabrication of diverse sensing devices, and solar cells. The outlines of this thesis can be organized as follows: First a general introduction to nanotechnology potentials and challenges motivated by the research and developments of nanomaterials with especial emphasis on oxides nanomaterials is given. A brief description of some of the important oxide nanomaterials and their potentials in various applications areas is introduced, with especial emphasis on ZnO and CuO as they are studied in this thesis. This introductory chapter is followed by background and literature survey on the structural properties of ZnO, CuO, and polymer materials. In chapter 3 the synthesis and characterization of ZnO, CuO, and CuO/ZnO nanomaterials is presented. After that, the realization and results of ZnO/polymer hybrid LEDs, CuO NFs pH sensor, and CuO/ZnO NCs RH sensing applications are discussed in details. Finally, conclusions that are evident from the work results are summarized and accompanied by a short outlook, which may boost additional efforts in this exciting and promising field.
Chapter 2

2. Background and Literature Survey

ZnO is a wide bandgap material possessing many attractive properties which have gained huge research interest in various aspects of material science as well as device technology development. Similarly, CuO material offers many stimulating characteristics which can be used for different applications such as sensing, field emission, and solar cell, etc. Likewise, semiconducting organic polymers which have already invaded the market place with diverse applications such as display technology, thin film transistors, and photovoltaics applications. In this chapter, comprehensive description of the properties of these materials is presented.

2.1 ZnO Material Properties

ZnO is a unique material with both semiconducting and piezoelectric properties. These properties in addition to its relatively large family of nanostructures compared to all semiconductors of interest pave the way for ZnO to occupy a pioneering place as an advanced material for future applications. In this section the fundamental properties of ZnO will be described with especial emphasis on the properties related to the present work such as crystal structure, optical, and electronic characteristics of ZnO.

2.1.1. Crystal Structure

As a member of group II-VI binary compound semiconductors, ZnO crystallizes in either zinc blende or hexagonal wurtzite structure. In the wurtzite structure Zn and O are arranged into a hexagonal form with interpenetrating lattices where each Zn$^{2+}$ ion is coordinated by tetrahedral of O$^{2-}$ ions, and vice-versa (Figure 2.1). Even though ZnO is II-VI compound semiconductor with covalent bonding, it exhibits significant ionic character as well [68]. The crystal lattices of ZnO are organized into a wurtzite (B4) space group P63mc or C6v4, zinc blende (B3) and rocksalt (B1). At ambient conditions the thermodynamically favorable crystal structure is the wurtzite, while the zinc blende crystal structure can be obtained by growing ZnO on cubic substrates. The rocksalt
phase of ZnO is rare crystal structure and can be observed at relatively high pressures [68]. ZnO in the wurtzite structure has polar surface (0001) which is either Zn or O terminated surface as shown in Fig. 2.1, and non-polar surfaces (1120) and (1010) having an equal number of Zn and O atoms. Due to the metastable nature of the polar surfaces of ZnO, these surfaces exhibit many interesting properties such as piezoelectricity, physical, chemical, and high sensitivity. The lattice parameters of the wurtzite unit cell of ZnO were measured by x-rays diffraction technique [68, 69] to be \(a = 3.2490 \text{Å} \), and \(c = 5.2069 \text{Å} \), with axial ratio \(c/a = 1.6018 \), and the density is 5.605 gcm\(^{-3}\) [70]. The discussion in the present thesis will be limited to the wurtzite crystal structure of ZnO since ZnO nanorods synthesized using the low temperature method demonstrated hexagonal structures as confirmed by the characterization techniques used.

![Figure 2.1: The hexagonal wurtzite crystal structure of ZnO. One unit cell is outlined for clarity. (Reproduced from Wikipedia.org).](image)

**2.1.2 Electronic Band Structure**

Understanding the band structure of a semiconductor material is of great importance when this material is considered for device applications. ZnO is a direct bandgap semiconductor with energy gap of 3.37 eV at ambient conditions (for a direct
bandgap materials the uppermost valence and the lowermost conduction bands occur at the same point in Brillouin zone known as Γ-point see Fig. 2.2). Due to the substantial ionic character of ZnO the bottom of the conduction band is mainly formed by the 4s levels of Zn\(^{2+}\) or the antibonding sp\(^3\) hybrid states, while the valence band is created by the 2p levels of O\(^{2-}\) or the bonding sp\(^3\) orbitals [71]. The group theory predicts that the bottom of the conduction band (CB) has a Γ\(_1\) symmetry without inclusion of spin and symmetry Γ\(_1\)⊗Γ\(_7\) = Γ\(_7\) with spin [71]. The effective electron mass of ZnO has a value of about \((0.28\pm 0.02) \, m_0\) [71]. The hexagonal crystal field of ZnO splits the valence band (VB) into two states, Γ\(_5\) and Γ\(_1\). Also, the involvement of spin introduces further splitting of the VB and giving rise to three twofold-degenerate sub-VB with symmetries of (Γ\(_1\)⊗Γ\(_5\))⊗Γ\(_7\) = Γ\(_7\)⊗Γ\(_9\)⊗Γ\(_7\) these sub-VB are labeled as from the highest to the lowest energies as A, B, and C bands as shown in Fig. 2.2. The effective masses of the holes in ZnO for the various bands A, B and C are rather isotropic with typical values of \(m_\text{h\parallel A,B} = 0.59 \, m_0\), \(m_\text{h\parallel C} = 0.31 \, m_0\), and \(m_\text{h\perp C} = 0.55 \, m_0\) [71].

The wide bandgap of ZnO has many important implications in the electronic and optoelectronic fields. For example ZnO can operate at high power, sustain high breakdown voltages, with minimum electronic noise. Additionally, its wide bandgap can accommodate large number of intrinsic defects that emit various light wavelengths. Also, among other II-VI semiconductors, ZnO possesses a relatively high and stable exciton binding energy of 60 meV at room temperature [68, 71, 72]. The high exciton binding energy of a material ensures that the excitons will recombine radiatively at higher probability. The native defects and impurities in ZnO such as oxygen vacancies (V\(_O\)), hydrogen, aluminum, gallium, etc., are responsible for the observed n-type semiconductor behavior of ZnO as well as Schottky diode properties [68, 73-76].

### 2.1.3 Optical Properties

As discussed above ZnO is a direct wide bandgap semiconductor, it has a number of unique optical properties which make ZnO a promising material for short wavelength photonics. The optical properties of ZnO are highly affected by the
electronic band structure and the lattice dynamics of the hexagonal crystal field as pointed out in the previous section. In general high purity ZnO crystal is optically transparent in the visible range of the spectrum, with a typical refractive index of \( n_\omega = 2.008 \) [70, 77]. But, ZnO crystals usually are red, green or yellow colored which are the results of unintentional doping of the grown crystals. The source of coloration centers in ZnO is a subject of long standing debate [73, 78]. Both intrinsic and extrinsic defects were assigned as potential coloration centers (levels) within the bandgap of ZnO. These deep level defects (DLE) include oxygen vacancies, Zn vacancies, interstitial Zn and oxygen, in addition to impurities such as Li, Ga, Cu, H, … etc.

![Figure 2.2: Schematic illustration of the band structure (CB and VB) of ZnO in the vicinity of the fundamental bandgap [71].](image)

Number of investigations on the photoluminescence (PL) of ZnO have suggested that within the bandgap of undoped ZnO (3.37 eV) there are intrinsic point defects that are responsible for the observed green emission (~2.36 eV) which have been assigned as \( V_0 \) [73]. While for the red luminescence (~1.9 eV) it has been attributed to \( \text{Zn}_i \) in ZnO [68, 73]. On the other hand, the violet-blue and blue luminescence was ascribed to \( \text{Zn}_i \) and Zn vacancy (\( V_{\text{Zn}} \)), respectively [68]. Finally, the yellow luminescence of ZnO which
is commonly observed in the low temperature grown samples, has been attributed to surface defects [79]. The formation energy along with the various deep level defects in ZnO has been studied by many researchers [79-81], and the results are summarized in the schematic diagram of Fig. 2.3. An intensive attention is being shown in studying the defect emissions in ZnO in general and ZnO nanomaterials in particular, because of their huge potential for a variety of optical applications.

![Figure 2.3: Schematic band diagram of intrinsic point defects in ZnO, based on the value of different defects extracted from the literature [68, 73, 80].](image)

**2.1.4 Summary of ZnO Properties**

Besides, the electronic and optical properties of ZnO, there are many other favorable aspects in this attractive material such as relatively low-cost production of large single crystals, relatively abundant source material, and chemical stability to name a few. Furthermore, the large family of ZnO NSs demonstrates that this material has great potential in diverse applications in the near future. In particular, ZnO nanorods are potentially attractive for various nanodevices such as LEDs, chemical sensors, solar cell, and piezoelectric nanogenerators ensuring high efficiency and high sensitivity on these applications. Some of the common properties of ZnO bulk material are summarized in Table 2.1.
Table 2.1: Important properties of bulk wurtzite ZnO.

<table>
<thead>
<tr>
<th>property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = b = 3.25 Å</td>
<td></td>
<td>[82-84]</td>
</tr>
<tr>
<td>c = 5.21 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>u = 0.348</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c/a = 1.593-1.6035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>5.606 gm/cm³</td>
<td>[84]</td>
</tr>
<tr>
<td>Melting point</td>
<td>2248 K</td>
<td></td>
</tr>
<tr>
<td>Stable crystal structure</td>
<td>Wurtzite</td>
<td>[84]</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>8.66</td>
<td>[85]</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008</td>
<td>[86]</td>
</tr>
<tr>
<td>Band gap (E_g)</td>
<td>3.37 eV, (direct)</td>
<td>[84, 87]</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
<td>[88]</td>
</tr>
<tr>
<td>Electron/Hole effective mass</td>
<td>0.24-0.28 m_e/0.59 m_o</td>
<td>[71, 82]</td>
</tr>
<tr>
<td>Hole mobility (300K)</td>
<td>5-50 cm²/ V s</td>
<td>[89]</td>
</tr>
<tr>
<td>Electron mobility (300K)</td>
<td>100-200 cm²/ V s</td>
<td>[89]</td>
</tr>
</tbody>
</table>

2.2 Copper Oxide

As mentioned earlier, copper oxide has two types of polymorphism, namely, cuprous oxide (Cu₂O) and cupric oxide (CuO). These oxides are the two most important stoichiometric compounds in the Cu-O system. Both oxides are intrinsic p-type semiconductors with relatively small bandgaps and show many attractive properties that can be utilized in a diversity of applications. The potential applications of copper oxides include solar cells [90], Li-ion battery where they have been used as negative electrode material [91], superconductor [92], magnetic storage, gas sensors [93], and photoconductive systems [94]. Due to its peculiar properties, CuO has been chosen in this thesis work to profit from the unique properties of CuO/ZnO composites in RH sensing application.
2.2.1 Cupric Oxide

Cupric oxide (CuO) is an intrinsic p-type semiconductor with a bandgap in the range of (1.2-1.85 eV). The CuO has a C2/c monoclinic crystal structure [95-97]. The unit cell of CuO comprises Cu$^{2+}$ ions which are coordinated by four O$^{2-}$ ions in an approximately square planar configuration (Figure 2.3) [98].

![Monoclinic crystal structure of cupric oxide (CuO). (Reproduced from Wikipedia.org).](image)

The abundance of its source material (Cu) together with other features such as low-cost production, good thermal stability, and electrochemical properties make CuO a promising material in various applications. Furthermore, the ionicity of the Cu-O bonds increases when the size of the material approached the nanodomain. This property combined with the relatively large aspect ratio of CuO nanomaterials is very attractive for applications such as gas sensing and catalyst for degradation of hazardous chemicals. Also, the synthesis of CuO/ZnO NCs and their application as fast and sensitive RH sensor was accomplished. Some of the important properties of CuO bulk material are given in Table 2.2.
Table 2.2: Some of the key properties of CuO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants (300K)</td>
<td>(a = 4.68 \text{ Å})</td>
<td>[82, 99]</td>
</tr>
<tr>
<td></td>
<td>(b = 3.42 \text{ Å})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c = 5.13 \text{ Å})</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>6.31 gm/cm(^3)</td>
<td>[100]</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975 °C</td>
<td>[100]</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
<td>Monoclinic</td>
<td>[99]</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>18.1</td>
<td>[100]</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.4</td>
<td>[100]</td>
</tr>
<tr>
<td>Band gap ((E_g))</td>
<td>1.21-1.85 eV, direct</td>
<td>[101, 102]</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.24 (m_o)</td>
<td>[82]</td>
</tr>
<tr>
<td>Hole mobility</td>
<td>0.1-10 cm(^2)/Vs</td>
<td>[100]</td>
</tr>
</tbody>
</table>

2.3 Polymers

Among the materials used in the present thesis are conjugate polymers which were employed with ZnO nanorods to fabricate various LEDs. So, here I will briefly describe some of the general properties of this class of unique organic semiconductor materials.

2.3.1 Conjugated Polymers

In general polymers are materials that consist of long chains of identical species of organic molecules called monomers linked together by covalent bonds. Polymer word has originated from the Greek language where poly means “many” and mer means “part”. Polymers exist in variety of shapes and forms such as rubber and protein as natural products along with large number of synthetic polymers such as nylon and polyethylene. The easy synthetic and controllability of polymers made them versatile materials that have very wide applications in industrial packaging and insulation. The conjugated polymers are characterized by their alternating single and double bonds in
the polymer chain. The three hybridized sp\(^2\) electrons of each carbon atoms create three single bonds known as sigma bonds. The remaining electron of the carbon atom is characterized by a P\(_z\) orbital perpendicular to the plane created by the sigma bonds [103]. The interactions of the P\(_z\) orbitals of adjacent carbon atoms create two molecular orbitals: occupied \(\pi\)-bonding orbitals which also known as the highest occupied molecular orbitals (HOMO), and an unoccupied \(\pi^*\)-antibonding orbitals which are called the lowest unoccupied molecular orbital (LUMO) [104]. The electronic and optical properties of conjugated polymers are critically determined by these molecular orbitals. The analogy of the HOMO and the LUMO orbitals in inorganic semiconductors are the valance band and the conduction bands, respectively.

In this thesis two semiconducting light emissive polymers were used to fabricate ZnO/p-polymer hybrid LEDs.

\subsection{2.3.2 Poly(9,9-dioctylfluorene) (PFO)}

Poly(9,9-dioctylfluorene) (PFO) is a p-type semiconducting and blue light emissive conjugated polymer. This polymer has many attractive properties such as simple solution processability, good thermal and chemical stabilities at elevated temperatures (\(\approx 300^\circ\)), good hole conduction, and high luminescence yield. PFO has a LUMO level locating between 2.12 eV- 2.6 eV and a HOMO level in the range of 5.6 eV-5.8 eV resulting in \(\sim 3\) eV energy bandgap [105]. Moreover, the PFO exhibits liquid crystalline phase transition at 170 °C which allows the realization of oriented films and polarized light emission devices [105]. Also, the PFO has a planar polymer chain with different types of amorphous (glassy \(\alpha\)-phase) and sometimes extended conjugation encompassing the entire chain which is known as (\(\beta\)-phase), the chemical structure of the PFO is shown in scheme 1 [105]. The formation of the \(\beta\)-phase is a consequence of the \(n\)-alkyl crystallization of the PFO side chains [106, 107]. This phase exhibits characteristic red-shift absorption and luminescence spectrum with resolved vibronic features. Both phases of the PFO are very attractive for investigating the photophysical properties and energy transfer processes in conjugated polymers [108]. On the other
hand, particular processing of the PFO such as thermal, optical, electro-optical, and chemical treatments can induce significant changes in the absorption and luminescence as a result of new intrachain states [109].

Among the observed states in the PFO chains is the fluorenone defect which associated with the oxidation of the polymer backbone [109]. This on-chain defect contributes to the low energy emission band in the polyfluorene derivatives and turns their blue emission into blue-green emission.

2.3.3 MEH-PPV

Among the intensively studied conjugated polymers is the poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), due to its interesting emissive and electrical properties.

The MEH-PPV has relatively small optical bandgap of 2.1 eV as estimated from the HOMO-LUMO energy difference [105]. As a result of the slightly small energy bandgap of the MEH-PPV it emits in the orange-red (590 nm), and it has been explored for potential application in solar cells [110]. The relatively high hole mobility and simple preparing/processing of MEH-PPV allow its applications in thin film transistors [111]. The chemical structure of the MEH-PPV is shown in scheme 2 above.
Chapter 3

3. Synthesis and Processing of Nanostructures

In this chapter, the details of the experimental procedures used to synthesize reproducible, uniform, and good quality ZnO, CuO, and CuO/ZnO NSs are described. These procedures were based on low temperature wet chemical routine either by one step protocol for individual nanomaterial or two steps for the composite NSs. The processing of these NSs and composites into functional devices such as hybrid light emitting diodes (HyLEDs), (pH) and relative humidity (RH) sensors will also be given.

3.1 Substrate Preparation

There are a number of important steps that have to be performed before the synthesis of the NSs in the wet chemical synthesis procedures. These steps include the pre-cleaning of the substrate, preparation of the seed nanoparticles in case of ZnO. This is followed by spin coating of these colloidal nanoparticles on the substrate. Adjusting these entire parameters play a significant role in the quality of the synthesized NSs.

3.1.1 Standard Substrate Cleaning

Prior to the synthesis step the substrates were sequentially and repeatedly immersed in acetone and iso-propanol under sonication for 5 minutes at 45 °C. This cleaning step is followed each time by rinsing the substrates in deionized water (DI-water) and finally the substrates were blown dried by nitrogen gun. The purpose of this cleaning step is to eliminate organic contaminant and unwanted particles. This is essential in the subsequent materials deposition and the NSs synthesis.

3.1.2 Thin Films Deposition

In this thesis the synthesis of ZnO nanorods were achieved on a number of thin films of metal, metal oxides semiconductor and polymer coated substrates. These thin films include silver (Ag) gold (Au), copper (Cu), (CuO), (Cu2O) and poly(3,4
ethylenedioxythiophene)/poly(strenesulfonate) (PEDOT:PSS). So, for preparing the substrates for ensuing growth procedure these thin films were deposited as follows: Metals thin films were thermally evaporated using Satis metal evaporator under a high vacuum of \((2.5 \times 10^{-6} \text{ mbar})\). A 10 nm thin film of chromium (Cr) was first deposited on the substrates to improve adhesion properties of the targeted metals. Then 125-150 nm (as measured by the quartz crystal thin film controller) of the appropriate thin film was evaporated. The metal evaporation rate (Å/s) was extra-carefully adjusted to the lowest possible level for metals deposited on soft plastic to avoid burning. For the case of copper oxides (CuO, Cu₂O) a 150 nm thin film of Cu was deposited on a glass slide and then transferred to a horizontal quartz tube furnace for heat treatment. The conditions necessary to obtain the desired copper oxide were achieved by annealing of the substrate under an oxygen-rich environment at 500 °C for 25 min to produce CuO, while for Cu₂O formation, the coated glass was transferred to the same oven held at 400 °C for 5 min in an inert environment. A color transition on the films was observed indicating the production of both Cu oxides. For polymers thin films used in this thesis, a specific spin coating speed and baking at 75 °C were applied.

3.1.3 ZnO Seed Layer Preparation

One of the main benefits of using ZnO nanoparticles acting as a seed layer in the hydrothermal growth method is to provide nucleation sites for ZnO nanorods by reducing the thermodynamic barrier between heterogeneous materials [112]. Also, ZnO seed layer was found to be a critical factor in the final product morphology e.g. alignment and uniformity of the grown ZnO nanorods. The seed layer was prepared by dissolving zinc acetate dehydrate \((\text{Zn(CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})\) in absolute methanol (99%) to obtain 0.01 M solution concentration, which was then heated at 60 °C on a hotplate. A solution of potassium hydroxide (KOH) in methanol was added dropwise to the Zn acetate solution under vigorous stirring, and the whole solution was kept at 60 °C for 2 hours. The prepared solution is expected to contain dispersed ZnO nanoparticles with an average size of 3-5 nm [113]. This colloidal solution is then ready for spin coating on
the substrate without any post treatment [112]. For the synthesis of ZnO nanorods the seed solution was spin coated 3-4 times at spin speed of 3000 rpm (rounds per minute) for 30 seconds each. During the growth, ZnO nanorods preferentially nucleate and grow at the seed layer grains. By controlling the spinning speed of the seed layer one can control the thickness of the seed layer and its surface coverage. This in turns can be used as a way to control the density and placement of the grown ZnO nanorods.

3.2 Hydrothermal Synthesis of Nanostructures

As mentioned earlier, ZnO possesses the richest family of NSs among all known materials. Various types of ZnO NSs can be found in the literature with unique morphologies, structure, and properties. ZnO NSs that have been chosen in this work is 1D ZnO nanorods (NRs). This is due to the unique structural and physical properties along with their simple growth steps using the hydrothermal technique [114, 115]. The hydrothermal synthesis approach is a very attractive low temperature solution based synthetic method due to many reasons. This growth method is simple and does not require sophisticated equipment; it is cost efficient, environmental friendly, scalable for large area applications [116], and can be used to grow various NSs by simply varying the growth parameters such as the solution pH [117]. Therefore, the hydrothermal approach holds great aptitudes for NSs synthesis on flexible/soft substrates such as polymers and paper. In this work, the hydrothermal approach was used in the synthesis of ZnO NRs [112], petal-like and flower-like CuO NSs [118], and CuO/ZnO nanocorals [119].

3.2.1 Synthesis of ZnO Nanorods

In the hydrothermal synthesis of ZnO NRs many attempts have been carried out before reaching the optimum conditions for the synthesis of high density and high quality ZnO NRs. After systematic studies of these conditions, the following optimized conditions were used in the entire thesis. The growth solution used in this work is a mixture of 100-150 mM of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and 100 mM of
hexamethylenetetramine (C₆H₁₂N₄, HMT) with a volume ratio between 1:1 to 1.5:1, respectively. It is widely accepted that the addition of HMT to the aqueous solution of zinc nitrate regulates the solution pH value and supplies addition OH⁻ ions [114, 115]. Moreover, Sugunan et. al [120] proposed that the HMT is preferably attached to the non-polar facets of the zincite crystal and this means preventing the access of Zn²⁺ ions to reside on the sides of the structure, leaving to the Zn²⁺ ions access only to the polar facet (0001) for further nucleation and vertical growth. The prepared aqueous solution is then vigorously stirred for 5 minutes to ensure that the precursor materials are completely dissolved. The pre-seeded substrates using the procedure described in section (3.2.3) were immersed into the nutrient solution (Figure 3.1a). The nutrient solution containing the pre-coated substrates was then transferred to a conventional oven held at 50 °C for several hours. After the synthesis time is elapsed the beaker was withdrawn (Figure 3.1b) and the samples were collected (Figure 3.1c) and then were rinsed well in DI-water under sonication to remove unreacted salts. The optical photograph of all samples grown by the one or the two steps hydrothermal approach is shown in Fig. 3.1e. These samples include ZnO NRs grown on Au substrate, CuO NSs grown on Au substrate and CuO/ZnO composite NSs which will be discussed below. As mentioned above, the pre-seeded substrates were immersed in the nutrient solution which resulted in the c-axial oriented ZnO NRs normal to the substrate. This growth behavior can be explained from the wurtzite crystal structure of ZnO together with its strong ionicity nature. The c-axis ± (0001) facets of ZnO are polar surfaces and thus possess the highest energy among low indices surfaces. As a consequence, any new deposited ZnO nucleus will preferably be adsorbing to the polar surfaces rather than on other low indices (low energy) surfaces. Furthermore, after the deposition of each ZnO monolayer the polar surface transforms into new polar surface with inverted polarity and so forth with time until the source materials are consumed. This process will lead to a fast growth along the polar surfaces, exposing the non-polar surfaces to the solution [53]. Finally, the possible chemical reactions involved in the synthesis of ZnO NRs can be summarized as follows [53, 112,
In the hydrothermal method described in this thesis, the dissolved zinc nitrate provides the Zn$^{2+}$ ions required for forming ZnO NRs. The HMT on the other hand hydrolyzes in the water and gradually produces formaldehyde (HCHO) and ammonia (NH$_3$) as described by equations (1-2). The ammonia acts as a pH buffer and regulates the solution pH value (OH$^-$ ions), during the entire experiment, the pH value retains close to the neutral pH.

The main chemical reactions occurring during the growth process can be described according to:

\[ C_6H_{12}N_4 + 6H_2O \leftrightarrow 4NH_3 + 6HCHO \quad (1) \]
\[ NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2) \]
\[ Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \quad (3) \]

\[ \]
The Zn(OH)$_2$ is a metastable compound that is dehydrolyzed under the given conditions to produce ZnO according to:

$$\text{Zn(OH)}_2 \leftrightarrow \text{ZnO} + \text{H}_2\text{O} \quad (4)$$

All these reactions (1-4) are in equilibrium and can be controlled by adjusting the reaction parameters such as the source material concentration, the reaction temperature and the growth duration. The density of the grown NRs is generally determined by the concentration of the reactants, while the reaction temperature and duration can precisely be used to control the aspect ratio (length/diameter) [53, 112].

### 3.2.2 Synthesis of CuO Nanostructures

The hydrothermal synthesis of CuO NSs was realized by using copper nitrate trihydrate (CNH, Cu(NO$_3$)$_2$.3(H$_2$O), HMT and aqueous solution of NaOH without prior pre-seeding process of the substrates. In a typical experiment, a (~ 0.121 g) of CNH was dissolved in 100 mL of DI-water targeting 5 mM and vigorously stirred for 5 min. a 1 mM aqueous solution of HMT was then added to the CNH and kept for extra 10 min under continuous stirring. The pre-cleaned substrate was immersed in the nutrient solution and then transferred to a laboratory oven held at 90 °C for 4-5 h. This experiment results in the growth of black CuO NFs on the substrate as well as powder on the bottom of the reaction vessel. For the growth of CuO nanopetals (NPs) 1 mL of NaOH (30%) was added to the nutrient solution of CNH and HMT, while other steps were kept identical. The optical photograph of the sample is shown in Fig 3.1e. For the detailed chemical reaction and CuO NSs formation mechanisms the reader is referred to [121, 122]. In addition, time-dependent synthesis of CuO NSs was studied to identify the intermediate products. This experiment was performed using the CNH+ HMT+ NaOH aqueous solution and the reaction products were collected and characterized using a transmission electron microscope (TEM). The intermediate products obtained in this study were ultra-thin CuO nanowires (NWs) with ~ 2-5 nm diameters and length up to 1 µm, which later self-assemble to form higher dimension CuO NSs. These CuO nanomaterials are still under investigation and will be discussed elsewhere.
Furthermore, pH dependent hydrothermal synthesis of CuO NSs was carried out for a better understanding of the effect of the pH on the morphology of the CuO NSs. This was performed by adjusting the nutrient solution of CNH+HMT to a pH value between 2-11 using HNO₃ and NH₃.OH as pH controlling agents to decrease and increase the pH of the nutrient solution, respectively.

3.2.3 Synthesis of CuO/ZnO Composite Nanostructures

The synthesis of composite NSs of CuO/ZnO was developed using a two-step hydrothermal method, in which the CuO NSs were self-assembled and selectively deposited on ZnO NRs. The growth was divided into lengthwise growth (ZnO NRs) and branched growth of CuO NSs. The lengthwise synthesis of ZnO NRs was performed as discussed in section 3.2.1 above following the same procedure developed before [112]. For the branched growth of CuO NSs two procedures were adopted. First, a 5 mM aqueous solution of CNH only solution was prepared according to our recently reported method [119]. In the second procedure a 1 mM aqueous solution of the HMT was added to the CNH to form (CNH+HMT) solution as described in 3.2.2. The freshly grown ZnO NRs used as substrates were dipped having faced up in the precursor solution that was held at 60 °C for 0.5- 4 h. Finally, when the color of the precursor solution was turned into light gray the reaction was ended as the branch growth of CuO NSs was obtained. The substrates were then thoroughly washed with DI water and then dried by a N₂ gun. The photograph of the grown sample is shown in Fig. 3.1e. It is important here to mention that the growth duration/reactant and the solution pH value in the branched growth play a critical role in the final products. For instance, increasing the growth duration more than 4 h will lead to complete dissolution of ZnO NRs, since they are vulnerable in low pH solutions [123]. Also, using the CNH+HMT solution resulted in a fast growth of CuO/ZnO composite NSs due to the relatively abundant (OH⁻) as will be discussed later. So, by optimizing the growth conditions one can get excellent control over the final composite NSs e.g. by shorten the growth time partial coverage of ZnO NRs by CuO NSs can obtained.
3.3 Device Processing

Engineering of the variety of nanostructures obtained using the above discussed synthetic procedures into functional devices were the major objectives of the present work. After collecting sufficient knowledge about the materials used in this thesis and gaining wide controllability over their respective nanostructures, the exploration of their potential applications in diverse technologically important areas was the stimulating factor behind the present thesis. These applications include hybrid heterojunction of ZnO/p-polymer LEDs for lighting, and RH sensing application using hierarchical CuO/ZnO NCs heterojunction diodes, and finally CuO NFs were utilized as an electrochemical pH sensor.

3.3.1 Hybrid ZnO nanorods/p-polymer Heterojunction LEDs

The fabrication of ZnO/p-polymer hybrid heterojunction LEDs (HyLEDs) in this thesis was conducted using commercially available high conductivity PEDO:PSS flexible foils. The choice of this polymer was based on its many attractive properties such as excellent electrical properties, transparency, flexibility, long term stability, and simple processability. Recently, we have also demonstrated a ZnO/p-polymer HyLED fabricated directly on paper [60]. The fabrication steps of the flexible ZnO/p-polymers HyLEDs can be summarized as follows: after performing the standard cleaning process (see 3.1.1), the light emitting polymers were spin coated on the substrates. The light emitting polymers consist of PFO (sec 2.3.2) purchased from (American Dye Source ADS 129BE), MEH-PPV (sec 2.3.3) (Sigma-Aldrich Sweden), and their blended polymer. These polymers were prepared by dissolving few mg (milligrams) depending on the experimental approach (see below) in 1 ml of either chloroform or toluene under constant sonication. The polymer solution was then spin coated using 2000-3000 rpm spinning speed for 30 sec and consequently, baked at 70-100 °C for few minutes in order to evaporate the solvents. The seed solution containing ZnO colloidal nanoparticles (see 3.1.3), instantly was repeatedly spin coated on the substrate to make uniform seeding layer for ensuing a successful hydrothermal synthesis step [60, 124, 125]. As discussed
previously (see section 3.2.1), the substrates were loaded in the nutrient solution of ZnO for several hours at 50 °C. After careful cleaning of the substrate and in order to complete the fabrication of the HyLEDs few additional processes were performed. First, spin coating of an insulating layer to electrically isolate adjacent ZnO NRs and to avoid metal diffusion to the underlying polymer layer(s) was required. For this purpose, insulating materials such as polystyrene and polymethyl methacrylate (PMMA) were used. The typical process of insulation involves spin coating a 3000 rpm for 30 sec. and baking at 90 °C for 1-3 minutes. This process results in an excellent coverage of the NRs. Reactive ion etching (RIE) with oxygen plasma was then utilized to etch away the insulating layer and expose the upper part of ZnO NRs tips for the final metallization step.

*Figure 3.2:* a) Schematic diagram illustrating the fabricated HyLED, b) optical photograph of the HyLED on PEDOT:PSS commercial foil, c) bending of the HyLED shown in b), and d) optical image of the fabricated ZnO/p-polymer HyLED on disposable paper substrate. Reproduced from [60].

The metallization step was accomplished using aluminum with 20-50 nm thickness which was thermally evaporated through a shadow masks having an average
diameters of 0.5-2 mm. While for the bottom contact conductive Ag paint was bonded to the PEDO:PSS layer. The schematic diagram of the fabricated HyLED is illustrated in Figure 3.2, along with the optical photographs of the HyLEDs fabricated on flexible/disposable paper substrates which were bent without any significant degradation of the devices.

### 3.3.2 CuO nanoflowers Based-Electrochemical pH Sensor

The CuO NFs were initially synthesized on Au coated glass slide by the method described in section 3.2.2 while the optical image of the sample is shown in Figure 3.1.

![Figure 3.3: Schematic diagram of the potentiometric measurement setup of the pH sensor.](image)

The electrochemical study was conducted using two electrodes configuration in which the CuO NFs on Au acted as a working electrode and Ag/AgCl as a reference electrode. The response of the electrochemical potential difference to the changes in the buffer was measured at room temperature in wide range of pH values (2-11) using Metrohm pH meter. The schematic depiction of the pH sensor consisting of CuO NFs electrode is shown in Figure 3.3.
3.3.3 CuO/ZnO Nanocorals Humidity Sensor

The newly developed CuO/ZnO composite NSs were employed to fabricate fast and high sensitivity humidity sensor. Taking into account all advantages offered by this composite nanomaterial an exploration of their performance as a functional nanodevices that exhibits unique characteristics was among the objectives of the present work. For instance, the formation of the composite NSs is simple, cost-effective, relatively fast (1.5 h), high selectively of CuO NSs to ZnO NRs, intrinsic p-n heterojunction of CuO/ZnO, respectively, high diode rectification behavior, and high porous structures. The combination of these unique advantages enabled us to fabricate very high sensitivity RH sensor that was able to change its diode characteristics for minute change in the humidity of the surroundings.

Figure 3.4: a) Schematic diagram of the fabricated CuO/ZnO NC RH sensor. Reproduced from [119], and b) the computerized environmental chamber at ITN cleanroom.

The fabrication of the RH sensor begun with the hydrothermal synthesis of the nanomaterials on indium tin oxide (ITO) substrate using the same procedure described previously. However, after the growth of ZnO NRs there was additional step before advancing to the growth of CuO NSs on ZnO NRs. Here, the polystyrene was spin coated on top of ZnO NRs and RIE etched to expose 2/3 of the NRs for the subsequent
growth of CuO NSs. After the growth of CuO NSs was established for 4 h, the polystyrene was coated again on the top of CuO/ZnO NCs to ensure there would be no leakage/shortage in the sensor active area [119]. Finally, a 100 nm Au thin film was thermally evaporated through a shadow mask (1.5 mm diameter) to act as ohmic contact to CuO NSs junction, while the ITO worked as ohmic contact on ZnO side. The electrical characterization together with the humidity sensing investigations was conducted at 25 °C inside an environmental chamber that is controlled by a computer program. The schematic diagram of the RH sensor and the environmental chamber are shown in Figure 3.4.

3.4 Characterization Techniques

In-depth understanding of the materials structures, morphology and properties and their correlation to the functional device is a key element in all technological achievement of mankind. There are number of characterization techniques that were used in this thesis including structural characterization equipment such as TEM, high resolution TEM (HRTEM), and selected area electron diffraction (SAED) [126], scanning electron microscopy (SEM) [127], and x-rays diffraction (XRD) technique using Bragg-Brentano geometry [128]. On the other hand, the fabricated devices for lighting/sensing application were characterized using electrical measurements (current-voltage), electrochemical measurements, and electroluminescence/photoluminescence characterization techniques. Here, a brief description of the working principles of these characterization techniques is given, except for the electrochemical measurement which was discussed earlier (see section 3.3.2).

3.4.1 Transmission Electron Microscopy (TEM)

The TEM is a microscopy technique in which high energetic beam of electrons that were first generated by an electron gun (field emission), is focused by a series of magnetic lenses. This beam is then transmitted through the ultra-thin sample on TEM grid, and interacting with the atoms of the specimen as it passes through. The
transmitted electrons through the specimen then create an image as the result of the interaction of the electrons and the specimen. This image is magnified and focused onto a fluorescent screen or a CCD camera. Thus, the working principle of the TEM is quite identical to the optical microscope. The TEM has many advantages and is used extensively on materials and life sciences in general. However, there are a number of disadvantages associated with TEM characterization such as the preparation of specimen is time consuming process, only local information can be gathered, destructive analysis, and difficult operation of the equipment [126].

3.4.2 Scanning Electron Microscopy (SEM)

The working principle of the SEM is similar to the TEM, where a high energy electron beam (few keV) is focused by condenser magnetic lenses and passes through a scanning coil inside the electron column. The scanning coil deflects the electron beam in the x and y axes and hence scans in a raster manner over the specimen surface. The interaction of the incident beam with the specimen involves random electron scattering, absorption, penetration, and backscattering. These interactions result in various emitted signals that are detected by a different types of electron/photon detectors [127]. In the present work, the SEM images were collected by secondary electron detector, which is useful technique for observing topographical features of nanomaterials.

3.4.3 X-rays Diffraction (XRD)

X-rays diffraction is a powerful structural characterization technique used for studying crystalline structures. It is a non-destructive analytical technique that provides unprecedented detailed information of the crystal structures, orientations, phases and chemical composition of materials and thin films. The working principle of the XRD technique is simple in which a monochromatic characteristic x-rays produced by the impact of accelerated electrons with heavy metal such as Cu, which then gets filtered and collimated by nickel filters. If this x-rays beam with a characteristic wavelength $\lambda$ strikes the solid with an incident angle $\theta$ then the scattered radiation is determined by Bragg’s law which states:
Where \( n \) is an integer known as the diffraction order, \( d \) is the distance between the diffracting planes. The set of \( d \)-planes in a typical XRD experiment is unique for each material and is used to identify the crystal structure of the studied solid [128]. In this thesis, the XRD characterization of the nanomaterials were performed using (X’pert PANaytical) equipped with Cu K\(_{\alpha 1}\) (\( \lambda = 1.5406 \) Å).

3.4.4 Current Density-Voltage (J-V) Measurements

The current density-voltage (J-V) measurements of a p-n junction give valuable information to evaluate the performance of the fabricated diode. The J-V characteristics of the fabricated HyLEDs and the CuO/ZnO NC RH sensor were conducted by means of a multiple source-measure units (SMUs) semiconductor parameter analyzer Agilent 4155B. Two terminals of the SMUs were connected via coaxial cable and micromanipulators (probes) to the \( p \)- and \( n \)-metal contacts of the diode. When the voltage sweeps in constant intervals the current response is measured accordingly. From this simple measurement important information can be extracted such as turn-on voltage of the diode, ideality factor using the diode equation, break-down, and the diode resistances [129].

3.4.5 Electroluminescence (EL) Measurements

The electroluminescence (EL) measurement is a very important electro-optical technique that enables understanding the characteristics of the emitted light photons and their original radiative centers in the material. In a typical EL measurement the light emission of the LED for instance is driven by and electrical injection of carriers (electron/hole). These carriers then undergo radiative recombination within the diode junction and as a result photons are emitted. The emitted photons then traverse the LED through the contact window and being collected by an optical fiber that is attached to the spectrometer. The transmitted photons are then disperse by diffraction grating within the spectrometer and finally detected by a CCD camera. The dispersion of the
light helps in defining the distribution of the emitted light. In the present thesis we used source meter Keithley 2400 to inject the carriers into the HyLED, while an Andor-Shamrock 303i spectrometer supported by Andor-Newton Du-790N CCD was used to investigate the emitted light characteristics of the fabricated ZnO/p-polymer HyLEDs.

3.4.6 Photoluminescence (PL) Measurements

The photoluminescence (PL) technique is an important method for characterizing the optical properties and electronic structure of semiconductors; the simplicity of the PL operation makes it a popular characterization tool. The main principle of the PL technique is to investigate the luminescence emitted from the sample under examination, when it is excited by light photons with certain wavelength. In a typical PL experiment the sample is illuminated with a monochromatic light (usually laser) having an energy above the bandgap of the sample. This excites the carriers from the valence band to the conduction band. The carriers (electrons/holes) will subsequently recombine in a direct radiative process with energy equals to the bandgap of the semiconductor. Other recombination pathways are also encountered in low purity samples as the case for ZnO NRs grown at low temperature. In this thesis, room temperature PL measurements were conducted using Coherent MBD 266 diode laser operating at $\lambda = 266$ nm (4.66 eV).
Chapter 4

4. Results and Discussion

The experimental results of hydrothermally synthesized nanomaterials as well as their functional devices including ZnO/p-polymer HyLEDs, CuO/ZnO NC RH sensor, and CuO NF based pH sensor are given in this chapter. To create a good sequence of this chapter and to avoid breaking the flow of information, I will present the results in the following order: the structural and optical properties of the obtained NSs will be dealt with in the first part. In the second part the results and discussion of the fabricated HyLEDs on flexible substrates using single light emitting polymer i.e. PFO, and the effect of the polymer concentration on the electrical and emitted light properties of the HyLEDs will be explained. Thirdly, the prepared HyLEDs using blended polymers targeting white light emission will be described. And finally, the results of the fabricated pH and RH sensors will be discussed in the end of the chapter.

4.1 Structural Characterization of Nanomaterials

4.1.1 ZnO Nanorods

As discussed in section 3.2.1 above, the synthesis of ZnO NRs was performed using the popular hydrothermal technique at low temperature of 50 °C using the seed layer as preferential nucleation sites. This method have been used to synthesize ZnO NRs on various substrates including metals, copper oxides, and PEDOT:PSS coated flexible foils. The main idea behind conducting this experiment was to develop a low temperature synthetic routine to apply later for fabricating ZnO NRs HyLEDs with p-type semiconducting and light emitting polymers on non-conventional substrates such as plastic. We have conducted several attempts and experiments to assess the possibility of obtaining ZnO NRs at very low temperature that is close to room temperature or below. These attempts led us to finally adopt the procedure mentioned in sec 3.2.1 above, which gave rise to many interesting results that is published in paper 1, and here I will go through these results.
Figure 4.1 below shows typical SEM images of ZnO NRs grown at 50 °C on different substrates using the hydrothermal technique.

As shown, ZnO NRs exhibited preferential growth habit normal to the substrate; this preferential growth is independent on the substrate nature and only dependent on the seed layer deposited prior to the synthesis process. As discussed earlier the seed
layer minimizes the thermodynamic barrier between the substrate and the deposited material [112]. Hence, the seeding process of the substrate plays a critical role in the hydrothermal synthesis of ZnO NSs, since it provides nucleation sites for the growth, minimizes the overall Gibbs free energy, which in turns leads to a uniform growth of ZnO NRs see Figure. 4.1. As shown in Figure 4.1, well-aligned and uniform ZnO NRs were obtained and are characterized with clear hexagonal facets of their wurtzite crystal structure (see insets). After careful examination of ZnO NRs we have observed that there is some size distribution variation which was governed by the substrate used in the experiment, this results in different aspect ratios (length/diameter). The average diameter of these ZnO NRs falls in the range 100-235 nm, while the length spans from 1.2 µm to about 2 µm as can be seen in Figure 4.1f. The most striking result of using lower growth temperature (50 °C) was the increase of the aspect ratio of the grown ZnO NRs, which is contrary to what was believed. We found that the axial length of ZnO NRs has increased as compared to the 90-100 °C grown samples.

*Figure 4.2: Schematic depiction of the proposed nucleation/growth steps of ZnO NRs at (a) ≥ 90 °C and (b) 50 °C. Reproduced from ACS [112] with permission.*

This was explained according to the schematic diagram shown in Figure 4.2. In the schematic diagram of Figure 4.2 two possible scenarios were proposed, in the first (a) the situation when synthesis of ZnO NRs is carried out at temperatures ≥ 90 °C is described. In this case the nucleation rates of ZnO nanoparticle increases while their
Results and Discussion

critical radius of nucleation decreases due to the increase in zinc solubility with temperature [130, 131]. In other words, at higher temperature the competition between the nucleation and axial growth will lead to shorter ZnO NRs despite the fact that their density is maximized see Figure 4.2a [112]. However, in scenario (b) for the case of lower growth temperatures \( \leq 50 \, ^\circ\text{C} \) the radius of nucleation remains almost constant over the entire growth duration which will give rise to longer ZnO NRs.

The structural properties of ZnO NRs were studied using the XRD technique in the Bragg-Brentano geometry. The typical XRD pattern of only one of the samples discussed above is shown in Figure 4.3.

![Figure 4.3: XRD pattern of ZnO NRs hydrothermally grown at 50 \(^{\circ}\text{C}\) on CuO thin film coated on glass substrate. Modified from ACS [112] with permission.](image)

As visible in Figure 4.3, the XRD pattern composed of several peaks that are characteristic of ZnO in wurtzite crystal structure (JCPDS 36-1451). The strongest XRD peak locating at 34.47 \(^{\circ}\) is the (002), which indicates the preferential growth of ZnO along the c-axis of the hexagonal wurtzite crystal structure. This also indicates that ZnO NRs
were grown normal to the surface of the substrate. Furthermore, other diffraction peaks related to the zincite crystal planes are rather weak compare to the (002) peak. Additionally, the contribution from CuO crystalized in monoclinic structure is also visible in Figure 4.3, however, it is quite weak as compared to that of ZnO [112]. Other ZnO NRs samples were also examined by the XRD technique which has shown similar results to the one shown in Figure 4.3.

The optical properties of ZnO NRs grown using the hydrothermal method at 50 °C were studied using both the UV-Visible absorption technique and photoluminescence (PL) and both were conducted at room temperature.

![Figure 4.4: Room temperature PL spectra of ZnO NRs grown at 50 °C and 95 °C. Inset shows the typical absorption of ZnO NRs grown at 50 °C. Modified from ACS [112] with permission.](image)

The typical PL of ZnO NRs grown at 50 °C and that of sample grown at 95 °C using the same procedure are shown in Figure 4.4. The absorption spectrum of ZnO NRs grown at 50 °C is depicted in the inset of Figure 4.4. As clearly seen ZnO NRs demonstrated strong ultra violet (UV) emission at 388 nm that is corresponding to the
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near band edge (NBE) emission (bandgap of 3.37 eV) [68, 71, 73]. We have observed a slight shift in the position of the NBE for different ZnO NRs samples which we have attributed to the difference in the concentration of the point defects (native defects) (see section 2.1.3) [112]. The concentration of point defects was reported to be higher on the surface of ZnO NSs as compared to their bulk [73]. The effect of these native point defects can be seen in the lower emission part of the PL spectra of Figure 4.4. This involves the green emission (520 nm) and the red emission located at 650 nm. For detailed discussion about these emission bands and their origin the reader is directed to references [68, 73, 80]. Additionally, we have observed that the samples grown at 50 °C demonstrated relatively low defects emission as compared to those grown at 95 °C as can be seen in Figure 4.4. This was ascribed to the low concentration of intrinsic point defects on ZnO NRs samples grown at 50 °C. The UV-Visible absorption spectrum of ZnO NRs grown at 50 °C is illustrated in the inset of Figure 4.4. From the optical absorption spectrum it is obvious that ZnO NRs exhibited strong absorption in the UV range (300- 400 nm) with absorption peak at 373 nm. This peak is consistent with the other results in the literature [132]. Furthermore, the absorption efficiency of ZnO NRs drops drastically in the visible range. The origin of these absorption maximum is due to excitons absorption.

4.1.2 CuO Nanostructures

The synthesis of various CuO NSs was carried out using the hydrothermal approach as discussed previously (sec 3.2.2) at relatively low temperature of 90 °C with different growth durations and pH values. The SEM images of Figure 4.5 show the top view of the synthesized CuO NSs at low and high magnification. The obtained CuO nanomaterials comprised CuO NFs (figure 4.5b, d) and CuO NPs (figure 4.5a, c). The former consists of many layers of leafs like structure. Each leaf has a wider base that is coupled at the central part of the NF and diverges outside with very sharp tips (20-50 nm) as clearly visible in the inset of Figure 4.5b. The mean diameter of each NF is about 4-5 µm. However, each leaf has a diameter of about 400 nm. On the other hand, CuO
Results and Discussion

NPs exhibit uniform growth on the substrate and each CuO NP consists of 2-3 interpenetrating plates like structure as shown in Figure 4.5c. Time-dependent growth of CuO NSs was conducted to gain additional information about the crystal growth habit of CuO NSs. This investigation revealed that the formation of CuO NSs takes place as self-assembly of ultra-thin CuO NWs which are oriented and attached together to form higher dimension CuO NSs. Unlike the classical crystal growth via atom-by-atom addition to the existing nucleus (such as ZnO NRs growth), in the oriented-attachment the growth occurs through particle based aggregation modes involving the process of mesoscopic transformation [133].

Figure 4.5: SEM images of the hydrothermally grown CuO NSs, (a) CuO NPs, (b) CuO NFs, (c) high magnification image of CuO NP, and (d) single CuO NF, inset is high magnification of CuO NF.
The TEM was used to characterize CuO NSs grown at different growth durations, while the samples were collected directly by dipping the TEM grid inside the nutrient solution that was held at 90 °C. The typical TEM images of the grown samples are shown in Figure 4.6. From the TEM images of Figure 4.6; one can clearly observe the complete phase transformation of CuO NSs from 1D structure to quasi-3D nanomaterial. We have concluded that the oriented-attachment process was the driving force behind the formation of the presented CuO NSs.

**Figure 4.6:** TEM images of CuO NSs grown at different growth durations, (a) CuO NWs grown for 15 min, (b) the oriented attachment of CuO NWs to form CuO NPs, (c) embryonic CuO NP formed after 35 min, and (d) CuO NPs grown for 60 min. The SAED and the high resolution TEM are shown in the inset of (c) and (d), respectively.

In the beginning of the growth CuO (NWs) were formed with a diameter of 2-5 nm and a length approaching 1 µm as can be seen in Figure 4.6a. These NWs have
amorphous nature with Cu: O ratio of ~ 0.5 a value close to that of Cu(OH)$_2$. Further, we have observed that during the electron beam irradiation (inside the TEM) these NWs experienced a decomposition process and form more crystalline NWs. It was also perceived that the NWs prefer to self-assemble in bundles parallel to each other (white circles in Fig. 4.6a). The bundles then merged together to form a leaf like CuO NS which is clearly seen in Figure 4.6b with the NWs features obviously identified. Allowing the nutrient solution to react further lead to the formation of small CuO NPs (Figure 4.6c), which in turns grow larger in size after 60 min of growth.

Figure 4.7: SEM images of CuO NSs grown under different pH of (a) inherent pH= 6.5, (b) pH= 7, (c) pH= 8, (d) pH= 9, (e) pH= 10, and (f) pH= 11. Reproduced from Elsevier [134] with permission.
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The crystallinity of the grown NSs was investigated using the SAED as shown in the inset of Figure 4.6c. The SAED revealed that CuO NP has single crystalline structure with the main growth direction along the [010] which lead to monoclinic structure of CuO. The stretching of the diffraction spot of the SAED indicates that the NPs were formed by CuO NWs which were arranged in almost same orientation. The HRTEM image shown in the inset of Figure 4.6d indicates the single crystalline nature of CuO NPs.

In addition to time-dependent growth experiments, we have investigated the influence of the nutrient solution pH on the morphology of CuO NSs [134]. Figure 4.7 depicts the SEM images of various CuO NSs that were attained at different pH values.

![Figure 4.8: The XRD pattern of hydrothermally grown CuO NPs.](image)

Under inherent pH values 6.5-7 CuO NFs and NPs were observed as the only CuO NSs. By further increasing the nutrient solution pH value in the range of 8-10 the general morphology remains petal-like, however, the diameter was found to
considerably decrease as shown in Figure 4.7c-e. At a pH value of 11 or higher the petals fuse together to create aloe-vera like structure with ultra-sharp tips [134].

The XRD technique was used to examine the crystallinity of all CuO NSs samples, the results are shown in Figure 4.8 for CuO NPs hydrothermally grown on glass slide. Form Figure 4.8, it can be seen that all the major XRD peaks can be readily indexed to CuO (JCPDS 05-0661) of the pure phase monoclinic structure. The XRD pattern of Figure 4.8 further demonstrates that high purity tenorite phase of CuO was obtained without any impurities such as Cu$_2$O and Cu(OH)$_2$ phases [134].

4.1.3 CuO/ZnO Composite Nanostructures

By using the procedures we have developed (see section 3.2.3), we were successfully able to synthesize CuO/ZnO composite NSs at low temperature of about 60 °C. As mentioned before two routes were applied for this purpose by either using single source material for CuO NSs growth (CNH), or by using the regular two source materials, namely, CNH+HMT. The results of both procedures will be given in this section. After the hydrothermal synthesis of well-aligned ZnO NRs, CuO NSs started to selectively assemble on the lateral surface of ZnO NRs at short growth duration independent on the nutrient solution. When the CNH nutrient solution was used it required 1.5 h for the CuO NSs to selectively deposit on ZnO NR lateral surface. However, by adding HMT to the CNH nutrient solution the growth duration was reduced to about 0.5 h. This nutrient solution dependent growth was attributed to the relatively higher pH of the CNH+HMT as compared to that of the CNH. The nutrient solution pH values for both cases were further investigated using a typical pH meter. The results indicated that for the case of CNH only, the introduction of ZnO NRs as a substrate raises the solution pH and over time the pH tends to decrease as a result of CuO NSs growth. While in the other case (CNH+HMT) the pH value was higher than the first case and it was remained constant during the entire growth duration (see appended paper VII).
Figure 4.9 shows the SEM images of the hydrothermally grown nanomaterials using both nutrient solutions.

**Figure 4.9:** SEM micrographs of the hydrothermally synthesized CuO/ZnO composite NSs using the CNH and CNH+HMT nutrient solutions, (a) after 1.5 h or 0.5 h (see text), inset shows high magnification tilted SEM image of (a), (b) low magnification SEM of showing the selective growth of CuO NSs on ZnO NRs, (c) CuO/ZnO NCs grown using CNH solution for 4 h, (d) 40° tilted SEM image of CuO/ZnO NSs grown using CNH+HMT for 1.5 h, (e) 40° tilted SEM image of CuO/ZnO NCs, inset shows the etching effect, and (f) high magnification SEM of single CuO/ZnO NC of fig. 4.9c. Reproduced from RSC [119] with permission.
As can be seen from Figure 4.9a, the Cu O NSs robustly and selectively grew on the lateral sides of ZnO NRs while the NRs tips were left bare upon short time growth process. Allowing the growth to proceed for longer time was led to complete coverage of the branched CuO NSs on the whole surface of ZnO NRs independent on the reactants type. However, the growth duration in both experiments is quite different. Figure 4.9b demonstrates the selective affinity of CuO NSs to deposit on ZnO NRs, as the uncovered places by ZnO NRs in the first growth procedure remain empty after CuO NSs deposition in the second one [119]. Furthermore, after 4 hrs of the synthesis using the CNH solution the CuO/ZnO composite transforms into NCs (Figure 4.9c) in which ZnO NRs play the role of their stem. Each NC composed of dozens of CuO NSs that were oriented-attached to each other’s and selectively decorated the NR as visible in Figure 4.9f. Additionally, strong etching effect on ZnO NRs was observed when the CNH is applied for the growth (inset of Fig 4.9e). The etching on ZnO NRs was attributed to the low pH value ~ 4.9 of the CNH nutrient solution. At such low pH media ZnO starts to etch as recently reported [123]. In the case of CNH+HMT the pH (~ 5.78) is relatively close to the inherent pH, and hence no etching effect on the NRs was apparent. This high pH value helps increasing the size of the grown CuO NSs which at short time (1.5 h) completely covered the NRs (Fig. 4.9d).

The CuO/ZnO composite NSs were further studied by TEM technique and the results are shown in Figure 4.10 a-d. Figure 4.10a shows a low magnification TEM image of ZnO NR with a number of CuO nanoleaves attached to its lateral surface. This sample was grown using the CNH solution for 1.5 h at 60 °C. As can be shown the etching effect is visible on the tip of the NR as well as on its sides (see 4.10c-d), which is consistent with the SEM image shown in Figure 4.9e. The notches on the sidewalls of ZnO NR represent an excellent nucleation sites for the secondary grown CuO NSs [119]. The HRTEM image taken from the tip of the NR is presented in Figure 4.10b. This image demonstrates that the NR is preferentially grown along the [0001] of ZnO wurtzite crystal structure in agreement with the XRD pattern of Figure 4.3. Magnified TEM
images of CuO nanoleaves attached to ZnO NR are shown in Figure 4.10 c–d. As can be seen, CuO nanoleaves exhibit rough surfaces which have been attributed to the self-assembled CuO nanocrystals that have limited misorientation as discussed before (see sec. 4.1.2). The misorientation of CuO nanocrystals results in stretching of the SAED diffraction spots as clearly visible in the inset of Figure 4.10d.

**Figure 4.10**: TEM images of the grown CuO/ZnO NSs, (a) single ZnO NR decorated by a number of CuO nanoleaves the insets show the HRTEM and the SAED from the interface of the heterostructure, (b) HRTEM image from the tip of the NR, (c) and (e) high magnification TEM images of the white circles in (a), and the inset of (d) the SAED of CuO nanoleaf. Reproduced from RSC [119] with permission.
The HRTEM image and the SAED pattern of CuO nanoleaf adhered to ZnO NR are illustrated in the insets of Figure 4.10a. From the SAED pattern and the HRTEM it is obvious that there are no epitaxial relations between these nanomaterials, which is consistent with [135]. However, very recently Q. Simon et.al reported the synthesis of CuO/ZnO nanorods array using combined plasma assisted chemical vapor deposition of ZnO NRs, followed by RF sputtering of Cu and subsequent annealing for the conversion to CuO. Their results show hetero-epitaxial relation between the CuO/ZnO nanocomposite [136]. The crystal structure of the grown CuO/ZnO composite NSs was studied by the XRD technique (Figure 4.11). The XRD pattern of ZnO NRs (black curve) is repeated here for the sake of comparison. As shown the XRD pattern of the composite NSs (red curve) consists of the major diffraction peaks of both crystal phases (wurtzite and monoclinic) of both materials.

**Figure 4.11:** Typical XRD patterns of ZnO NRs and CuO/ZnO NCs samples grown by the hydrothermal method.
The XRD peak located at about 34.5 ° is the (002) peak of ZnO as discussed before, while the relatively weak and broad XRD peaks at 35.5 ° and 38.8 ° are belonging to CuO (compare with Figure 4.8). The origin of the broadening in the XRD peaks is ascribed to the small grain size of CuO nanocrystals comprising CuO NSs and/or their poor crystallinity. Based on the results discussed above, we have developed a growth model to describe our grown composite NSs [119]. This model takes into account the etching behavior of ZnO NRs when the CNH solution is used. It also involved the dissociative adsorption of water molecules on the defective surface of ZnO NRs. The dissociative adsorption of water takes place on the vacancy sites on the surface of ZnO, and as a results two hydroxyl molecules are generate per oxygen vacancy [137]. The locally created OH⁻ molecules interact with the dissolved Cu²⁺ ions to form [Cu(OH)₂] intermediates, which under the given conditions dehydrate to produce CuO nanocrystals. The nanocrystals is then attach to each other to create CuO NWs, which then self-assemble to give rise to CuO nanoleaf [119] via the oriented attachment process [133]. We have proposed another growth model to describe the deposition of CuO NSs when the CNH+HMT nutrient solution was used. This model explains the large size and the fast growth habits of CuO NSs on ZnO NRs.

4.2 Devices Based on ZnO, and CuO Nanostructures

The development of functional devices using nanomaterials realized by the low temperature synthesis method was the prime objective of this thesis work. The synthesized ZnO and CuO nanomaterials possess many unique properties that were explored for potential use in lighting and sensing applications. In this section, the experimental results of the fabricated devices based on ZnO/p-polymer HyLEDs, CuO/ZnO NC heterojunction RH sensor, and CuO NF based electrochemical sensor will be given and thoroughly discussed. To achieve white light emission we have fabricated ZnO/p-polymer composite HyLEDs on flexible substrates. Moreover, some efforts have been devoted to reach full color emission by blending different polymers and to further analyze their effect on the quality of the emitted light. In addition, the
influence of the polymer concentration on the HyLED performance characteristics was also investigated. Likewise, some sensing applications of CuO and CuO/ZnO NSs were realized and evaluated. The electrochemical sensor based on CuO NFs showed excellent pH dependence over wide range together with good reproducibility. While the CuO/ZnO NCs RH sensor demonstrated excellent sensor characteristics for humidity variations at short response/recovery times. The present section will be divided into number of subsets in the first set the results of HyLEDs based on ZnO NRs/p-polymer(s) will be discussed. The second subsection will be devoted for the results obtained from CuO NFs pH sensor. And finally the experimental outcomes of the CuO/ZnO NCs RH sensor will be described.

4.2.1 ZnO nanorods/p-polymer HyLEDs

The emergence of light emitting diodes as possible efficient replacement of conventional incandescent and fluorescent lighting sources is attracting enormous investments in the areas of research and development. The LEDs exhibit many unique advantages over the traditional lighting sources. These advantages include smaller size, higher efficiency, longer lifetime, and improved controllability, to name a few. Nevertheless, fabrication of full color LEDs (white) is typically utilized either by mixing red, green and blue (RGB) LEDs to obtain white emission, or by using the harmful phosphorus conversion technique. Hence, the full color emitted from single LED device is needed with low cost, good stability, and high color quality white emission. In this regard, ZnO represents an excellent candidate due to its many unique opto-electrical properties. However, homojunction ZnO LEDs are scarcely reported in the literature due to the lack of reproducible and stable p-type ZnO [68]. Thus, the heterojunction of ZnO with other host p-type materials can be one of the possible options for fabricating LEDs. The p-type polymers appear as an excellent choice, since they are solution processable and suitable for large area lighting applications [138-142]. Conjointly, the advantage of the low temperature synthesis of ZnO NRs which is compatible with the temperature sensitive p-polymer, and simple integration of their composites into device,
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allowed us to fabricate flexible, disposable and printable ZnO NRs/p-polymers HyLEDs [60, 116, 124, 125]. By applying the procedures described in chapter 3 (sec. 3.3.1), we successfully fabricated ZnO NRs/p-polymer HyLED on flexible plastic substrates. The schematic structures of these HyLEDs as well as their optical photographs are presented in Figure 3.2a-d. After the fabrication processes we applied standard characterization techniques that involve room temperature J-V characteristic to judge the device quality. The optical and electro-optical properties of the fabricated devices were investigated using UV-Vis absorption spectroscopy, PL, and EL measurements. Here, some of the results will be presented to shed light on the performance of the fabricated HyLEDs. Figure 4.12a demonstrates typical J-V characteristics of our ZnO NRs/p-polymer HyLEDs fabricated using different polymers with ZnO NRs.

![Figure 4.12](image)

**Figure 4.12**: The J-V characteristics of the fabricated ZnO/p-polymer HyLEDs, (a) different ZnO/p-polymers HyLED configurations. Reproduced from Springer [124] with permission, (b) ZnO/PFO HyLED with different PFO concentrations Reproduced from AIP [143] with permission.

These polymers include PFO, MEH-PPV, and their blended polymer PFO: MEH-PPV with ratio of 9:1 [124]. In contrast, Figure 4.12b shows the J-V characteristics behavior of the ZnO/PFO HyLED when the concentration of the polymer is varied over a wide range (2-20 mg/ml). As can be seen from Figure 4.12a-b, the rectifying behavior
of the HyLEDs is evident for all samples. Moreover, the turn-on voltages of the HyLEDs shown in Figure 14.12a exhibited slight variation depending on the polymer used. This dependence can be explained by the difference in the HOMO-LUMO orbital levels of the PFO and the MEH-PPV, which in turns influence the electron injection from the conduction band of ZnO to the polymer LUMO [124]. On the other hand, we have observed that as the PFO concentration increases (2-20 mg/ml) the turn-on voltage of the HyLED increases considerably and the corresponding J-V curve shows lower current injection. This increase in the turn-on voltage was attributed to the increase in the diode parasitic resistance, which resulted from the imperfect ZnO/PFO interface when the PFO concentration increases. We have found that by increasing the concentration of the PFO the spin coated film possesses rough surface as compared to those prepared by relatively lower concentration PFO solutions. The conventional diode equation was applied to analyze the J-V characteristics of the HyLEDs shown in Figure 4.12a. The results showed that the ideality factors of the HyLEDs are far from unity which implies that surface defects on ZnO side as well as interface states exist on the ZnO/PFO junction [124]. The optical properties of the prepared hybrid structures are presented in Figure 4.13 a-c which includes UV-Vis absorption spectra of the PFO with various concentrations, MEH-PPV, and their blended polymer. The room temperature PL spectra of the PFO, ZnO NRs, and the hybrid ZnO NRs/PFO: MEH-PPV film are illustrated in Figure 4.13c. From Figure 4.13a for the bare and blended polymer, one can see that the PFO exhibits strong and broad absorption peak at approximately 395 nm due to the $\pi-\pi^*$ electronic transition that is consistent with the literature [105]. While the MEH-PPV possesses broad absorption with a maximum located at 510 nm [105]. For the case of the blended PFO:MEH-PPV polymer the UV-Vis absorption of the PFO was clearly dominating the absorption spectrum compared to the MEH-PPV (black curve). Various blending ratios of PFO:MEH-PPV were investigated to reach a proper blended polymer ratio with excellent light emission properties. By increasing the ratio of the MEH-PPV against the PFO we found that the optical properties of the MEH-PPV (absorption/emission) dominate over the PFO, so we restricted our study to (9:1) ratio
The absorption spectra of various PFO layers prepared on PEDOT:PSS flexible foils by using different concentrations of the PFO are displayed in Figure 4.13b. As can be seen by increasing the PFO concentration from 2 up to 20 mg/ml the relative absorption intensity of the glassy phase of the PFO is increased. At higher concentrations another absorbing phase of the PFO starts to emerge as a shoulder at about 437 nm and this is called the β-phase.

Figure 4.13: The optical properties of the prepared composite materials, (a) UV-Vis absorption of the PFO, the MEH-PPV, and their blended polymer, Reproduced from Springer [124], with permission, (b) absorption spectra of the PFO as a function of the concentration, Reproduced from AIP [143] with permission, and (c) the PL spectra of ZnO NRs, the PFO thin film, and the ZnO/blended polymer. Reproduced from Springer [124] with permission.

The appearance of the β-phase associated with the transformation of a fraction of the glassy phase into more crystalline phase. This β-phase is created by the
crystallization of the \textit{n-alkyl} side chains of the polyfluorene, as a result forcing the polymer main chains into coplanar arrangement of the fluorene building blocks. Figure 4.13c demonstrates the representative PL spectra of the deposited materials. As shown ZnO NRs sample possesses a dominant peak at 378 nm which is corresponding to the NBE as mentioned before. Furthermore, visible emissions related to the DLE of ZnO are also visible in the PL spectrum. These emissions comprised a green band at 525 nm (green circle) and a weak orange/red band located at approximately 665 nm. For more details about the defect related emissions in ZnO see the discussion in section 4.1.1 above and the references therein. The near infrared (NIR) peak located at 756 nm is ascribed to the second harmonic emission of the NBE of ZnO [144]. The PL spectrum of the PFO demonstrates two resolved blue peaks at 430 nm and 456 nm in addition to one less resolved peak at 490 nm. These blue peaks are attributed to the 0-0, 0-1, and 0-2 interchain singlet transition in polyfluorenes [145]. The featureless broad green band (green circle) with a maximum at 525 nm is commonly observed in the pristine as well as thin films of polyfluorene. This broad band is originating from defects related to the oxidation of the polymer backbone [109] as mentioned in section 2.3.2 above. As can be seen in Figure 4.13c, the blended polymer/ZnO PL spectrum (red curve) exhibits predominant low energy band covering the entire visible range. The contribution of both the NBE of ZnO NRs and the PFO blue emissions are indicated by arrows. The DLE of ZnO NRs and the defects emission of the PFO were intermixed with that of the MEH-PPV (orange/red) band. The orange/red emission of the MEH-PPV at 585 nm and 615 nm are ascribed to the single chain exciton transition and to the intrinsic vibronic structure, respectively, [105]. Therefore, the stemmed PL emission of the composite is covering a wide range of the visible spectrum, so one expects a broad light emission from the hybrid junction in the case of EL measurements which will be discussed next.

The EL measurements of various ZnO/p-polymers HyLED were conducted at room temperature using a source meter for current injection and probing the emitted light by a spectrometer connected to a CCD camera. The EL results are depicted in
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Figure 4.14a-c for various fabricated HyLEDs. From Figure 4.14a it is interesting to observe that by blending two polymers with ZnO NRs we can achieve excellent control over the emitted light from the HyLEDs. The resemblance of the EL spectrum of the ZnO NRs/blended polymer HyLED to that of the PL spectrum Figure 4.13c is clear. However, slight blue shift of the EL spectrum can be seen in Figure 4.13c. This can be attributed to the overlapped emissions of ZnO and the PFO green bands and the orange/red emission of MEH-PPV.

![Figure 4.14](image)

**Figure 4.14**: A typical EL spectra of the various ZnO NRs/p-polymer(s) HyLEDs, (a) the EL spectra of ZnO/PFO, ZnO/MEH-PPV, and ZnO/blended polymers HyLEDs. Reproduced from Springer [124] with permission, (b) the EL spectra of ZnO/PFO HyLEDs at low polymer concentrations 2-8 mg/ml, and (c) the EL spectra of the same HyLEDs configurations with higher polymer concentrations. Reproduced from AIP [143] with permission.
It was found that even at lower concentrations of the MEH-PPV in the blended polymer the energy transfer is a predominant process which results in strong emission from the MEH-PPV. The fabricated ZnO/MEH-PPV HyLED (red curve) on the other hand showed broad emission covering the orange/red with a peak centered at 608 nm and a shoulder at 640 nm. These emissions are originating from the PPV backbone that arises from the relaxation of the excited $\pi$-electrons to the ground states, and to the interchain states, respectively, [146]. The absence of ZnO NRs emission in this case can be elucidated to the large holes offset (2.5 eV) between the HOMO level of the MEH-PPV and the valence band edge of ZnO, as compared to 1.2 eV for electrons injection barrier from ZnO conduction band to the LUMO level of the MEH-PPV [147]. As a consequence, the electron-hole recombination takes place in the MEH-PPV side with photons energy corresponding to the HOMO-LUMO gap of the polymer [147]. For the HyLED composed of ZnO NRs/PFO (blue curve) shown in Figure 4.14a, the EL spectrum consists of three dominant emission peaks covering a large part of the visible range from 435 nm – 600 nm. The blue peaks at 456 nm and 470 nm are corresponding to exciton emissions in PFO and its vibronic progression from non-interacting single chains, respectively, [148]. Additionally, the broad green emission of the ZnO/PFO HyLED comprises two features at 510 nm and 540 nm. The first blue/green feature is more likely to be due to the electrochemical degradation of the PFO as a result of electron induced transformation of the polymer chains [149]. The green emission feature at 540 nm can be ascribed to the $V_O$ in ZnO NRs, which as discussed earlier are frequently observed in low temperature grown ZnO NSs. Another possible source of this feature can be related to the PFO which has defect emission caused by the oxidation (C=O) of the polymer chain (see Figure 4.13c).

The influence of the polymer concentration on the EL characteristics is shown in Figure 4.14b-c, for cases of low concentrations (b) and high concentrations as compared to the lowest one (c). As can be seen the influence of the polymer concentration is playing a significant role in the EL emission characteristics. It was noticed that by
increasing the concentration of the PFO from 2 mg/ml to 20 mg/ml the EL spectra tend to significantly change as illustrated in Figure 4.14b-c. This change of the emitted light can be explained as follows. The exciton emission at 452 nm of the PFO predominates at low polymer concentrations 2-4 mg/ml (Figure 4.14b), then by increasing the concentration to 6 mg/ml the exciton emission is gradually quenched. At the same time the peak at 473 nm starts to gradually dominate over the exciton emission and at 8 mg/ml to 10 mg/ml the 452 nm peak has completely disappeared (Figure 4.14c). The quenching of the exciton peak at 452 nm can be correlated with the emergence of the β-phase in the absorption spectra at 6 mg/ml or above [143] (see the red box in Figure 4.13b). The formation of the β-phase at higher concentrations implies that efficient energy transfer of the excitons from the glassy phase (α-phase) to the β-phase takes place which results in the quenching of the 452 nm peak [150]. In addition the β-phase can act as a low energy trap for the excitons owing to its lower energy gap compared to the α-phase [107]. Likewise, the intensity of the broad green emission was also enhanced by increasing the PFO concentration. This can be attributed to the increased fluorenone defect density in the polymer at higher concentrations and/or the density of ZnO NRs defects associated with the green emission. It was observed that the formation of places with very high density of ZnO NRs was created at relatively higher polymer concentrations. Simultaneously, two processes encompassed in the green emission of the PFO: first the fast and effective energy transfer from the excitons on the polymer chains to the low energy fluorenone defects. Secondly, a low energy trapping of the excitons by the fluorenone defects followed by radiative recombination. Therefore, three competitive processes are involved in capturing the created excitons within the PFO main chain and as a consequence quenching of the exciton emission is resulting [143].

4.2.2 CuO nanoflowers Based Electrochemical pH Sensor

Electrochemical sensors are rapid, precise, and quantitative sensors that exhibit sensitive response together with simplicity of construction which make them very attractive class of sensors. The electrochemical sensors are generally organized based on
their measuring technique into potentiometric, amperometric and conductometric sensors. In potentiometric the sensing step is performed by measuring the potential of an electrochemical cell while drawing negligible current. While, in amperometric sensors changes in current generated by electrochemical reactions (oxidation/reduction) are measured directly with time while a constant voltage is maintained at the working electrode with respect to a reference electrode [151]. Metal oxides such as CuO NSs have drawn much interest due to their large surface area to volume ratio, high electron transfer properties, and relatively strong adsorption ability. The high aspect ratio offered by CuO NSs enabled short diffusion distance of the analyte toward the electrode surface, thereby providing a relatively faster response and improved analytical performance. The measurement of the pH is very important in many areas such as biology, medicine, and industry. For example the human body is critically influenced by the pH value of the blood, since small change in the pH of the body fluids can lead to serious health problems. Thus monitoring the pH is extremely important in medical fields as well as in biochemical applications. Also, electrochemical pH sensors have been widely used in industrial hygiene, pollution monitoring, process control and combustion control. The application of metal oxides as sensitive pH sensor has been widely explored and reported see e.g. [152-154]. These metal oxides based pH sensors demonstrate fast response and excellent pH sensitivities. As mentioned above the characterization of a pH sensor is conducted by measuring the electrochemical accumulated charges on the electrode (potentiometric). Figure 4.15a displays the pH changes from 2-11 versus the potential response of CuO NFs based electrochemical pH sensor. As can be seen good linear relation has been observed with relatively good sensitivity of 28 mV/decade and a correlation coefficient r² of about 0.997 which has been calculated from near-Nernstian response [134]. The stability and reproducibility of the CuO NFs pH sensor were examined by repeating the electrochemical measurements several times. The results indicated that CuO NFs electrode is reasonably stable and reproducible potentiometric responses can be achieved.
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Figure 4.15: The pH measured characteristics using CuO NFs sensor, (a) calibration and linear fit curves of the NFs pH electrode for a pH range of 2-11, and (b) time response versus the output voltage of the fabricated pH sensor. Reproduced from [134].

The mechanism by which CuO NFs pH sensor works was ascribed to the protonation-deprotonation processes at the electrolyte/NFs interface, which lead to accumulation of surface charges (potential difference) that is dependent on the electrolyte pH [155]. Furthermore, we have examined the time response of the fabricated pH sensor at a certain pH value of 4 versus the output voltage. The pH sensor showed relatively fast electrochemical response of 25 seconds to reach stable output signal. This response time is slightly slower than other reported sensors which can be attributed to the porosity nature of CuO NFs electrode (figure 4.5 b, d). It has been reported that the sensor response time is affected by the porous properties of the sensing material [154].

4.2.3 CuO/ZnO Nanocorals Humidity Sensor

The control and monitoring of humidity is crucial in various areas, such as food processing, hospitals, paper and textile industries, to name a few. Diversity of materials have been explored and developed for humidity sensing purpose [156]. Both resistive and capacitive humidity sensors have been investigated using ceramics, conjugated polymers and metal oxides semiconductors materials [156, 157]. Among these materials, ceramic resistive-type have received more attention in humidity sensing applications
due to their easy fabrication, relatively high sensitivity, thermal and chemical stabilities, and reproducibility. In this class of humidity sensors, the variations in the resistance are originating from the chemical reaction between the water vapor and the porous surface of the sample. Recently, many researchers have reported the realization of humidity sensors based on nanostructured ZnO [158-160] and CuO [161] alone as a good humidity sensors. However, development of new nanostructured materials and intelligent sensing capabilities are highly desirable in technology, as they can resolve many challenges and problems. The ordered hierarchical nanostructures and heterostructures based on metal oxides emerge as a good candidate for gas sensing applications. These heterostructures exhibit many interesting structural and chemophysical properties that enabled them to compete with existing technology. In this regard, CuO/ZnO heterostructures with intrinsic $p$- and $n$-type junctions have attracted vast attention since the time they were first studied by Nakamura et. al for gas detection [162]. With their intelligent sensing characteristics, gas selectivity, and relatively low working temperature, several investigations on CuO/ZnO heterostructures for gas and humidity sensing applications were conducted [163-168]. Yet, most of these reports on CuO/ZnO heterostructures were based on either mechanical heterocontacts by pressing CuO and ZnO pellets which result in poor sensitivity and reproducibility, or by depositing CuO thin film on polycrystalline ZnO [167]. Which it is however, relatively expensive and compromises the reproducibility of the heterocontacts. Therefore, it is very attractive and cost-efficient to fabricate humidity (gas) sensors using composite nanostructures with relatively large surface to volume ratios and exhibiting hierarchical morphology that is promising in these applications as compared to film-type sensors. As described in (sec 3.3.3) the fabricated CuO/ZnO NCs sensor was inserted inside an environmental chamber and the temperature was maintained at 25 °C while the relative humidity was varied in the range of 30-90 % in steps of 5 %. The NC RH sensor shows high responsivity to humidity variation even if the RH is changed by only 1 %. However, we allowed 20 minutes period after the desired RH value was reached to ensure that the adsorbed water was equilibrated with
the vapor phase. The results of the fabricated RH sensor based on CuO/ZnO NCs are shown in Figure 4.16a-d. From Figure 4.16a one can readily judge the formation of excellent p-n heterojunction between CuO NSs and ZnO NRs.

![Figure 4.16](image)

**Figure 4.16:** (a) The J-V characteristics of the CuO/ZnO NC RH sensor measured at 25 °C, the inset is the ohmic contact characteristics of Au and ITO to CuO and ZnO, respectively, (b) the J-V characteristics of CuO/ZnO NC RH sensor at various RH values, the inset shows the sensor responses at 85 % and 90 % (c) the NC sensor DC resistance in the ascending-descending recovery cycle, and (d) the dynamic response curve of the fabricated NC sensor. Reproduced from RSC [119] with permission.

The heterojunction showed obvious rectifying diode behavior with a typical turn-on voltage of 1.52 V [169]. This value is consistent to the reported value of 1.55 V for sputtered CuO thin on polycrystalline ZnO [167]. The inset of Figure 4.16a demonstrates
the ohmic contact behavior of Au/CuO and ITO/ZnO, both contacts showed relatively low contact resistance to the respective nanomaterial. Furthermore, as visible the heterojunction exhibited negligible reverse saturation current ($J_R$), which results in high rectification factor of $320 \pm 3V$ [119]. Some of the fabricated CuO/ZnO NC p-n heterojunctions showed even higher rectification factor of $\sim 760$ [169]. Figure 4.16b displays the impact of humidity variations on the fabricated NC heterojunction. The forward current density (as shown) has increased tremendously by almost four times when the RH was varied from 30-90 %. In contrast, the reverse current $J_R$ remained insignificant up to 70 % and then starts to increase notably above that as shown in the inset of Figure 4.16b. In Figure 4.16c, the corresponding results of the DC resistance for the sensor when it was biased at 1.6 (above the turn-on) as a function of RH is illustrated. It was observed that the sensor DC resistance dropped significantly by increasing the RH. The sensitivity factor of the NC sensor was calculated according to the simple formula ($S_f = R_{30\%}/R_{90\%}$) which yielded $6045$ ($\pm 731$) [119]. This value is significantly higher than the reported $S_f$ value of individual nanomaterials junctions [158, 168]. However, the present sensor shows low stability under repeated RH measurements as the one presented in the ascending and descending curve of Figure 4.16c. A large hysteresis of about 21 % was observed, which indicates that in the case of descending experiment the surface reactions between the water and the NC pores prevent its desorption. The calculated standard deviation is 12 % which is rather high but can be attributed to the variation in the density of ZnO NRs from area to area, which in turns affects the selective growth of CuO NSs [119]. The response/recovery time of the NC sensor was determined by switching the sensor between two sealed chambers containing saturated solutions of MgCl$_2$ and KNO$_3$ having RH values of 32 % and 96 %, respectively, [170]. The results of the dynamic response are shown in Figure 4.16d, it was found that the response and recovery times of our NC RH sensor were about 6 s ($\pm 1$) and 7 s ($\pm 0.6$), respectively [119]. The humidity sensing mechanism of our present sensor was discussed in details in view on their high porosity, high surface/interface defect densities, and the relatively high surface to volume ratio. Thus, the carrier
transport at the p-n junction of the NC heterojunction under forward bias is mostly due to both the pinning of Fermi level by the interfacial states and the injected current. Hence, the sensitivity of our RH sensor can be due to the saturation of these states by the physisorbed water at low RH, while at high RH the water electrolyzes at the CuO/ZnO interface [156, 157].
Chapter 5

5. Conclusion and Future Prospects

The present thesis dealt mainly with nanostructured ZnO, CuO, and their composites, study of their low temperature growth mechanisms, as well as their various combinations for potential sensing and lighting applications. This thesis can be divided into two parts (i) synthesis of nanomaterials and composites, and (ii) applications, which is further divided into two parts (a) lighting applications, and (b) sensing applications.

5.1 Research Summary

In the first part of this research our work on the synthesis of various nanostructures using the low temperature wet chemical route was discussed. In paper I, well-aligned ZnO NRs grown at 50 °C on both conventional and nonconventional substrates was presented. It was found that lowering the growth temperature is advantageous for the axial alignment of ZnO NRs. A model explaining this finding was proposed. Also, lowering the growth temperature was observed to enhance the NBE/DLE ratio of ZnO as compared to the conventional growth at 95 °C. In paper II and VII, a two-step hydrothermal method was developed to selectively synthesize CuO NSs on ZnO NRs. In these experiments two nutrient solutions were used to deposit CuO NSs and to understand the growth mechanism in both cases. It was established that the CuO NSs tend to deposit on the lateral surfaces of ZnO NRs at short growth durations independent of the nutrient solution. However, by extending the synthesis duration the CuO NSs completely covered ZnO NRs. Also, it was observed that the CuO NSs can be grown on ZnO NRs without using any pH controlling agent which was ascribed to the presence of locally generated OH\(^{-}\) group in the vicinity of ZnO NRs. The composite of these nanomaterials exhibits broad light absorption covering the entire visible range together with excellent electrical properties as discussed in paper III.
In papers IV-V, the realizations of white light emission based on ZnO/p-polymer HyLEDs were demonstrated. By applying the low temperature chemical growth of ZnO (in paper I), we have investigated the characteristics of the HyLEDs fabricated on nonconventional flexible substrates. The effects of the polymer concentration on the electro-optical properties of the fabricated HyLEDs were studied over a wide range of polymer concentrations. The results indicated that the polymer concentration can be utilized as a tuning parameter toward white light emission. Furthermore, by blending two polymers the emitted light characteristics can also be modified over a wide range.

In the third part of this research work, the sensing application of the CuO/ZnO nanocorals and the CuO NFs were investigated in papers II and VI, respectively. In the case of the CuO NFs we have scrutinized the effect of the nutrient solution pH on the grown NSs, which were further utilized to fabricate a pH sensor. The fabricated CuO NFs pH sensor exhibited good sensing characteristics over a wide range of pH values, and the sensor also demonstrated excellent reproducibility and relatively high sensitivity. For the fabricated humidity sensor based on CuO/ZnO NCs, the sensor showed improved sensitivity for RH variations. The NCs sensor revealed the highest sensitivity factor for its constituent materials (CuO, ZnO) and a fast dynamic response to humidity change. However, the sensor suffered from instabilities associated with surface reactions that hindered water desorption for recovery conditions.

5.2 Future Prospects

Regarding the future prospects of the present research work there are many issues that have to be upraised. First, concerning the synthesis part of the nanomaterials studied in the present thesis further studies are necessary to investigate the reproducibility part of these nanomaterials especially for the CuO NSs, and the CuO/ZnO NCs. For example, we observed during the synthesis experiments of the CuO NPs the presence of large quantity of CuO NFs on the substrate. This also applies for the CuO/ZnO nanocorals synthesis in which larger CuO entities were deposited on top of the NCs. These CuO bulky structures will have a direct effect on the fabricated devices
as they will push the nanoscale device with its unique properties into more bulk related behavior. On the other hand, the density of ZnO NRs has to be controlled in order to achieve a better device performance. This issue has critically influenced the reproducibility of the RH sensor as discussed in section 4.2.3 above. This was also observed to affect to a large extent the electro-optical characteristics of ZnO NRs/p-polymer HyLEDs as mentioned in section 4.2.1. Therefore, extensive controlled hydrothermal synthesis experiments of these nanomaterials are crucial if they are to be integrated into low-cost and efficient nanoscale devices for lighting and sensing applications. Secondly, some extra work is also necessary to fully understand the selective growth behavior of CuO NSs on ZnO NRs. Although, we have developed simple models to describe the growth behaviors that were encountered during the synthesis of CuO NSs on ZnO NRs samples. But, these models were based only on indirect measurements and observations, which are so far not examined with direct experiments. Hence, designing new experiments such as in-situ analysis measurements are important to reveal their growth mechanisms as well as the crystallographic relationship between CuO and ZnO which was not evident in our experiments. Furthermore, by understanding the fundamental characteristics of the CuO/ZnO system at low dimensions, investigating potential applications such as sensors and solar cells are then feasible and attractive. For example, by controlling the low temperature synthesis of the CuO/ZnO NCs in powder form and then print this powder on a large area flexible plastic foil, one can achieve a large area humidity/gas sensors at low cost. This method can also be applicable in solar cell application. As this composite is exhibiting extended light absorption covering the UV-Vis-NIR range and intrinsic p-n diode characteristics. However, the interface of this system has to be intensively studied and modified by doping to achieve better band alignment appropriate for solar cells applications.

Future directions related to ZnO/p-polymer HyLEDs include a number of queries to access the ultimate potential of this promising technology. Among these
queries is the fast degradation of the HyLEDs under continuous operation owing to the electrochemical oxidation of the polymer. This issue requires more studies such as investigating more stable polymers, optimization of the ZnO/polymer interface properties, and introduces instantaneous encapsulation of the HyLEDs after fabrication to avoid ambient exposure. Moreover, power efficiency measurements of the HyLEDs were not conducted in our research work which is an important figure of merit in judging the performance and feasibility of this system for lighting applications. The observed relatively high voltages $\geq 8$ V to trigger the light emission from these HyLEDs need to be addressed in future work. Finally, the choice of an optimal contacts quality and configurations that possess both transparency and long term stability for LED applications, along with the selection of a better polymers and blends are crucial for some white light applications such as indoor lighting.

Some of these future directions are challenging especially when it is related to nanomaterials interfaces. However, the unique opportunities that they offer are extremely enormous in all technological aspects. In addition to the lighting and sensing applications that we have successfully demonstrated during the last few years there are many other possible applications of these nanomaterials. The nanostructured ZnO, CuO, and their composites carry much potential in a diversity of fields such as catalysis, photovoltaics, energy conversion and storage applications.
References

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