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**Synthesising Metal Oxide Materials and Their Composite
Nanostructures for Sensing and Optoelectronic Device
Applications**

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Dedicated to:
My family and teachers

Synthesising Metal Oxide Materials and Their Composite Nanostructures for Sensing and Optoelectronic Device Applications

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Abstract

Research on nanomaterials has been revolutionized in the last few years because of the attractive properties they have in comparison to the bulk phase of similar materials. These properties are physical, chemical, catalytic and optical. Among these nanomaterials, the metal oxide nanostructures have become of particular interest to scientists for the development of different optical, biochemical and biomedical nanodevices. In the present research work using the advantageous features of nanotechnology, high performance nanodevices for optoelectronics with a wide band gap compound nanostructure and highly sensitive sensor devices have been demonstrated. The nanotechnology is used to fabricate sensitive and precise nanodevices based on nanomaterials for the application of sensing.

Among metal oxide nanostructures, ZnO, CuO and NiO are attractive materials because of their unique properties; their high surface area to volume ratio, their energy band gap of 3.37 eV, 1.2 eV and 3.7 eV, respectively, biocompatibility, high electron mobility, fast electron transfer rate and they are environmental-friendly in many applications. When used in sensor devices, nanomaterials have indicated high selectivity for possible use to detect the various analytes even in small volumes. Metal oxide nanostructures have shown to be good for optoelectronic nanodevices because of their electrical characteristics, high optical absorption and low-processing temperature.

In this thesis, the synthesis of different morphologies of metal oxide semiconductor nanostructures and their composite using the hydrothermal method are demonstrated for various applications. This thesis is divided into three parts:

In the first part of this research work, the fabrication of well-aligned ZnO nanorods using different concentrations of composite seed layer of inorganic and organic materials when using the hydrothermal growth method is presented. The effect of the composite seed layer on the

alignment, density and optical properties of the grown ZnO nanorods is investigated (paper I). Utilizing the advantage of ZnO nanostructure, a comparative study of ZnO nanorods and thin films for chemical and biosensing application was carried out. The ZnO nanorods and thin films were functionalized with strontium ionophore membrane, immobilized the galactose oxidase and lactate oxidase for determining the strontium ions, D-galactose and L-lactic acid, respectively (paper II).

In the second part, the effects of different urea concentrations on the morphology of CuO nanostructures is studied as described in paper III. Moreover, CuO nanoflowers were functionalized with cadmium ion ionophore for the detection of Cd ions, while CuO nanosheets were grown by the low temperature growth method and were used for the development of a non-enzymatic glucose sensor, respectively (Paper IV).

In the last part of this thesis, composite nanostructures of CuO/ZnO and NiO/ZnO were applied to develop dopamine sensor and fast sensitive UV photodetector, respectively. A nano-hybrid of CuO/ZnO nanostructure was used as a non-enzymatic electrode to detect dopamine by cyclic voltammetry and amperometric techniques (Paper V). In paper VI, we have demonstrated a strong UV absorption from ZnO nano-sheets achieved by the supramolecules-assisted growth solution using the hydrothermal method. The synthesized nanomaterial was used in the fabrication of UV photodetector based on p-NiO/ n-ZnO heterostructures.

Keywords: Hydrothermal method; metal oxide nanostructure; composite seed solution; well-aligned ZnO nanorods; composite structures; glucose and dopamine non-enzymatic sensors; heavy metals; supramolecular; UV photodetector sensor.

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List of publication included in this thesis

Paper I

Fabrication of well-aligned ZnO nanorods using a composite seed layer of ZnO nanoparticles and chitosan polymer

K. Khun, Z.H. Ibupoto, M.S. AlSalhi, M. Atif, A.A. Ansari and M. Willander

Materials 2013, 6, 4361-4374

Paper II

Comparative study of ZnO nanorods and thin films for chemical and biosensing applications and the development of ZnO nanorods based potentiometric strontium ion sensor

K. Khun, Z. H. Ibupoto, C.O. Chey, J. Lu, O. Nur and M. Willander

Applied Surface Science 2013, 268, 37-43

Paper III

Urea assisted synthesis of flower like CuO nanostructures and their chemical sensing application for the determination of cadmium ions

K. Khun, Z. H. Ibupoto and M. Willander

Electroanalysis 2013, 25, 1425 – 1432

Paper IV

Synthesis of novel CuO nanosheets and their non-enzymatic glucose sensing applications

Z.H. Ibupoto, **K. Khun**, V. Beni, X. Liu and M. Willander

Sensors 2013, 13, 7926-7938

Paper V

An electrochemical dopamine sensor based on the ZnO/CuO nano-hybrid structures

K. Khun, Z.H. Ibupoto, X. Liu, N. A. Mansor, A.P.F. Turner, V. Beni, and M. Willander

Journal of Nanoscience and Nanotechnology 2014, 14, 6646-6652

Paper VI

Supramolecules-assisted ZnO nanostructures growth and their UV photodetector application

K. Khun, S. Elhag, Z.H. Ibupoto, V. Khranovsky, O. Nur and M. Willander

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Journal of Applied Physics 2011, 110, 104702
- 2. ZnO nanorods based enzymatic biosensor for selective determination of penicillin**
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- 5. Development of a disposable potentiometric antibody immobilized ZnO nanotubes based sensor for the detection of C-reactive protein**
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- 6. Potentiometric glucose sensor based on the glucose oxidase immobilized iron ferrite magnetic particle/chitosan composite modified gold coated glass electrode**
K. Khun, Z.H. Ibupoto, J. Lu, M.S. AlSalhi, M. Atif, A.A. Ansari and M. Willander,
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- 7. Electrochemical L-lactic acid sensor based on immobilized ZnO nanorods with lactate oxidase**
Z.H. Ibupoto, S.M. Usman Ali, **K. Khun** and M. Willander
Sensors 2012, 12, 2456-2466.
- 8. Indirect determination of mercury ion by inhibition of a glucose biosensor based on ZnO nanorods**
C. O. Chey, Z. H. Ibupoto, **K. Khun**, O. Nur and M. Willander
Sensors 2012, 12, 15063-15077

9. **Iron ion sensor based on functionalized ZnO nanorods**
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Z.H. Ibupoto, **K. Khun**, X. Liu, M. Willander
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Physica Status Solidi A 2013, 210, 2720-2724
26. **The Synthesis of Co₃O₄ Nanowires; Structural Characterization and their Application as Glucose Non-enzymatic Sensor**
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Submitted manuscript
27. **Ethylene glycol-assisted ZnO nanorods growth and their Schottky diode for UV photodetector application**
K. Khun, S. Elhag, V. Khranovskyy, O. Nur and M. Willander
Manuscript

Review articles

1. **ZnO based potentiometric and amperometric nanosensor**
M. Willander, **K. Khun** and Z.H. Ibupoto
Journal of Nanoscience and Nanotechnology 2014, 14, 1–12
2. **Metal oxide nanosensor using polymeric membranes, enzymes and antibodies receptors as ion and molecular recognition elements**
M. Willander, Z.H. Ibupoto, **K. Khun**
Sensors 2014, 14, 8605-8632

Invited articles

1. **UV detectors and LEDs in different metal oxide nanostructures**
M. Willander, M.A. Abbasi, **K. Khun**, M. Hussain, Z.H. Ibupoto, and O. Nur
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Conference papers

- 1. Fabrication and characterization of light emitting diodes based on n-ZnO nanotubes grown by a low temperature aqueous chemical method on p-GaN**

C.O. Chey, S. M. Usman Ali, Z.H. Ibupoto, C. Sann, **K. Khun**, K. Meak, O. Nur and M. Willander

CLV-02, Vinh City, 2011, Vietnam

- 2. Synthesis of ZnO nanorods in PBS solution, their morphological and optical characterization**

K. Khun, Z.H. Ibupoto, S. Chen, W.M. Chen, I.A. Buyanova, M. Willander,

CLV-03, Phnom Penh, 2013, Cambodia

List of abbreviations

Abbreviation	Word or Phrase
AFM	Atomic Force Microscope
CuO	Copper (II) Oxide
I-V	Current Voltage
CV	Cyclic Voltammetric
EDX	Energy Dispersive X-ray
EHT	Extra High Tension or high voltage
FESEM	Field Emission Scanning Electron Microscope
FTO	Fluorine Doped Tin Oxide
FTIR	Fourier Transform Infrared Spectroscopy
GCGS	Gold Coated Glass Substrate
HMT	Hexamethylenetetramine
JCPDS	Joint Committee on Powder Diffraction Standards
Mag	Magnification
NRs	Nanorods
NSs	Nanostructures
NiO	Nickel Oxide
1D	One dimension
O_{Zn}	Oxygen anti-site
O_i	Oxygen interstitial
V_o	Oxygen vacancies
PBS	Phosphate Buffer Solution
PL	Photoluminescence
PVC	Polyvinyl Chloride
pH	Power of Hydrogen
TEM	Transmission Electron Microscope
TOSs	Transparent Oxide Semiconductors
UV	Ultraviolet
WD	Working Distance
XRD	X-Ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
Zn_o	Zinc anti-site
Zn_i	Zinc interstitial
ZnO	Zinc Oxide
V_{Zn}	Zinc vacancies

List of units

Symbol	Unit
A	Ampere
Å	Angstrom
°C	Degree centigrade
eV	Electronvolt
g	Gram
Hz	Hertz
keV	Kiloelectronvolt
kHz	Kilohertz
kV	Kilovolt
µm	Micrometer
mbar	Millibar
mg	milligram
ml	Milliliters
mM	Millimolar
mV	Millivolt
M	Molar
nm	Nanometer
N	Newton
Ω	Ohm
rpm	Revolutions per minute
V	Volt
W	Watt

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Chapter 1

Introduction

Nanomaterials are now being used for a wide variety of device applications because of their unique properties. Several nanodevices have been fabricated for different fields such as electronics, chemical sensing, biosensing and health care. Nanomaterials are expected to be useful in the near future for applications that include medicine, biotechnology and for the food industry. Nanotechnology based devices have many advantageous features but there are concerns about their effect on both human health and environment [1]. The classification and understanding of the impact of nanomaterials is very important for the development of future based industrial applications.

1.1. Background

1.1.1. Nanotechnology

Nanotechnology describes the manipulation of matter on an atomic, molecular and supramolecular level (dimension from 1 to 100 nm); to achieve the fabrication of new devices with superior properties [2, 3]. The idea of nanotechnology was presented by the American Physicist Richard Feynman in his lecture “There is Plenty of Room at the Bottom” at an American Physical Society meeting in Caltech in 1959. He had suggested that it will be possible to successfully manipulate and control materials on the atomic and molecular size for electronic and mechanical systems with nanoscale components; the development of technologies into such small systems would be created from combined fields such as chemistry, biology and physics [4]. In 1974, the first term “nanotechnology” was introduced by the Japanese Scientist Norio Taniguchi at The International Conference on Production Engineering, Tokyo, from 26-29 August. He presented the process of using semiconductors, such as thin film deposition and ion beam milling characterized at a level of 1 nm length. He further defined “nanotechnology” as the process of separation, integration and deformation of the materials by using one atom or one molecule [5, 6]. In the 1980s, the idea of nanotechnology had been applied in the invention of instruments such as a scanning tunneling microscope (STM), developed by Gerd Binnig and Heinrich Rohrer. They received the Nobel Prize in Physics in 1986 [7, 8]. It was also used in the development of the atomic force microscope (AFM), invented by Calvin Quate and Christoph

Gerber. In 1985 the fullerenes (C_{60}) was investigated by Harry Kroto, Richard Smalley and Robert Curl [9, 10]. Carbon nanotubes were discovered by L. V. Radushkevich and V. M. Lukyanovich in 1952 [11]. They published a clear image of carbon nanotubes with a diameter of 50 nm in the Soviet Journal of Physical Chemistry, but this discovery was unnoted because of the fact that it was published in Russian language during the cold war.

The research and development of nanomaterials and the nanotechnology fields have been greatly improved by the fabrication of nanodevices and their unique properties of nanomaterials, such as:

1. The large surface area to volume ratio increases the surface reactivity around nanomaterials. This is useful for chemical and biosensing applications.
2. Increased optical emission and absorption due to electron transfer from one state to another state. This phenomenon is useful for optoelectronic nanodevices.

1.1.2. Biosensors

A biosensor is an analytical device, which combines a sensitive biological component such as tissue, microorganisms, enzymes, antibodies, cellular structure, nucleic acid etc. with a physicochemical detector [12]. A biosensor tool converts the signal of the interaction between the analyte and the biological element into an easily detectable signal such as light, voltage, current, mass, etc. Biotransducers are made from sensitive elements such as optical, electrochemical, piezoelectric, electronic, gravimetric and pyroelectric materials [13]. Biosensors have attractive applications in human care, food industry, controlling the environment and for genetic applications. The greatest advantage of such biosensors are in their application being user friendly, having a fast response, high sensitivity, strong selectivity, and their practical use for real sampling [14-17]. The first oxygen sensor was invented by Leland C. Clark Jr in 1956, for oxygen detection in blood, water and other liquids [14]. He is also known as the father of the chemical-/bio-sensor field [18]. In 1962, his idea was to develop the experiment of an immobilized glucose oxidase with a membrane on a Clark electrode to determine the glucose concentration with decreased oxygen concentration [15]. At the end of 1967 glucose detection based on an independent and operational enzymatic electrode was developed [16]. The first investigation of potentiometric urea detection, based on urease with an ammonium selective membrane immobilized electrode, was published in 1969 [17]. In 1970, the pH ion selective field effect transistors electrodes were demonstrated [19]. By the end of the 1980s several scientists

were conducting experiments that focused on the biosensor field, to develop different methods for the determination of various ions and analytes [20]. Among the different biosensors, biosensors based on nanomaterials are very useful for biomolecular recombination pathogenic diagnosis and environmental monitoring applications [20-23]. The nano-size of a surface and the fast interaction with the target analytes on the surface make biosensors based on a nanomaterial able to detect analytes even in small volumes. Nanomaterials also have the ability to be inserted inside a biological cell. This property of a nanomaterial demonstrates a clear difference in ease of application, to the more bulky material used currently in biosensor applications. To have a highly sensitive biosensor with a fast response and a specific application, the choice of the material of sensor is very important. Several nanomaterials such as nanowires/nanotubes [24], gold nanoparticles [23], magnetic nanoparticles [25], carbon nanotubes [26] and quantum dots [27] have been investigated to evaluate their application as biosensors. Experiments have looked at their physical, chemical, mechanical, magnetic and optical properties for increased sensitivity, faster response and specific biomolecules recognition. Such high selectivity, fast response and sensitivity of biosensors based on these nanostructures (NSs) can be assigned to their dimensions relative to the biological or chemical analyte.

1.1.3. Metal oxide semiconductor nanostructures

The nanostructures of metal oxide semiconductors are attractive and important for nanosensors research because of their practical and theoretical importance in biological, environmental science and analytical chemistry applications [28-31]. The semiconducting, piezoelectric and pyroelectric properties of one dimension metal oxide NSs are very important. The most popular research areas of these nanostructures are optoelectronics [31], sensors [32], and actuators [33]. Metal oxide NSs have a high surface area to volume ratio, low toxicity, are environment-friendly, have chemical stability and biocompatibility. So metal oxide NSs also show fast electron transfer properties required to improve nanomaterials performance when used as a biomimetic membrane that will detect e.g. proteins and retain their activity [29, 31, 32]. Among these metal oxides, ZnO, CuO and NiO have different and attractive morphologies as nanowires, nanorods (NRs), nanotubes, nanoleaves, nanoflowers, etc. that make them useful to fabricate nanodevices for optoelectronic and sensing applications.

In the last two decades, research on ZnO has been successful because of their physical and chemical properties. ZnO NSs have become increasingly popular, because of the different

morphologies grown by various growth methods including the vapor-liquid-solid (VLS) technique [34], chemical vapor deposition (CVD) [35, 36], electrochemical deposition (ED) [37], and hydrothermal methods [38, 39]. Among these methods, the hydrothermal method has several advantages such as; they can be processed at a low temperature ($<100^{\circ}\text{C}$), cheap, environment-friendly and give a high yield of ZnO NSs on substrates. One dimension (1D) ZnO (NRs) are highly important compared to other ZnO NSs because of the simple synthesis and the higher surface areas to volume ratio that enhance the fabrication of electronic, optoelectronic and biomedical devices [40, 41]. By using the hydrothermal methods, ZnO NRs can easily be grown on a broad range of substrates that include paper, glass, metal, and other semiconductors [42, 43]. ZnO has a wide direct energy band gap of 3.37 eV at room temperature (25°C), many radiative deep level defects and relatively large exciton binding energy of 60 meV, which makes ZnO useful for sensing and optoelectronic device applications [44, 45].

Copper (II) oxide (CuO) is known as a p-type semiconductor with narrow energy band gap of 1.2 eV and monoclinic crystal structure. This material has also high potential in several nanodevices applications that include sensors, high critical temperature superconductors, lithium ion batteries, field emission emitters and catalysts [46-50]. CuO NSs have shown many attractive properties such as; they can easily be grown on various substrates, prepared as different morphologies, low cost, and they are non-toxic. The researchers have been interested in the synthesis of various morphologies of CuO because the size and morphology of the CuO have a large effect on the electrochemical and catalytic nanodevices performance [51]. Several morphologies of CuO have been grown by the hydrothermal methods such as NRs [52], nanosheets [53], nanoflowers [54] and nanotubes [55].

Nickel oxide (NiO) is a p-type semiconductor with a wide energy band gap of 3.6 eV to 4 eV and interesting properties such as magnetic, optical, catalytic and electrochemical [56, 57]. NiO NSs have been used in the fabrication of nanodevices such as electrochemical energy-storage devices, gas sensors, dye-sensitized solar cells, and as an optical active counter-electrode tool. There are many methods for the synthesis of NiO NSs, but most of these have disadvantages except the hydrothermal method which is low cost, user friendly, easily controllable and environment-friendly. The morphologies and size of NiO NSs grown by the hydrothermal method are dependent on the growth parameters. Such as temperature, composition of growth solution, and growth time [58].

1.2. Outline and objectives

The outline and objective of this thesis is about the synthesis of different morphologies of metal oxide semiconductor NSs (ZnO, CuO and NiO) by the hydrothermal method and their application as UV photodetectors, catalytic and chemical biosensors.

This thesis is divided into three parts:

1. The fabrication of well-aligned ZnO NRs, thin film and the synthesis of CuO nanoflowers and nanosheets. The morphologies and the crystal structure quality were investigated using field emission scanning electron microscope (FESEM), x-ray diffraction (XRD) and a transmission electron microscope (TEM).

2. Using ZnO, CuO NSs and their composites to fabricate chemical sensors and biosensors. We used two methods for sensing applications; potentiometric (enzymatic or ionophore type) and amperometric (non-enzymatic type) including the detection of heavy metals, dopamine and glucose.

3. The fabrication of a fast and sensitive UV photodetector using p-type NiO/n-type ZnO heterostructures. ZnO nanosheets were grown on fluorine doped tin oxide glass substrate (FTO) with supramolecular assisted solution using the hydrothermal method. This device was characterized by current-voltage (I-V) characteristics.

Chapter 2

Materials and their properties

Among the transparent oxide semiconductors (TOSs), ZnO and NiO have a wide energy band gap and many other attractive properties. CuO is a narrow energy band gap semiconductor and has unique physical and chemical properties. In this chapter we describe the properties of ZnO, CuO and NiO that we investigated in this research work for the fabrication of different devices.

2.1. Zinc Oxide (ZnO)

ZnO is a wide energy band gap, compound semiconductor; it is n-type native doped semiconductor material with a piezoelectric property [59]. ZnO has two main crystalline structures, hexagonal wurtzite and cubic zincblende. Of these structures, the wurtzite is the most common and is stable under ambient conditions. The image of the hexagonal wurtzite structure of ZnO is shown in figure 2.1. The wurtzite structure is obtained by alternate stacking along the c direction of two interpenetrating hexagonal-closed-pack (HCP-type) sub lattices. The unit cell of sub lattices forms a tetrahedron structure which consists of 5 atoms; one atom belongs to oxygen and is surrounded by four Zn atoms and vice versa [60]. In its most common form, the hexagonal wurtzite structure of ZnO has two different surfaces; one is the polar plane and includes (0002), and the (000 $\bar{2}$) and the other is the nonpolar plane and includes (11 $\bar{2}$ 0) and the (10 $\bar{1}$ 0). The nonpolar surface has an equal number of O and Zn atoms. The polar surface is the most important characteristic in determining the chemical and physical properties of ZnO; it also has a higher surface energy compared to the nonpolar surface. Due to this high surface energy of the polar plane, 1D ZnO NRs grow well along the C-direction [0001] [41], this shown in figure 2.2. The ZnO material has attractive electro-optical properties because of the presence of intrinsic and extrinsic point defects in the crystal structure, which are useful for optoelectronic devices. The direct wide energy band gap of approximately 3.4 eV and the relatively high exciton-binding energy (60 meV) of the ZnO semiconductor are useful for short wavelength optoelectronic devices and allow efficient excitonic emission at room temperature (25 °C), respectively [61]. ZnO does not only emit in the UV region, it also emits covering the whole visible spectra which emits green, yellow and in the red region [62-64].

Figure 2. 1 : The hexagonal wurtzite structure of the ZnO semiconductor.

Figure 2. 2: Schematic diagram of 1D ZnO NSs grown on a substrate, along the c-axis.

The UV spectrum is associated with near band-edge transition in ZnO, namely, the recombination of the free excitons. The visible emission is produced because of the presence of the defect levels in ZnO such as Oxygen and Zinc vacancies (V_o , V_{Zn}) [65, 66], Oxygen and Zinc interstitial (O_i , Zn_i) [67, 68], Oxygen and Zinc anti-site (O_{Zn} and Zn_o) [69] as shown in figure 2.3. Due to the native defects in the ZnO like V_o and Zn_o and hydrogen incorporation, the ZnO material will natively be n-type semiconductor. However, there are many reports about p-type doping of ZnO semiconductor but it is still uncontrollable and not reproducible which is a

problem to fabricate p-n homojunctions based on ZnO [70]. ZnO nanostructures also have other attractive physical and chemical properties that include high mobility, high electron transfer rate and high surface area to volume ratio. They are also bio-safe, bio-compatible and environmental-friendly which make ZnO useful for intra/extra biosensing applications [71, 72]. Table 2.1 shows the summary of the basic physical parameters of ZnO semiconductor material at room temperature.

Figure 2. 3: Energy band diagram showing some of the defect levels in ZnO structures [73].

Table 2. 1: Summary of the basic physical properties of ZnO at room temperatures [59, 74, 75].

Parameter properties	Values
Lattice constants	a= 0.325 nm, c=0.527 nm
Stable crystal structure	Wurtzite
Density	5.675 g/cm ³
Molecular mass	81.389g/mol
Melting point	1975°C
Specific heat	0.125 cal/g°C
Refractive index	2.008
Static dielectric constant	8.656
Direct energy band gap	3.37 eV
Exciton binding energy	60 meV
Electron mobility	210 cm ² /Vs
Effective mass of electron/hole	0.28 m ₀ /0.59 m ₀

2.2. Copper (II) Oxides (CuO)

CuO is another native p-type metal oxide semiconductor with a narrow energy band gap of 1.2 eV. CuO belongs to the monoclinic crystal structure system with the space group $2/m$ or C_{2h} as shown in figure 2.4. In a unit cell of the CuO structure, the copper atom is surrounded by four oxygen atoms in a square planar configuration [76]. Due to the unique physical and chemical properties of CuO NSs and the simplicity in the synthesis of different morphologies using the hydrothermal method, CuO NSs can widely be used in various applications. CuO NSs have many popular advantages such as non-toxicity, cheap production and a high surface area to volume ratio, good electrochemical activity and electron transfer at low potential, which is good for bio and chemical sensing applications [77]. CuO NSs are also used for the fabrication of solar energy (cells) transformation, dry cell batteries and as an anode in lithium ion batteries [78, 79]. CuO NSs work effectively as high critical temperature superconductors, as field emission emitters and for magnetic storage media [80, 81]. The summary of the basic physical properties of CuO material is shown in the table 2.2.

Figure 2. 4: The unit cell of CuO structures.

Table 2. 2: Summary of the basic physical properties of the CuO material [82-84].

Parameter properties	Values
Lattice constants	$a = 0.468 \text{ nm}$, $b = 0.342 \text{ nm}$, $c = 0.513 \text{ nm}$ $\alpha = 90^\circ$, $\beta = 99.54^\circ$, $\gamma = 90^\circ$
Crystal structure	Moniclinic
Space group	C_{2h}
Molecular mass	79.545 g/mol
Density	6.315 g/cm ³
Boiling point	2000 °C
Melting point	1326 °C
Refractive index	2.63
Direct energy band gap	1.2 eV
Hole mobility	0.1-10 cm ² /Vs

2.3. Nickel Oxide (NiO)

NiO is a native p-type 3d transition metal oxide semiconducting material with a wide energy band gap from 3.6 eV to 4.0 eV [85, 86]. NiO shows good electric, electro-chromic and thermoelectric properties as well as high chemical resistance [87-89]. Due to these properties, NiO has been used in reaction catalysis, batteries, sensors, photo-catalysts and electro-chromic devices [90-95]. The crystal structures of NiO material is commonly known as a cubic rock salt structure; the nickel atom is placed in a six fold octahedral coordination as shown in figure 2.5 [96]. The synthesis of NiO NSs has been achieved using several different methods such as evaporation, electrochemical deposition, chemical vapor deposition, sol-gel and hydrothermal growth [97-100]. The hydrothermal method is the best technique for growing the NiO NSs. Advantages of this method include inexpensive apparatus, low temperature operation, it is user friendly and it is substrate independent [101]. The hydrothermal method produces non-pure NiO material because of the hydroxide produced in the growth solution. The non-pure NiO NSs was annealed at 300-500 °C to produce pure NiO nanostructure phase [101]. Table 2.3 shows a summary of the basic properties of the NiO metal oxide semiconductor material.

Figure 2. 5: The unit cell of a NiO structures.

Table 2. 3: Summary of the basic physical and chemical properties of the NiO material [102, 103].

Parameter properties	Values
Appearance	Green crystalline solid
Molecular mass	74.69 g/mol
Density	6.67 g/cm
Melting point	1995 °C
Refractive index	2.18
Energy bandgap	3.6-4.0 eV
Hole mobility	2.8 cm ² /Vs
Electrical conductivity	1.5 ×10 ⁻³ Ω ⁻¹ .cm ⁻¹

Chapter 3

Synthesis and characterization of metal oxide nanostructures

This chapter describes the preparation and characterization of the nanostructures metal oxide semiconducting grown materials such as ZnO, CuO, NiO and their composites. The hydrothermal growth method was chosen for preparation of the above metal oxides. After preparation of the nanostructures, their morphologies, crystal quality, structure and chemical bonding were investigated. The techniques that were used for the characterization in this work are: field emission scanning electron microscope (FESEM) for the morphologies, transmission electron microscope (TEM) for studying the lattice crystal structure, X-ray diffraction (XRD) for the crystal purity characterization, X-ray photoelectron spectroscopy (XPS) for surface analyzing, Fourier transform infrared spectroscopy (FTIR) for chemical bonding and the molecular structure and photoluminescence (PL) spectroscopy for studying the optical properties of metal oxide NSs.

3.1. The preparation of the substrate

The substrate preparation is the most important step for the growth of metal oxide semiconducting NSs. In order to avoid contamination, impurities and dust on the substrate from grease, hands, the environment and the cutting/breaking of the substrate, careful cleaning was required. There are two ways of substrate cleaning; wet cleaning and dry cleaning. For these experiments the wet cleaning method was used, it has advantages such as low cost, easy and it is environmental-friendly.

3.1.1. Standard substrate wet cleaning method

The substrates were cleaned separately with acetone and isopropanol in an ultrasonic bath for 5 minutes each to remove any organic contaminant and residual particles on it. Afterward the substrate was cleaned with de-ionized water and flushed with nitrogen gas at room temperature. Finally the clean substrates were annealed in oven at 120 °C for 10 to 15 minutes to remove water molecules from the surface of the substrate.

3.1.2. The deposition of the gold or silver thin layer on glass substrates

In this work, a thin layer of gold and silver were used as the contact for the electrical measurement and to grow various metal oxide semiconducting NSs on the substrate. We used

Satis Evaporator (725) to deposit the thin gold or silver layers on the substrates. Firstly, the glass substrate was cleaned by using the standard substrate wet cleaning method. The cleaned substrate was then placed into the Satis Evaporator (725). Satis Evaporator at a pressure of 2×10^{-6} mbar, was used to evaporate the metal on the glass substrate. First 10 nm layer of Titanium (Ti) or Chromium (Cr) was deposited on the substrate to be used as the adhesive layer, followed by the addition of a 100 nm layer of gold or silver. The schematic diagram of deposition of gold or silver on the glass substrate is shown in figure 3.1.

Figure 3. 1: Schematic diagram of gold or silver coated on a glass slide.

3.1.3. ZnO, CuO and NiO seed solutions

The next step for the growth of metal oxide semiconducting material NSs is the seed solution. The seed solution consists of embedding seed particles onto the substrate before the growth of the nanostructures material; this step produces nucleation sites by decreasing the thermodynamic barrier [104]. The seed particles play an important role for the metal oxide NSs growth for controlling the density, morphology and direction of growth of the metal oxide NSs. The ZnO seed solution was prepared with 0.01M zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and 0.03 M potassium hydroxide (KOH) dissolved in 125 ml and 65 ml of methanol, respectively. The potassium hydroxide was added drop wise to the zinc acetate solution at constant stirring and heating at 60 °C for 2 hours. The complete seed solution has a cloudy color and contains the dispersed ZnO nanoparticles with a diameter of approximately 3-5 nm [105].

We used the same method to prepare the CuO and NiO seed solution, with 0.01M copper acetate monohydrate ($\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$) and nickel acetate monohydrate ($\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$) in methanol, respectively. After preparation of a seed solution it was placed on the surface of the substrate using the spin coating method.

3.2. Fabrication of metal oxide nanostructures on gold coated glass substrate (GCGS) using the hydrothermal method

There are several techniques to grow metal oxide semiconducting NSs (ZnO, CuO and NiO) that have been reported in the literature. Among those techniques, the hydrothermal method is the most useful technique because of its attractive advantages such as low cost, simple, and environmentally safe. ZnO is one of the most important metal oxide semiconducting materials and it has the richest family of nanostructures. In this work, we studied ZnO NRs, CuO nanoflowers, nanosheets, NiO nanoflowers, and their composite NSs that were grown on gold coated glass substrate and the FTO glass using the hydrothermal method [55, 106, 107].

3.2.1. ZnO nanorods

The growth solution for ZnO NRs was prepared by dissolving 0.05 M of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) in 100 ml of deionized water. The hydrothermal method was used to grow ZnO NRs on GCGS. First a gold substrate was cut to small sizes and cleaned by using the standard substrate cleaning method. The cleaned gold substrates were coated with ZnO seed solution by spin coating method for 30 seconds in one or two times at 2000 rpm; the spin coated substrate was annealed at 120 °C for 15 to 20 minutes. Finally the annealed gold substrates were placed in a Teflon holder and dipped into ZnO NRs growth solution in the oven at a temperature range of 90 to 95 °C for 5 to 7 hours. The schematic diagram of the grown metal oxide semiconducting NSs by the hydrothermal methods is shown in figure 3.2. At the end of the growth time the nanostructures samples were washed with de-ionized water to remove some salt particles from the nanostructures surface. The chemical reactions involved in the fabrication of ZnO NRs are shown below:

During the growth time, hexamethylenetetramine plays an important role as a buffer medium and also produces ammonia as shown in eq. (1). In eq. (2) and (3), ammonia reacts with water and produces hydroxide ions; the hydroxide ions react with zinc ion and produces the zinc hydroxide. Finally, the zinc hydroxide produces ZnO NRs growth on the gold substrate. The diameter, length and density of the ZnO NRs can be controlled by the growth parameters that include the concentration of the growth solution, the temperature and the growth time.

Figure 3. 2: Schematic diagram of the growth of metal oxide nanostructures by the hydrothermal method.

3.2.2. The synthesis of CuO nanoflowers and nanosheets onto GCGS

The synthesis of CuO NSs onto GCGS was done using the hydrothermal method. Cleaned gold substrates with a CuO seed layer was placed in the sample holder and dipped into the CuO growth solution of 0.025 M of copper nitrate hemi(pentahydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$) and $\text{C}_6\text{H}_{12}\text{N}_4$. The CuO nanoflowers were grown by adding urea to the growth solution so that we could investigate the effect of urea on the size of the CuO nanoflowers. Various amounts 0.1, 0.4, 0.5, 0.6, 0.8 and 1.0 g of urea were added to 100 ml of the CuO growth solution. The urea was used as a template for controlling the size and density of the CuO nanoflowers. The CuO nanosheets were grown in the CuO growth solution at an alkaline pH of 11. The pH of the CuO growth solution was changed by adding 0.1 M of nitric acid and 25% ammonia solution. The nanostructures growth solutions were kept in the electric oven at 80-85 °C for 4-6 hours. At the end of the growth time the CuO nanostructures sample was washed with de-ionized water to remove some salt particles on the nanostructures surface. The FESEM images of CuO nanoflowers and nanosheets are shown in figure 3.3.

Figure 3. 3: FESEM images of CuO NSs: (a) nanoflowers, and (b) nanosheets grown using the hydrothermal method [55].

Figure 3. 4: FESEM images of NiO NSs: (a) nanowalls and (b) nanoflowers [108].

3.2.3. The fabrication of nickel oxide (NiO) nanowalls on the GCGS

The hydrothermal method was also used to fabricate NiO NSs on GCGS. The GCGS was deposited using NiO seed particles on the surface by the spin coating method at a speed of 2000 rpm for 30 seconds for one to two times. The seed particle coated gold substrate was annealed in the electric oven at 120 $^{\circ}\text{C}$ for 15 to 20 minutes. After the completion of the annealing time, the gold substrate was fixed in the Teflon sample holder and dipped into the NiO growth solution of

the equimolar concentration of 0.1 M nickel nitrate hexahydrate and $C_6H_{12}N_4$. The growth solution was kept in the oven at 90-95 °C for 4 to 6 hours. At the end of the growth time, the sample was washed with de-ionized water, flushed with nitrogen gas and then dried at room temperature (25°C). This dried sample was annealed at 450 °C for 2-4 hours, to transfer the $Ni(OH)_2$ NSs into the NiO NSs phase. The FESEM images of NiO nanowalls and nanoflowers is shown in figure 3.4.

3.3. The characterization tools for the study of metal oxide nanostructures

3.3.1. The X-ray diffraction (XRD)

Figure 3. 5: XRD pattern of ZnO nanorods grown using the hydrothermal method [109].

The XRD is a useful technique to characterize the crystal quality and the composition of the synthesized material. From the XRD pattern, we can calculate the arrangement of the atoms, lattice parameters and identify crystal planes of the metal oxide semiconducting material. Also, the XRD is a powerful tool for identifying amorphous from crystalline materials. There are more information which is obtained about the prepared material using the XRD method below:

1. Lattice parameters, units cell structure and crystal plane
2. The formation mechanism of a specific material
3. The existence of different crystal phases in the prepared material
4. The ratio of crystalline and amorphous structures in the synthesized material

5. The average crystal size can be calculated from the width of the peak in the crystal array (the particle size is inversely proportional to the peak width).
6. The structural distortion is calculated by the interplanar distance.

In this work, the XRD patterns are measured using XRD scans (0.1/sec) made with the Phillips PW 1729 powder diffractometer and CuK α radiation with wavelength ($\lambda = 1.5418\text{\AA}$). The full width at half maximum (FWHM) of the XRD peaks are calculated by pseudo-Voigt curve fitting. A typical XRD pattern of the ZnO NRs measured using the XRD model Phillip PW 1729 powder diffractometer is shown in figure 3.5.

3.3.2. The field emission scanning electron microscope (FESEM)

The FESEM is a powerful technique to study the surface morphology of the synthesized material. This technique produces images of materials by scanning it with a focused electron beams. The electrons interact with atoms in the material, producing a signals that contain the surface morphology and composition of the material. The FESEM can has a high resolution that is better than one nanometer due to short wavelength and high energy electron beam. The FESEM can produce different types of signals such as secondary electrons (SE), characteristic X-ray, back scattered electrons (BSE), light cathodoluminescence (CL), sample current and transmitted electrons. The SE detector is the standard tool in all FESEM. The FESEM can make high-resolution images of a material surface with size less than one nanometer. Due to the very narrow electron beam, the FESEM has a large range of magnifications from 10 to more than 500,000 times compared to the magnification of the best light microscope. The BSE uses the reflection of electrons beam from the synthesized material by elastic scattering. Due to the strong intensity of the BSE related to atomic number (Z) of the material, the BSE is used in analytical FESEM with the spectra that is made from the characteristic X-ray. The BSE image can provide information about the different elements in the material. A characteristic X-ray is emitted by removing an inner shell electron from the sample using the electron beam; a higher energy electron then fills the shell and releases energy. The characteristic X-ray that is emitted can be used for identifying the composition and measuring the abundance of elements in the synthesized material. For the FESEM, a sample is normally needed to be completely dry and hard such as wood, bone or feathers because the sample chamber works at high vacuum. For a soft sample such as living cells, tissues or a soft bodied organism, chemical fixation must be used to save and stabilize their structures.

Figure 3. 6: FESEM top view and cross section images of ZnO nanorods [109].

An electron beam in the FESEM is thermionically emitted by a tungsten filament cathode or lanthanum hexaboride (LaB6) in an electron gun that moves towards an anode. Tungsten metal is usually used in the thermionic electron gun due to its higher melting point and lower vaporisation pressure and lower cost compared to other metals. Typically the electron beam has a high energy ranging from 200 eV to 40 keV which is focused by one or two magnetic condenser lenses to a very small spot size of 0.4 nm to 5 nm. The electron beam moves through a pair of deflector plates in the electron column; this allows deflection of the electron beam in the horizontal and vertical direction so that it can scan a rectangular area of the sample surface. Due to the interaction of the primary electron beam with the sample surface, the electrons lose energy due to the repeated scattering and absorption in a volume of specimen which is called the interaction volume. This extends from less than 10 Å to approximately 5 μm under the surface. The interaction volume size depends on several parameters such as electron landing energy, the atomic number of the sample (Z) and the density of the specimen on the sample. The energy exchange between the sample and the electron beam produces elastic scattering (high energy electron), inelastic scattering (secondary electron) and electromagnetic radiation which can be used to create an image of the specimen.

In this work the FESEM images of metal oxide nanostructures materials were investigated by the LEO 1550 Gemini field emission gun and JEOL JSM-6301F. Some FESEM images of the metal oxide semiconducting NSs is shown in figure 3.6.

3.3.3. The transmission electron microscopy (TEM)

Figure 3. 7: TEM images of ZnO nanorods grown using the hydrothermal method [109].

The transmission electron microscopy (TEM) is used to characterize the internal structure of the material such as the lattice parameter, the miller indices and the lattice distances. A high energy electron beam used in the TEM interacts with the sample to give elastic scattering radiation and particles. These signals provide the information to characterize the sample by using energy-dispersive X-ray spectroscopy (EDS), back scattered and secondary electron beam images. TEM has two ways to provide specimen information, the diffraction method and the image method. In the diffraction method, an electron diffraction pattern is created by the electron beam. The TEM diffraction and the X-ray diffraction patterns are similar; a single crystalline structure material provides a spot pattern on the screen. However, the polycrystalline structures provide a powder or ring pattern at the illuminated area on the screen. A glassy or amorphous sample will show a chain of diffused halos. With the image method, the image of the illuminated sample area can be created by several different mechanisms; mass contrast due to the spatial separations between specific atomic constituents, thickness contrast due to the non-uniform thickness of the sample and diffraction contrast which is created by the interaction of the incident

electron beam phase contrast and the structural defects of the sample. The TEM also has several disadvantages, the preparation of the samples is a time consuming technique in order to make a sample thin enough to be transparent for electrons.

In this work, TEM images of metal oxide NSs were made using an FEI Tecnai G2 TF20 UT (Hillsboro, OR, USA) with a field emission gun operating at 200 kV and a point resolution of 1.9 Å and equipped with an EDS. Figure 3.7 shows TEM image of a metal oxide NSs.

3.3.4. The X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-analytical tool that is used to characterize the elemental composition, chemical state and electronic state of the material by photoionization. The principle process of the XPS method can be explained by irradiating a material with the X-ray beam onto the surface of the sample; electrons of the atoms at the surface will escape from the material because of the incident X-ray energy. When the photon energy of the X-ray is enough, core electrons at the surface will escape from the atom with a specific kinetic energy ($E_{kinetic}$). These are photoelectron. The kinetic energy of these photoelectrons can be experimentally determined by the equation:

$$E_{kinetic} = h\nu - E_{binding} - W \quad (1)$$

where the photon energy of the X-ray is $h\nu$, $E_{binding}$ is the binding energy and W is the work function of the spectrometer. For atoms with a larger number of electron orbits, the electron in each orbital is related to a binding energy like a “finger print”. Due to the X-ray excitation, each element will show specific peaks on the XPS spectra that are related to the electron kinetic energies of specific radius. In the XPS spectrum, the electron kinetic energy is plotted as a function of the elements binding energy. From the XPS data, we can identify all elements other than Hydrogen and Helium by calculating the binding energy of their core electrons.

In this work, XPS measurements were performed by the ESCA200 spectrometer in an ultrahigh vacuum and a base pressure of 10^{-10} mbar. The chamber was fitted with a monochromatic Al ($K\alpha$) x-ray source using photons with energy ($h\nu = 1486.6$ eV) for the identification of the chemical composition of the sample. Carbon was used as a reference substance to calibrate the binding energies for all XPS measurement. Figure 3.8 shows high resolution XPS spectra of CuO NSs obtained using the x-ray photoelectron spectroscopy model ESCA 200.

Figure 3. 8: XPS spectra of CuO nanosheets grown using the hydrothermal method [110].

3.3.5. Photoluminescence spectroscopy (PL)

Photoluminescence spectroscopy (PL) is the method used to characterize the various properties of a material such as purity, crystalline quality and the minority carrier lifetime of semiconductors. The PL is the light emission from any material after they absorb photons (electromagnetic radiation). A PL spectrum gives accurate and precise information about the nature of the surface, interface, the impurity level of the material and it also provides knowledge about an estimate of interface disorder and roughness of the sample. For a semiconductor with a low indirect band gap it is not easy to use PL because these materials have less radiation efficiency. The recognition of impurity and defect levels of materials are related to their optical activity. The tools required for the normal PL measurement are an optical light source and a spectrophotometer.

In this work, the PL was performed at room temperature with experimental third harmonics ($\lambda_e = 266$ nm) from a Coherent Ti; a sapphire laser used and the detection was observed with a Hamamatsu CCD camera. To measure the dispersion of the PL signal a monochromator of one

meter focal length (model Brucker Optics Chromex 25, Bruker Corp., Billerica, MA, USA) was used with a diffraction grating of 150 lines/mm. A typical PL spectrum of ZnO NRs at room temperatures is shown in figure 3.9.

Figure 3. 9: PL spectrum of ZnO nanorods at room temperatures (25 °C) [109].

3.3.6. Atomic force microscopy (AFM)

The AFM is used for imaging, measuring and manipulating materials at nanoscale. The AFM equipment was invented in 1986 by G. Binnig, C. Quate and C. Gerber. It has a very high resolution scanning probe microscope. The AFM equipment provides an image of a surface that is 1000 times better than an optical diffraction device. The AFM has a cantilever with a sharp tip (probe) at the end that is used to scan the material surface. The cantilever is made of silicon or silicon nitride with a nanometer tip radius. During the experiment, a force is generated between the tip and the sample surface which results in the deflection of the cantilever, which follows Hooke's law [111]. The size of deflection is measured by using a laser spot which is reflected from the cantilever top surface into photodiodes. The laser deflection provides the information of the hills and valleys on the sample surface; this makes the image of the surface. In the AFM equipment there are two ways to perform the experiment with the scanning probe microscope;

one is the contact mode where the tip touches on the sample surface, the other is the tapping mode where the tip taps across the sample surface.

In this work, the AFM measurements were performed using Veeco Dimension 3100 (Veeco Instruments, Inc., Plainview, NY, USA), operated in tapping mode with a silicon tip (resistivity 0.01–0.025 $\Omega\cdot\text{cm}$; cantilever $T = 3.95\text{--}4.71\text{ }\mu\text{m}$; $W = 29\text{--}31\text{ }\mu\text{m}$; $L = 124\text{ }\mu\text{m}$; $C = 39\text{--}71\text{ N/m}$; and $f_0 = 330\text{--}399\text{ kHz}$). A typical AFM image of ZnO seed nanoparticle is shown in figure 3.10.

Figure 3. 10: AFM image of ZnO seed nanoparticle on the gold coated substrate [109].

3.3.7. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectroscopy is a useful tool to characterize an unknown specimen and provide information about the chemical bonding and molecular structure of inorganic and organic materials. The FTIR tool is used to obtain the characteristic infrared radiation absorption, emission, photoconductivity or Raman scattering of a sample (solid, liquid or gas). The FTIR spectrum gives molecular information of the sample from the different absorption peaks which relate to the bond formation between atoms and certain frequencies. The intensity of the absorption peaks in the spectrum provides data about the amount of the material contained in the sample. In this work, FTIR was used to investigate the bonding of the enzyme, ionophore membrane and metal oxide nanostructures on the sample.

3.4. The electrical measurement

The electrical and electrochemical characterizations of our devices in this research work were performed by several tools such as Auto-lab, semiconductor parameter analyses, pH meter and Keithley. Auto-lab with model PGSTAT 12 potentiostat/galvanostat FRA 2 Auto-lab Type (III) model that uses the general purpose electrochemical system software program (Eco Chemie, The Netherlands) was used to measure the current response of the free enzyme biosensor and UV photodetector device. The semiconductor parameter analyzer is the basic equipment used to investigate the electrical properties of semiconductor devices and is used to record the I-V data of the UV photodetector devices. The potentiometric measurement was carried out using the pH meter and Keithley equipment to measure the voltage output response and time response of the sensing devices, respectively.

Chapter 4

Fabrication and characterization of devices

This chapter focusses on my research results during my Ph.D. study at Linköping University, Sweden. There are three parts of the results that are presented and discussed;

1. The investigation of the well aligned growth of ZnO NRs using composite seed layer of ZnO nanoparticles and chitosan polymer on a GCGS. This was done using the hydrothermal method. We completed a comparative study of ZnO NRs and thin films based on the chemical sensing application.
2. The synthesis of novel CuO nanosheets, nanoflowers and the composite of ZnO/CuO NSs for developing enzyme free dopamine, glucose sensors and potentiometric Cd^{2+} ion sensor.
3. The synthesis of NiO NSs and ZnO nanosheets was investigated using the hydrothermal growth method and applied to the development of fast sensitive UV photodetector device.

4.1. The growth of well-aligned ZnO NRs and thin films based on strontium ion sensing application

In this section, we discuss our research work on the growth of well-aligned ZnO NRs; using a composite seed layer on gold coated substrate by the hydrothermal method and a comparison between the ZnO NRs and thin films based on the strontium ion sensor studied by the potentiometric method.

4.1.1. Fabrication of well-aligned ZnO NRs using ZnO nanoparticles and chitosan polymer as a composite seed layer (paper I)

In this paper, ZnO nanoparticles are combined with chitosan polymer and used as a composite seed layer to control the growth of well aligned ZnO NRs over the surface of a substrate using the hydrothermal method [112]. Some of the results of our research work are described below:

FESEM images of the fabricated ZnO NRs grown on GCGS with different composite seed layer concentrations are shown in figure 4.1 (a-d) and figure 4.2 (a-d). Figure 4.1 (a) shows the growth image of the ZnO NRs using only chitosan seed layer and that shows random growth of the ZnO NRs with low density on the substrate. With 10 mg of ZnO nanoparticles added to the

chitosan solution; an improved alignment of the ZnO NRs is observed, as shown in figure 4.1 (b). When the amount of ZnO nanoparticles is increased to 30 mg and 50 mg, the result shows a better alignment with high density of the ZnO NRs on GCGS, as shown in figure 4.1(c, d). A similar growth trend was studied for the different concentrations of composite seed layer with 70 mg and 90 mg of ZnO nanoparticles as shown in figure 4.2 (a, b). The reason behind this growth pattern might be the effect of the uniform distribution of the ZnO nanoparticles in the composite seed solution leading to a substrate providing better nucleation sites for controlling the aligned growth of ZnO NRs.

In addition to the top view FESEM images of well-aligned growth pattern, a cross-sectional FESEM image was provided to confirm the well-aligned growth pattern of the ZnO NRs on the GCGS as shown in figure 4.2 (c). It can be seen from the cross-sectional image that the ZnO NRs are perpendicular to the substrate with a length and average diameter of approximately 7 μm and 100 nm, respectively. The use of the composite seed solution of ZnO nanoparticle and chitosan polymer has shown two advantages: (i) the nucleation is provided by the Zn and O ions of the ZnO nanoparticles and (ii) the chitosan makes uniform distribution of the ZnO nanoparticles on the surface of substrate. Moreover, a combined bunch of the ZnO nanoparticle on the surface might be responsible for the well aligned and high density of the ZnO NRs growth [113]. The energy-dispersive X-ray (EDX) spectra of the well aligned ZnO NRs fabricated by the composite seed layer were shown in figure 4.2 (d). The results show that the composed nanorods have only Zn and O atoms; however, a peak of carbon atoms also appears in these spectra which may be due to the presence of carbon in the chitosan polymer. In the chitosan compound, there is also other atoms such as hydrogen, oxygen and nitrogen, but those atoms do not appear in the EDX spectra due to their low percentage in the chitosan molecule.

The HRTEM image and selected-area electron diffraction of a single crystal ZnO NRs is shown in figure 4.3 (a). This image shows that the growth of ZnO NRs leads to a single crystal with a hexagonal crystal structure (wurtzite structure), the growth direction is along the (0002) plane, as shown in figure 4.3 (b). Figure 4.3 (c) shows one nano-grain with the (0002) plane distance of approximately 0.26 nm which is consistent with the lattice spacing of the wurtzite crystal structure of ZnO. The diameter of the ZnO NRs was calculated by the HRTEM analysis, to be 90 nm approximately, which corresponds to the diameter that is observed from the FESEM data. Our results show single crystal nature of the ZnO NRs and good orientation of growth along

the c-direction when using ZnO nanoparticles and chitosan polymer as the composite seed layer. A uniform and heterogeneous nucleation on the other surfaces has been reported [114]. However, the nucleation of well-aligned grown ZnO NRs on substrate using the seed layer of ZnO nanoparticles is a simple and suitable method.

Figure 4. 1: FESEM images of the ZnO NRs grown with composite seed layer at different amounts of ZnO nanoparticles: (a) 0 mg, (b) 10 mg, (c) 30 mg and (d) 50 mg [112].

Figure 4. 2: FESEM images of the ZnO NRs grown with composite seed layer at different amounts of ZnO nanoparticles: (a) 70 mg and (b) 90 mg; (c) the cross sectional image of the ZnO NRs growth using 90 mg of ZnO nanoparticles and (d) The EDX spectra of the ZnO NRs using 70 mg of ZnO nanoparticles [112].

Figure 4. 3: HRTEM image of the ZnO nanorods grown with 70 mg of ZnO nanoparticle [112].

Figure 4.4 show PL spectra at room temperature of the grown ZnO NRs using the ZnO nanoparticle and chitosan polymer as composite seed layer. It can clearly be seen that a strong UV peak is observed at wavelength of 377 nm; and wide visible peaks appear at wavelengths of 528 nm and 676 nm. These represent a green emission and orange/ red emission, respectively. The broader green emission peak can be associated with the Oxygen vacancies [115], and the orange/red emission peak may be due to the interstitial atomic and defects in the ZnO [113]. The PL spectra of the ZnO NRs grown using the zinc acetate dihydrate seed solution is shown with dotted lines for comparison, in figure 4.4. From the PL data, the grown ZnO NRs with ZnO nanoparticles and chitosan as the composite seed layer have shown higher defect level compared to the ZnO NRs grown with the zinc acetate dihydrate seed layer. Therefore, the grown ZnO NRs with the composite seed layer shows intense luminescence properties in the visible region.

Figure 4. 4: PL data of the ZnO NRs grown with the composite seed layer using 70 mg of ZnO nanoparticle and the seed layer of zinc acetate dihydrate [112].

4.1.2. The comparative study of ZnO NRs and thin films, for chemical and biosensing applications and the development of a ZnO NRs based potentiometric strontium ion sensor (paper II)

In this study, ZnO NRs were fabricated on the GCGS by the hydrothermal method and the ZnO thin films grown was deposited with the electrodepositing method. The comparative study of ZnO NRs and thin films was performed for chemical and biosensing applications [109]. The ZnO NRs were used to develop the strontium ion sensor based on the potentiometric method. Results of this research work are discussed below;

The morphologies of ZnO NRs and thin films were investigated using the FESEM technique. The top view of the FESEM image shows clearly that the fabricated ZnO NRs were of high density, uniform and well-aligned on the GCGS, shown in figure 4.5 (a). The proposed ZnO thin films grown by the deposition method is shown in figure 4.5 (b). Figure 4.5 (b) shows that the ZnO thin films have been created by many nano clusters with a diameter of approximately 20 nm. At the insertion of the sensor into the analytic solution, there is a formation of a complex between the analytic molecules and the enzyme or ionophore, on the ZnO nanostructures material working electrode to detect the target molecules, is shown in figure 4.6. In the schematic diagram, it is shown how the ZnO NRs or thin films working electrode with immobilized enzyme

or ionophore and Ag/AgCl reference electrode are connected to a pH meter. The calibration curve for the strontium ion sensor which was based on ZnO NRs and thin films by using the potentiometric method is shown in figure 4.7 (a, b). It can be seen that the ZnO NRs have shown a better sensitive response and a wider detection range, compared to ZnO thin films. This result for the different morphologies of ZnO material could be the effect of the surface sensitiveness related to different morphologies. The electrode based on ZnO NRs provided a larger surface area to volume ratio and consisted of a greater number of surface possibilities to bind the selective strontium ionophore, resulting in higher sensitivity and wider detection range of strontium ion concentrations. The fabricated ZnO thin films showed a flat surface, which attached these exposed fewer surfaces to the strontium selective ionophore. The obtained results showed a less sensitive response and a lower detection range for strontium ion concentrations compared to the ZnO NRs. Because of this, the ZnO NRs showed a highly sensitive and wide detection range for chemical sensor devices. In order to clearly understand, the high chemical and biosensing sensitivity of ZnO NRs and thin films, two more experiments with different types of bioactive compounds were performed separately. The second experiment was performed with galactose oxidase immobilised ZnO NRs and thin films using the potentiometric method for the detection of D-galactose. The third experiment was with the ZnO NRs and thin films immobilised with the lactate oxidase and used for the detection of L-lactic acid by the potentiometric method.

Figure 4. 5: Top view FESEM image of ZnO NSs (a) NRs and (b) thin films [109].

Figure 4. 6: Schematic diagram of potentiometric measurement of immobilized ZnO nanorods and thin films based on a chemical and biosensing application.

Figure 4. 7: The calibration curve of the strontium ion sensor based on immobilized ZnO (a) nanorods and (b) thin films [109].

Both experiments with bioactive compound showed that the working electrode based on immobilised ZnO NRs has a highly sensitivity response and a wider detection range for analytes compared to immobilised ZnO thin films electrode. The summarised results of the comparative study of the ZnO NRs and the ZnO thin films for chemical and biosensing application are shown in table 4.1.

Table 4. 1: Summary of results for the comparative study of ZnO nanorods and thin films, for chemical and biosensing applications [109, 116, 117].

Sensing	Nanorods	Thin films
Strontium		
Slope (mV/decade)	28.65 ± 0.52	22.72 ± 0.66
Intercept (mV)	43.69 ± 2.03	46.58 ± 2.67
Detection range (M)	1.00×10^{-6} - 1.00×10^{-1}	5.00×10^{-6} - 5.00×10^{-3}
R ²	0.99	0.99
D-galactose		
Slope (mV/decade)	-89.14 ± 1.23	-37.89 ± 1.34
Intercept (mV)	235.45 ± 2.25	97.75 ± 2.61
Detection range (M)	1.00×10^{-2} - 2.00×10^{-1}	3.00×10^{-2} - 2.00×10^{-1}
R ²	0.99	0.99
L-lactic acid		
Slope (mV/decade)	41.33 ± 1.58	9.97 ± 0.25
Intercept (mV)	208.24 ± 3.66	44.05 ± 0.58
Detection range (M)	1.00×10^{-7} - 1.00×10^{-3}	1.00×10^{-7} - 1.00×10^{-3}
R ²	0.99	0.99

4.2. The synthesis of novel CuO nanostructures and their chemical and biosensing application

In this section, we will summarize the results of the urea assisted CuO nanoflowers and the CuO nanosheets by the hydrothermal method. The functionalized CuO nanoflowers with Cd²⁺ ion selective ionophore were used for the Cd²⁺ ion detection and the CuO nanosheets were used as a non-enzymatic electrode for the development of glucose sensor.

4.2.1. Urea assisted synthesis of CuO NSs and their chemical sensing application for the determination of cadmium ions (paper III)

This section describes the synthesis of novel urea assisted CuO nanoflowers by using hydrothermal method. The CuO NSs are immobilized with the tetrathia-12-crown-4 selective ionophore for the detection of Cd^{2+} ions [55]. The results of this work are discussed below;

Figure 4. 8: FESEM image of CuO nanoflowers synthesized by adding different amounts of urea in the growth solution: (a) 0.1 g, (b) 0.4 g, (c) 0.8 g and (d) 1.0 g [55].

The FESEM image of the highly dense and well aligned growth of CuO nanostructures is shown in figure 4.8 (a-d). The FESEM data has provided that nanobeads like morphologies of the grown CuO NSs using the urea as the template for controlling the CuO NSs morphology has been

achieved. Different amounts of urea: 0.1 g, 0.4 g, 0.8 g and 1.0 g were added into the growth solution (0.025 M concentration of copper nitrate and HMT) to control the effect on the CuO NSs. FESEM image shows that the morphology is slightly changed by increasing the urea concentration in the growth solution. The size of CuO NSs is decreased and finally turned into the CuO nanoflowers. Urea plays an important role in the change of the CuO NSs which may be due to hydroxide ions (OH^-) being provided in large quantities for higher concentrations of urea. In the presence of low concentrations of urea, HMT and urea both assisted the formation of CuO nanobeads. HMT and urea give the NH_3 and OH^- , respectively. NH_3 also provided OH^- ions and in doing so the OH^- concentration is increased in the growth solution for higher amounts of urea. This increases the growth speed that produces the CuO nanoflowers, as shown in figure 4.8 (d). CuO is one of the electrochemical materials and it was used as anodic material in some fabricated electrochemical batteries. Due to these advantageous properties of CuO material, we have grown CuO nanoflowers with urea using the hydrothermal growth method. They have also been used to develop cadmium ion sensor. Tetrathia-12-crown-4 is a neutral ionophore which has been used with the Polyvinyl Chloride (PVC) membrane electrode for the determination of cadmium ions [118]. Due to the advantages of CuO NSs such as high surface to volume ratio, high electro-catalytic activity, fast electron transfer and strong electrical signal generation, the Tetrathia-12-crown-4 ionophore is functionalized on the CuO nanoflowers to develop cadmium ion sensor.

Figure 4. 9: (a) The calibration curve of the proposed Cd^{2+} sensor and (b) the time response curve measured at a concentration $1.0 \times 10^{-6} \text{ M}$ [55].

The developed sensor has shown a wide detection range for cadmium ion concentration from 1.0×10^{-9} to 1.0×10^{-1} M with sensitivity of 29.3 ± 0.3 mV/decade as shown in figure 4.9 (a). The wide detection range of the proposed Cd^{2+} ion sensor based on tetrathia-12-crown-4 ionophore may be assigned to the advantageous properties of CuO nanoflowers. The proposed cadmium ion sensor has shown a stable and highly sensitive response for the detection of cadmium ion concentration. Moreover, this sensor has shown a fast time response of less than 10.0 s as shown in figure 4.9 (b).

4.2.2. The growth of CuO nanosheets and their non-enzymatic glucose sensor application (paper IV)

In this part of our research work, CuO nanosheets were grown in a highly alkaline medium on GCGS using the hydrothermal method. The fabricated CuO nanosheets were used for the development of non-enzymatic glucose sensor device [110]. Results of this research work are discussed below;

The CuO nanosheets were fabricated on GCGS in a growth solution of pH 11. The obtained CuO nanosheets could be due to the high concentrations of hydroxide ions which improved the speed for the formation of the nanosheets by increasing the number of growth nuclei for the CuO material. Initially during the growth, some CuO nuclei with negative or positive charge were produced. Therefore, oppositely charged species on the substrate, including OH^- or Cu^{2+} will be attracted by those nuclei. The collection of these opposite charges provides the formation of CuO nanosheets. H_2O also has a significant effect on the morphology and the number of nuclei in CuO multiple nanosheets nanomaterial. The fabricated CuO nanosheets have an average thickness of approximately 10-20 nm as shown in figure 4.10 (a, b). The XPS technique was used to determine the chemical composition of the grown CuO nanosheets. A full wide scan XPS spectrum of the synthesized CuO NSs is shown in figure 4.11 (a). In figure 4.11 (a) distinct peaks at 284.00 and 531.00 eV are corresponding to the C1s and the O1s, respectively [119]. The three main peaks at 933.30 eV, 121.10 eV and 77.00 eV are observed and belong to the Cu 2p, Cu 3s and Cu 3p, respectively [120]. The XPS spectra of the Cu 2p and the O1s are shown in figure 4.11 (b, c). The peak of 933.60 eV in the Cu 2p spectra corresponds to the binding energy of Cu 2p_{3/2} [120] as shown in figure 4.11 (b). The two shake up peaks show the formation of the CuO compound on GCGS.

Figure 4. 10: FESEM images of CuO nanosheets (a) low magnification image and (b) high magnification image [110].

Figure 4. 11: (a) The full XPS spectra of CuO nanosheets grown using the hydrothermal method, (b) Cu 2p XPS spectra and (c) O 1s XPS spectra [110].

The O1s spectrum shows two peaks at 529.47 eV and 531.15 eV which correspond to the O^{2-} ion and adsorbed oxygen in the CuO nanomaterials, respectively as shown in figure 4. 11 (c). The results of the XPS show that the fabricated CuO nanosheets are highly pure and composed of CuO material. In order to understand the oxidation process of the CuO nanosheets, the amperometric detection of glucose was studied. The amperometric measurement was performed at an applied potential of 0.50 V for different glucose concentrations in a 0.10 M NaOH of electrolyte solution. The relationship between the glucose concentration and the current response of the CuO nanosheets non-enzymatic electrode is shown in figure 4.12 (a). Figure 4.12 (a) show the linear range of glucose concentration from 5.00×10^{-1} – 1.00×10^1 mM with sensitivity of $5.20 \times 10^2 \mu A m M^{-1} c m^{-2}$ and a correlation coefficient of 0.998. The presented non- enzymatic glucose sensor exhibited good sensitivity due to the high electro catalytic properties of the CuO nanosheets. The proposed non-enzymatic glucose sensor based on CuO nanosheets has a fast response time of approximately 10s with a steady current signal upon the addition of glucose, as shown in figure 4.12 (b).

Figure 4. 12: (a) The calibration curve of the non-enzymatic electrode based on the glucose and (b) the response time curve of the proposed glucose sensor with successive addition of glucose in 0.10 M NaOH solution [110].

4.3. The growth CuO/ZnO and NiO/ZnO nanocomposite and their sensor and UV photoreaction application

In this section, we will present our results on heterostructures of ZnO/CuO and NiO/ZnO. These heterostructures are used for the development of non-enzymatic dopamine sensing device and highly sensitive UV photodetector device, respectively.

4.3.1. An electrochemical dopamine sensor based on the ZnO/CuO nano-hybrid structures (paper V)

In this part of this research work, a nanocomposite of ZnO/CuO was grown on GCGS by the hydrothermal method. The fabricated ZnO/CuO composite NSs were used for the detection of dopamine molecules by the amperometric method [107]. The results of this research work are discussed below;

The growth of the ZnO/CuO composite NSs on GCGS was performed in two steps by the hydrothermal method. Firstly, the ZnO NRs were grown on GCGS. Then the CuO NSs were grown on the fabricated ZnO NRs. The morphologies of the ZnO/CuO nanocomposite were studied by FESEM. Figure 4.13 (a, b) show the top and the cross section views of the ZnO/CuO composite NSs. It can clearly be seen that the CuO nanoflowers are grown on the ZnO NRs with enhanced surface. The cross sectional FESEM showed that the top surface of the ZnO NRs was etched due to the acidic nature of the copper nitrate growth solution. The crystal quality of the synthesized ZnO/CuO composited NSs was measured by XRD. The very intense (002) miller plane peak in figure 4.14 shows well aligned growth of ZnO NRs on the substrate. From figure 4.14, there are several peaks of ZnO NRs such as (100), (002), (101), (102), (103), (112) and (004) which are denoted by star sign in the XRD pattern. The CuO peaks in the XRD pattern are denoted by the sign of delta. These could be assigned to the monoclinic phase of CuO; there was no any other impurity related peaks that were found in the sample; the gold peak appeared due to the gold on the substrate. The fabricated ZnO/CuO nanocomposite was used for the development of non-enzyme dopamine sensor using the cyclic voltammetric (CV) and amperometric methods. To understand the catalytic kinetics of dopamine's oxidation with the ZnO/CuO composite NSs, the effect of the scan rate to the current peak response in 2 mM of dopamine was measured; the result of this measurement is shown in figure 4.15 (a). The scan rates were selected from 10 to 100 mVs⁻¹; the results show that the current response is linear to the square root of the scan rate.

This behaviour of the ZnO/CuO nanocomposite electrode shows that the electrochemical reaction take place at the electrode surface is diffusion controlled. CV characterization was investigated for the different dopamine concentrations (0, 2.0, 2.9, 3.9 and 5.7 mM) in the phosphate buffer solution (PBS) as shown in figure 4. 15 (b).

Figure 4. 13: FESEM image of ZnO/CuO nano-hybrid structures (a) top view and (b) cross sectional view [107].

Figure 4. 14: XRD pattern of ZnO/CuO composite NSs grown using the hydrothermal method [107].

Figure 4. 15: (a) The current response for the fabricated dopamine sensor versus the square root of the scan rate in 2.0 mM concentration of dopamine in PBS and (b) the CV curve at a scan rate of 10 mV⁻¹ of the fabricated sensor at different concentrations of dopamine [107].

Figure 4. 16: (a) The calibration curve of the current versus dopamine concentration by amperometric measurement at an applied potential of 0.50 V and (b) the interference response of the fabricated dopamine sensor for 1.0 mM of glucose, uric acid and ascorbic acid [107].

From figure 4.15 (b), it can clearly be seen that the anodic peak, related to the oxidation of the dopamine, and the cathodic peak, associated to the reduction of dopamine are increasing. Figure 4.16 (a) shows the obtained response of the anodic current at +0.5 V by amperometric technique versus the dopamine concentration. The anodic current response was found to be linear from 1.0×10^{-3} to 8.0 mM range of dopamine concentration with a sensitivity of $90.9 \mu\text{A mM}^{-1} \text{cm}^{-2}$

and a lower detection limit of 1.0×10^{-4} mM. For the monitoring of the stability and the usability of the ZnO/CuO nano-hybrid structures based sensor, a series of experiments were performed for a period of three weeks. This sensor has shown to retain 90% of its original activity during the period of study. The small loss in the activity can be due to the loss of CuO or ZnO material during measurement or washing steps. The selectivity is one of the most important parameters for the improvement of sensors. There are several common interferents and easily oxidative substances including glucose, uric acid and ascorbic acid, which are mixed with dopamine in the human serum. The selectivity of the fabricated dopamine sensor was measured by comparing the electrochemical response of the sensor in the presence of these interferents. The interference response of the fabricated sensor was tested by adding of 1 mM of each interferent concentration into the dopamine solution. The results showed that the current response of the sensor for these interferents is negligible compared to the dopamine, as shown in figure 4.16 (b).

4.3.2. Supramolecules-assisted ZnO NSs grown for the fabrication of a sensitive UV photodetector (paper VI)

This part of the research work studies the UV absorption of ZnO nanosheets synthesized on FTO substrate in a supramolecules-assisted growth solution by the hydrothermal method. The proposed ZnO nanosheets were used for the development of UV photodetector based on p-NiO/n-ZnO heterostructure. The results of this work are discussed below;

Figure 4.17 (a, b) show FESEM image of ZnO NRs and nanosheets grown on FTO by the hydrothermal method. From those figures it can clearly be seen that well-aligned ZnO NRs have been converted to nanosheets due to the effect of the supramolecules. The ZnO nanosheets have highly faceted grains of an average size of approximately 200 nm, and are densely packed in a polycrystalline layer. In figure 4.17 (c), it can be seen that the NiO nanoflowers are in fact a network of thin sheets which cover the ZnO nanosheets surface. The cross section image of the ZnO nanosheets and NiO nanoflowers show that the interface of the ZnO/NiO nanocomposite is in good connection as shown in figure 4.17 (d). Figure 4.18 (a) shows the crystal quality and the phase purity of the ZnO NRs, nanosheets, NiO nanoflowers and ZnO/NiO nanocomposite, which were characterized by XRD pattern. The XRD pattern of the ZnO/NiO nanocomposite has exhibited only peaks for the ZnO and the NiO NSs. However, a peak related to SnO_2 was also observed, which is due to the FTO substrate. The XRD pattern of the ZnO NSs (NRs and nanosheets), NiO nanoflowers and ZnO/NiO heterostructure matched the standard pattern of ZnO

hexagonal crystal (JCPDS 01-1136) and cubic NiO (JCPDS 44-1159). Both XRD patterns for the ZnO NRs and nanosheets show a (002) peak, although for the ZnO nanosheets the peak intensity is relatively much lower than for the ZnO nanorods. This is expected since the dominant growth direction of the ZnO nanosheets is not along the c-axis. This result clearly exhibits that the supramolecules affected the growth direction and resulted in a new morphology. In figure 4.18 (b), the PL spectra of the obtained ZnO nanosheets and nanorods that were grown on the FTO by the hydrothermal method are shown. This PL spectra have the main high intensity peak at approximately 380 nm, which is related to near band-edge transition in ZnO because of the recombination of free and bound donor exciton [121].

Figure 4. 17: FESEM images of metal oxide nanostructures: (a) ZnO nanorods, (b) ZnO nanosheets, (c) NiO nanoflowers and (d) cross section of ZnO/NiO nanocomposite.

Figure 4. 18: (a) XRD pattern of ZnO/NiO nanocomposite growth on FTO and (b) the PL spectra of ZnO nanosheets (blue solid line) and ZnO NRs (red dotted line).

Figure 4. 19: Plot of $(\alpha h\nu)^2$ versus the photon energy for the ZnO NRs and nanosheets.

The PL spectra also shows two other lower intensity peaks that are related to visible emissions. Those two peaks appeared due to a recombination from deep level defects in the ZnO materials, like e.g. Oxygen vacancies and other interstitial defects. The ZnO nanosheets have a stronger intensity of the UV emission than the ZnO NRs because of the effect of the supramolecular to the hydrogen bonding with ZnO [122]. The other reason for the stronger UV absorption of the ZnO nanosheets may be due to the presence of many thin leaves leading to relatively larger surface area to volume ratio than the ZnO nanorods. Beside the modified

morphology, growth direction and PL spectrum of the ZnO NSs, the optical band of the ZnO nanosheets and NRs were investigated using UV-visible absorption tool for comparison. In figure 4.19, the relationship between the $(\alpha h\nu)^2$ and the photon energy ($h\nu$) is plotted. The optical band-gap value of the ZnO nanosheets was smaller “2.80 eV” than ZnO NRs “2.98 eV”. Furthermore, for the ZnO nanosheets, two new bands with a non-pronounced intensity have been observed at around “2.56 eV and 2.79 eV”, respectively. Simply, all these modulation in the UV/visible spectra could be due to impurities as a direct influence of the added supramolecular species. They can result in electronic energy states within the band gap of the ZnO nanosheets [123].

Figure 4. 20: (a) The I-V data obtained in the dark current (solid red line) and under UV light (dotted black line), (b) The time response of ZnO/NiO UV photodetector in conditions of on/off UV light.

Figure 4.20 (a) show the rectifying I-V characteristics of the NiO/ZnO heterojunction devices performed in the dark and under UV light. The I-V response of the proposed device shows that it is highly rectifying, nonlinear and with a forward threshold voltage of ~ 0.5 V. The proposed UV photodetector device become highly sensitive to UV light by increasing the photocurrent response in the forward region due to the increased generation of electron-hole pairs in the device, when UV light is applied. The I-V response of the Ag-NiO and FTO-ZnO is shown in the inset in figure 4.20 (a). It can be seen that both I-V response are liner, which shows that the contacts are good ohmic conductors. Hence, the rectifying and nonlinear behavior of the proposed device is due to the ZnO/NiO heterojunction. The time response of the proposed UV photodetector device was measured in two conditions continuously: dark (UV off) and light (UV

on) as shown in figure 4.20 (b). We have repeated a number of cycles of the UV response during the on/off of the UV light. The results show that the proposed UV photodetector response is repeatable and stable. The free carrier electrons generated from the ZnO/NiO UV photodetector device corresponded to the adsorption/desorption of oxygen molecules. The oxygen molecules are absorbed onto the nanostructures surface and then they capture free electrons from the ZnO materials. When the UV light is illuminated onto the UV photodetector device, an electron-hole pair is generated. The holes move toward the ZnO surface for desorbing the oxygen ions, and due to this phenomenon, the thickness of the depletion layer at the surface is decreased. This result in the free carrier electron concentration is increased. The free electrons are collected with the passage of time at desorption and reabsorption of oxygen ions, producing an increasing photocurrent.

Chapter 5

Summary

The main objective of the presented work focused on the synthesis of metal oxide NSs (ZnO, CuO and NiO), some of their composites, their characterization and their chemical and optical sensing applications. All metal oxide NSs were grown using the low temperature growth method. This research work is divided into: (i) the growth of the well aligned ZnO NRs using a composite seed layer of nanoparticles and conducting polymer, and the synthesis of novel CuO nanoflowers and nanosheets using urea and the alkaline medium of pH 11 assisted growth solution, respectively. (ii) ZnO material, CuO material and their composite nanostructures were used for chemical and biosensing applications and (iii) NiO/ZnO composite NSs were used for UV photodetector application.

Well-aligned ZnO NRs were prepared by the hydrothermal growth method using a composite seed layer of ZnO nanoparticles and chitosan-polymer in paper I. This research work showed that different concentrations of ZnO nanoparticles in composite seed layer controlled the size, density, alignment and optical properties of ZnO NRs. In paper II, a comparative study of ZnO NRs and thin films have been carried out by investigating chemical and biosensing applications. The result showed that both fabricated sensor devices of ZnO NRs and thin films worked very well, but the sensor device based on ZnO NRs has shown better performance in terms of higher sensitivity and lower detection limit.

CuO nanoflowers have been prepared by different urea concentrations assisted growth solution in the hydrothermal method. This work showed that the obtained CuO NSs are highly dense, uniform and compromise pure CuO crystal phase. Moreover, Cd^{2+} ions has been detected with the obtained CuO nanoflowers (paper III). The fabricated sensor showed a wide detection range of Cd^{2+} ions concentration from 1.0×10^{-9} to $1.0 \times 10^{-1} \text{M}$ with a high sensitivity of 29.3 ± 0.3 mV/decade and fast response time of approximately 10.0 seconds. In addition, the proposed sensors have also shown a good repeatability, reproducibility, stability and selectivity. Non-enzymatic glucose sensors have been carried out with the growth of CuO nanosheets in paper IV. The proposed sensor showed wide advantages of compatible size, cheap and simple fabrication.

Further, the fabricated sensor have a high sensitivity of $5.20 \times 10^2 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$, a wide detection range, good selectivity and reproducibility.

In paper V, electrochemical dopamine sensors have been fabricated with the ZnO/CuO nano-hybrid structures. The presented devices exhibited a good sensitivity over a wide concentration range of dopamine from 1.0×10^{-3} to 8 mM with a lower detection limit of 1.0×10^{-4} mM. In addition, the proposed sensor showed good selectivity to ascorbic acid, glucose and uric acid; it has also been observed that good stability and reproducibility after using seven different electrodes. Further, supramolecules-assisted ZnO NSs were synthesized on FTO using the hydrothermal method (paper VI). The research work has exhibited that the supramolecular effected to the morphology, growth direction, crystal quality and improved the UV absorption of ZnO NSs. Furthermore, the obtained ZnO nanosheets and NiO nanoflowers have been used to fabricate UV photodetector devices. The proposed UV photodetector devices have shown a nonlinear and rectifying I-V characterization, high sensitivity, fast rising and decaying time response ~ 100 ms and relatively low leakage current.

Due to the bio-safe properties in many cases and the low cost for fabrication of the metal oxide semiconductors, especially ZnO nanomaterial, these will be of relevance in my future work. Such work will focus on the intracellular measurement of bio-molecules in blood cells, such as cholesterol and dopamine. This will require the development of ZnO nanomaterials. These nanomaterials will also be evaluated in my future work on the development of highly efficient and low cost solar cells and energy harvesting nanodevices.

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