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Chemically Modified Metal Oxide Nanostructures Electrodes for Sensing and Energy Conversion

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To My Family and the Soul of My Father

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Sami Elhag

Abstract

The goal of this thesis is the development of scalable, low cost synthesis of metal oxide nanostructures based electrodes and to correlate the chemical modifications with their energy conversion performance. Methods in energy conversion in this thesis have focused on two aspects; a potentiometric chemical sensor was used to determine the analytical concentration of some components of the analyte solution such as dopamine, glucose and glutamate molecules. The second aspect is to fabricate a photoelectrochemical (PEC) cell. The biocompatibility, excellent electro-catalytic activities and fast electron transfer kinetics accompanied with a high surface area to volume ratio; are properties of some metal oxide nanostructures that of a potential for their use in energy conversion. Furthermore, metal oxide nanostructures based electrode can effectively be improved by the physical or a chemical modification of electrode surface. Among these metal oxide nanostructures are cobalt oxide (Co_3O_4), zinc oxide (ZnO) and bismuth zinc vanadate (BiZn_2VO_6) have all been studied in this thesis. Metal oxide nanostructures based electrodes are fabricated on gold-coated glass substrate by low temperature ($< 100\text{ }^\circ\text{C}$) wet-chemical approach. X-ray diffraction, x-ray photoelectron spectroscopy and scanning electron microscopy were used to characterize the electrodes while ultraviolet-visible absorption and photoluminescence were used to investigate the optical properties of the nanostructures. The resultant modified electrodes were tested for their performance as chemical sensors and for their efficiency in PEC activities. Efficient chemically modified electrodes were demonstrated through doping with organic additives like surfactants. The organic additives are showing a crucial role in the growth process of metal oxide nanocrystals and hence can be used to control the morphology. These organic additives act also as impurities that would significantly change the conductivity of the electrodes. However, no organic additives dependence was observed to modify the crystallographic structure. The findings in this thesis indicate the importance of the use of controlled nanostructures morphology for developing efficient functional materials.

Key words: Metal oxide nanostructures, mixed metal oxide nano-compound, low temperature wet-chemical growth, chemically modified electrode, doping, surfactant, chemical sensor, potentiometric sensor and photo-electrochemical activity.

List of included papers

Paper I

Incorporating beta-cyclodextrin with ZnO nanorods: a potentiometric strategy for selectivity and detection of dopamine

Sami Elhag, Zafar H. Ibupoto, Omer Nur and Magnus Willander, *Sensors*, **2014**, 14, 1654.

My contribution: All experimental work. Wrote a large part of the first draft of the manuscript.

Paper II

Habit-modifying additives and their morphological consequences on photoluminescence and glucose sensing properties of ZnO nanostructures, grown via aqueous chemical synthesis

Sami Elhag, Zafar H. Ibupoto, Volodymyr Khranovskyy, Magnus Willander and Omer Nur, *Vacuum*, **2015**, 116, 21.

My contribution: Design of the growth experiments. I performed all measurements except the PL measurement. I analyzed the data and wrote the first draft of the manuscript.

Paper III

Effect of urea on the morphology of Co₃O₄ nanostructures and their application for potentiometric glucose biosensor

Zafar H. Ibupoto, Sami Elhag, Omer Nur, and Magnus Willander, *Electroanalysis*, **2014**, 26, 1773.

My contribution: Partial contribution to growth design, measurements and analysis of the data, and I wrote the first draft of the manuscript.

Paper IV

Dopamine wide range detection sensor based on modified Co₃O₄ nanowires electrode

Sami Elhag, Zafar H. Ibupoto, Xianjie Liu, Omer Nur and Magnus Willander, *Sensors and Actuators B*, **2014**, 203, 543.

My contribution: Design of the growth and all experimental measurements except the XPS measurement. I analyzed the data and wrote the first draft of the manuscript.

Paper V

Efficient donor impurities in ZnO nanorods by polyethylene glycol for enhanced optical and glutamate sensing properties

Sami Elhag, Kimleang Khun, Volodymyr Khranovskyy, Xianjie Liu, Magnus Willander and Omer Nur, *Sensors*, **2016**, 16, 222.

My contribution: I designed all growth experiments and performed all the experimental measurements except the XPS and PL measurements. I analyzed the data and wrote the first draft of the manuscript.

Paper VI

Low-temperature growth of polyethylene glycol-doped BiZn₂VO₆ nanocompounds with enhanced photoelectrochemical properties

Sami Elhag, Daniel Tordera, Tymèle Deydier, Jun Lu, Xianjie Liu, Volodymyr Khranovskyy, Lars Hultman, Magnus Willander, Magnus P. Jonsson and Omer Nur, J. Mater. Chem. A, **2017**, 5, 1112.

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Related work but not included in the thesis:

Synthesis of Co₃O₄ cotton-like nanostructures for cholesterol biosensor

Sami Elhag, Zafar H. Ibupoto, Omer Nur, and Magnus Willander, Materials, **2015**, 8, 149.

Photocatalytic properties of different morphologies of CuO for the degradation of Congo red organic dye

Azar S, Khani, Zafar H. Ibupoto, Sami Elhag, Omer Nur and Magnus Willander, Ceramics International, **2014** 40, 11311.

Fabrication of sensitive potentiometric cholesterol biosensor based on Co₃O₄ interconnected nanowires

Zafar H. Ibupoto, Sami Elhag, Omer Nur, and Magnus Willander, Electroanalysis, **2014**, 26, 1928.

Supramolecules-assisted ZnO nanostructures growth and their UV photodetector application

Kimleang Khun, Sami Elhag, Zafar H. Ibupoto, Volodymyr Khranovskyy, Omer Nur and Magnus Willander, Solid State Sciences, **2015**, 41, 14.

Conference articles

Comparison between different metal oxide nanostructures and nanocomposites for sensing, energy generation and energy harvesting

Magnus Willander, Hatim Alnoor, Sami Elhag, Zafar H. Ibupoto, Eman S. Nour, and Omer Nur, Proceedings of SPIE, Oxide-based materials and devices, **2016**, Volume 9749.

Zinc oxide nanostructures and its nano-compounds for efficient visible light photocatalytic processes

Rania E. Adam, Hatim Alnoor, Sami Elhag, Omer Nur and Magnus Willander Proceedings of SPIE, Oxide-based materials and devices, submitted, **2017**.

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List of abbreviations

Abbreviation	Word or Phrase
ISE	Ion Selective Electrode
IEP	Isoelectric Point
COx	Cholesterol Oxidase
GOx	Glucose Oxidase
ZnO	Zinc Oxide
Co ₃ O ₄	Cobalt Oxide
ACG	ACG Aqueous Chemical Growth
BiVO ₄	Bismuth Vanadate
BiZn ₂ VO ₆	Bismuth Zinc Vanadate
NCs	Nanocompounds
NBs	Nanobelts
NRs	Nanorods
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
PL	Photoluminescence
pH	Potential of Hydrogen
JCPDS	Joint Committee on Powder Diffraction Standards
HMT	HexaMethyleneTetramine
SDS	Sodium Dodecyl Sulfate
SDBS	Sodium Dodecyl Benzene Sulfonate
NaPTS	Sodium <i>P</i> -Toluenesulfonate
CTAB	Cetyl Trimethyl Ammonium Bromide
PEG	Polyethylene Glycol
PEC	Photoelectrochemical
PBS	Phosphate Buffered Saline
Ag/AgCl	Silver/Silver Chloride
LOD	Limit of Detection

List of figures

Figure 1.1: (a) Schematic diagram of a chemical sensor and (b) proposed ZnO nanorods based modified chemical electrode.....	3
Figure 2. 1: (a) The wurtzite crystal structure of ZnO and (b) the growth habit of the ZnO crystal. ^{54,55}	10
Figure 2. 2: (a) The hydrophobic part is interacting more strongly with oil drop than with water and (b) PEG with abundant hydrogen.....	14
Figure 3. 1: (a) Schematic diagram for the growth process of ZnO NRs and (b) optical photograph illustrating the substrates coated with ZnO seeds when introduced horizontally and upside-down in the growth solution in normal laboratory glass beaker.	19
Figure 3. 2: SEM images of Co ₃ O ₄ wire-like nanostructure synthesized with an equimolar concentration (0.1 M) urea and cobalt chloride in 100 mL deionized water. ¹¹²	20
Figure 3. 3: (a) Scheme showing the growth process of the BiZn ₂ VO ₆ NCs and (b) SEM image of the BiZn ₂ VO ₆ nanostructures grown for 4 h laying on the top of vertically aligned ordered ZnO nanostructure. ¹⁰⁶	21
Figure 3. 4: Illustration of the fabrication of modified electrodes: spin coating of seed layer on Au coated glass, growth of the nanostructures, immobilization of polymeric membrane by deep coating and proposed mechanism of CME where a DA accumulated. ¹⁰³	22
Figure 3. 5: (a) XRD pattern of ZnO NRs grown on Au-coated glass substrate and (b) the standard card of bulk ZnO.	25
Figure 3. 6: A digital photograph of the SEM at IFM Department at Linköping University, Sweden.	26
Figure 3. 7: (a) TEM image of a BiZn ₂ VO ₆ and the inset shows the corresponding selected area electron diffraction (SAED) pattern and (b) EDX mapping showing the Bi, Zn, and V distributions. ¹⁰⁶	26
Figure 3. 8: Room temperature PL spectra of BiZn ₂ VO ₆ NCs grown on Au with and without the presences of PEG. ¹⁰⁶	28
Figure 3. 9: UV-Vis. absorption spectrum of BiZn ₂ VO ₆ NCs, an absorption peak at around ~ 482 nm corresponds to an optical band gap of about 2.57 eV. ¹⁰⁶	28
Figure 3. 10: Basic principle of the XPS technique.	29
Figure 3. 11: XPS spectra of the as grown Co ₃ O ₄ nanostructures on Au (a) a wide scan, (b) Co 2p, and (c) O1s spectra. ¹⁰³	30
Figure 3. 12: (a) Schematic diagram showing a typical potentiometric glucose biosensor and (b) a photograph of the three-electrode cell setup using a metal oxide nanostructure based CMEs.	31
Figure 4. 1: SEM images of ZnO NRs, (a) as grown and before membrane immobilization, (b) high magnification showing the relatively large aspect ratio of the grown ZnO NRs, (c) after polymer membrane immobilization and (d) after measurements. ¹⁰²	33
Figure 4. 2: (a) The calibration curve for the presented dopamine chemical sensor giving the linear calibration equation as: $y = 49.857x + 246.6$ and (b) the response time measured in 0.01 mM concentration of dopamine. ¹⁰²	34
Figure 4. 3: XRD spectra of the ZnO nanostructures grown with and without the different surfactants. ⁵¹	36
Figure 4. 4: SEM images of the as-grown ZnO nanostructures after adding the surfactants (a) ZnO:SDBS nano-wurtzite structure, (b) ZnO:SDS nano-foam-like structure, (c) ZnO:NaTPS nano-hexagonal-like structure and (d) ZnO:CTAB interconnected nano-disk-like structure. ⁵¹	37
Figure 4. 5: Calibration curve for enzymatic glucose sensors where the ZnO nanostructures grown with assistance of: (a) CTAB, (b) NaPTS, (c) SDBS, (d) SDS, and (e) ZnO NRs with the standard growth condition i.e. without surfactants. The insets proposed Fermi lelevel position at ZnO surfaces. (f) Room temperature PL spectra of the product of ZnO nanostructures. ⁵¹	38

Figure 4. 6: SEM images of Co_3O_4 nano-flowers comprised on nanowires fabricated on the Au coated glass substrate using different concentrations of urea with a low and high magnification. ¹⁰⁴	39
Figure 4. 7: (a) Calibration curve of the fabricated $\text{GOx}/\text{C}_3\text{O}_4$ nanoflowers/Au electrode to detect glucose molecules for the concentrations from 1 μM to 10 mM and the linear calibration equation is: $y = -56,9x - 213,7$ and (b) the selective response of the CMEs in the presence of common interferents at concentrations of 100 μL of 100 mM copper, ascorbic acid, uric acid, or urea, respectively. ¹⁰⁴	40
Figure 4. 8: SEM images show the morphology of the Co_3O_4 nanostructures grown with a different amount of SDBS (a) 0.1 and (b) 0.05 g with high and low magnifications and both of them are dense with a high aspect ratio. ¹⁰³	42
Figure 4. 9: XRD pattern of the Co_3O_4 nanostructures on Au coated glass. ¹⁰³	43
Figure 4. 10: Calibration curve showing the sensitivity and the linear response range of our constructed CMEs. ¹⁰³	43
Figure 4. 11: (a) UV-Vis absorption spectra and (b) plot of $(\alpha E)^2$ versus photon energy for the Co_3O_4 nanostructures. ¹⁰³	44
Figure 4. 12: SEM images of the ZnO NRs obtained with different concentrations of the PEG. ¹⁰⁵	45
Figure 4. 13: Schematic represent the four H sites in ZnO. ¹⁴¹	46
Figure 4. 14: Room temperature PL spectra of ZnO NRs grown on Au coated glass with and without presences of PEG showing a sharp UV peak accompanied by two broad visible emission peaks. ¹⁰⁵	47
Figure 4. 15: (a) UV-Vis absorption spectra of ZnO NRs grown on glass with different amount of PEG and (b) the plot of $(\alpha E)^2$ versus photon energy. ¹⁰⁵	48
Figure 4. 16: XPS study of the as grown pristine ZnO NRs (solid line) and 0.1% w/v PEG doped ZnO NRs with 0.1% w/v PEG on Au (a) O 1s and, (b) Zn 2p spectra. ¹⁰⁵	48
Figure 4. 17: (a) Mott-Schottky plots of the pristine and PEG-doped ZnO NRs with different amount in 0.1 M LiClO_4 and (b) shows the increases of the capacitances upon the increase of the PEG amount. ¹⁰⁵	49
Figure 4. 18: Different properties of a potentiometric chemical sensor using ZnO NRs based CMEs to detect glutamate molecules (a) and (b) shows a comparison calibration curve between the pristine and the PEG-doped ZnO NRs, respectively, (c) the response time and (d) the selective response in the presence of 100 μL of 100 mM of common interferents. ¹⁰⁵	51
Figure 4. 19: SEM of (a) PEG-doped ZnO NRs, (b) PEG-doped ZnO nanobelts, (c) PEG-doped BiZn_2VO_6 NC grown in 4 h and (d) side view of (c). ¹⁰⁶	52
Figure 4. 20: (a) XRD patterns of ZnO nanobelts, PEG-doped ZnO nanobelts, BiVO_4 , and PEG-doped BiZn_2VO_6 nanocompound grown by the low-temperature aqueous solutions hydrothermal synthesis for 4 and 10h, (b) TEM image of a BiZn_2VO_6 and the inset shows the corresponding SAED pattern and (c) EDX mapping. ¹⁰⁶	53
Figure 4. 21: XPS spectra of (a) and (b) O1s and V2p of the as grown BiVO_4 and BiZn_2VO_6 NCs on Au coated glass, respectively, (c) Bi4f for both the BiVO_4 and the BiZn_2VO_6 and (d) Zn 2p spectrum for BiZn_2VO_6 NCs. ¹⁰⁶	54
Figure 4. 22: (a) UV-Vis absorption spectrum of the BiZn_2VO_6 grown on glass with the same procedure as that which was used for the Au coated glass (b) the room temperature PL spectra of BiZn_2VO_6 NCs grown on Au with and without the presences of PEG. ¹⁰⁶	56
Figure 4. 23: (a) Linear sweep voltammetry of the ZnO nanobelts, PEG-doped ZnO nanobelts, BiZn_2VO_6 and PEG-doped BiZn_2VO_6 NCs electrodes in dark and under solar illumination (AM 1.5G) and (b) Chronoamperometry I-t curves of all electrodes at an applied voltage of +0.5 V with 50 s light on/off cycles. ¹⁰⁶	56

Table of contents

Abstract.....	II
Key words:.....	II
List of included papers.....	IV
Related work but not included in the thesis:.....	V
Acknowledgment.....	I
List of abbreviations.....	II
List of figures.....	III
Table of contents.....	V
Chapter 1 Background and introduction.....	1
1.1. Nanotechnology.....	1
1.2. Chemical sensors.....	2
1.2.1. Biosensors.....	4
1.3. Chemically modified electrodes.....	5
1.4. Metal oxide nanostructures.....	6
1.5. Outline and goals.....	7
Chapter 2 Properties of some metal oxides.....	9
2.1. Zinc oxide (ZnO).....	9
2.1.1. Biological properties.....	10
2.1.2. Zinc oxide based sensors.....	11
2.2. Cobalt oxide (Co ₃ O ₄).....	12
2.3. Bismuth zinc vanadate (BiZn ₂ VO ₆).....	13
2.4. Organic additives (surfactant).....	13
Chapter 3 Synthesis and characterization of the CMEs.....	17
3.1. The fabrication and preparation of CEMs.....	17
3.1.1. Substrate preparation.....	17
3.1.2. Preparation of ZnO, Co ₃ O ₄ and BiVO ₄ seed solutions.....	18
3.1.3. Synthesis of ZnO nanorods.....	18
3.1.4. Synthesis of Co ₃ O ₄ nanostructures.....	20
3.1.5. Synthesis of the BiZn ₂ VO ₆ nano-compounds.....	21
3.2. Membrane, enzymes and CMEs preparation.....	22
3.2.1. Dopamine membrane preparation and the buffer solution.....	22
3.2.2. Immobilization of glucose oxidase on ZnO and Co ₃ O ₄ nanostructures.....	23
3.2.3. Immobilization of ZnO NRs with L-glutamate oxidase (GluOx, EC 1.4.3.11).....	23
3.3. Characterization techniques.....	24
3.3.1. X-ray diffraction.....	24

3.3.2. Scanning electron microscope	25
3.3.3. Transmission electron microscopy	26
3.3.4. Photoluminescence spectroscopy	27
3.3.5. Ultraviolet-visible spectroscopy	28
3.3.6. X-ray photoelectron spectroscopy	29
3.3.7. Electrochemical and photoelectrochemical characterizations	30
Chapter 4 Findings and summary	33
Incorporating β -cyclodextrin with ZnO nanorods: A potentiometric strategy for selectivity and detection of dopamine (paper I)	33
Habit-modifying additives and their morphological consequences on photoluminescence and glucose sensing properties of ZnO nanostructures, grown via aqueous chemical synthesis (paper II)	35
Effect of urea on the morphology of Co_3O_4 nanostructures and their application for potentiometric glucose biosensor (paper III)	38
Dopamine wide range detection sensor based on modified Co_3O_4 nanowires electrode (paper IV)	41
Efficient donor impurities in ZnO nanorods by polyethylene glycol for enhanced optical and glutamate sensing properties (paper V)	44
Low-temperature growth of polyethylene glycol-doped BiZn_2VO_6 nano-compounds with enhanced photoelectrochemical properties (paper VI)	51
Chapter 5 Conclusion and future prospects	57
References	61

Chapter 1 Background and introduction

1.1. Nanotechnology

The term nanotechnology^{1,2} comes from the combination of the Greek numerical prefix nano meaning one billionth used primarily with the metric system *i.e.* (10^{-9} m) and the word technology. Nanotechnology is *"the construction and utilization of functional structures with at least one characteristic dimension measured in nanometers"*.³ Despite the fact that nanotechnology has appeared only recently. However, in 1959 Nobel laureate physicist Richard Feynman first described nanotechnology while he did not name this new research field. He suggested "nanotechnology" during a famous speech entitled *"There is Plenty of Room at the Bottom"* at an American Physical Society meeting in Caltech. Feynman had envisioned and described the potential that can be gained when manipulating and controlling matter at small scale.⁴ In 1974, the term nanotechnology was introduced and defined by the Scientist Norio Taniguchi, Tokyo Science University in a conference paper as *"mainly consists of the processing, separation, consolidation and deformation of materials by one atom or by one molecule"*.^{1,5} In 1981, Nobel laureate physicist Gerd Binnig and Heinrich Rohrer have developed an instrument for imaging atoms and molecules on surfaces called scanning tunneling microscope (STM).^{6,7} After a while, in 1985 fullerenes have been discovered by Nobel laureates in chemistry Harry Kroto, Richard Smalley and Robert Curl.^{8,9} This was followed by the preparation of needle-like tubes of carbon by the physicist Sumio Iijima, from NEC Corporation in 1991.¹⁰ Since then the existence of nanoscale-materials have been revolutionizing towards the fabrication of nanodevices and the development of new devices with improved performance relative to that of the same bulk material.

Why do people are interested in nanoscale materials?

In fact, artificial nanoscale materials have been recognized according to the literature since the fourth century AD.¹¹ Romans have used nanoparticles of gold and silver to decorate glasses and cups. The first book on preparing and size measurements of gold nanoparticles during the first decade of the 20th century was written by Nobel laureates in chemistry Richard Adolf Zsigmondy.^{12,13} However, from the mid-1980s the

progress in nanometer-scale science and technology in general have been developed and has become popular.² At the present time, the impact of nanotechnology is clearly seen everywhere around us and is great support and help in solving many problems such as energy shortage, climate change, fatal diseases and also can create new products that would be appreciated in electronics, medicine and for many other fields.

Functional low dimensional (LD) nanostructures such as nanorods, nanowires, nanotubes and nanobelts are gaining vast consideration in the state of the art applications of the nanotechnology *e.g.* in electronics, optoelectronics and the medical filed. The most salient attribute of LD nanostructures is the use for both efficient transport of charged carriers combined with optical excitation. These two factors make LD nanostructures promising for a variety of applications. In particular, applications with great potential like the demonstration of photoelectrochemical (PEC) cell using visible light spectrum are becoming hot topic of research at the moment. In addition to the above mentioned advantageous of LD nanostructures, their relatively high surface area to volume ratio and their modified charged carriers transport properties makes quantum confinement effects very sensitive to relatively small perturbations.

1.2. Chemical sensors

The sensor field has grown enormously since the first well-known published paper on the oxygen electrode in 1956 by the biochemist Leland C. Clark Jr, who is known as the father of the biosensor concept.^{14, 15} Further, in 1962, Clark and Lyons introduced the “enzyme electrode,” as a new terminology in the field of biosensors. In their published work in which glucose oxidase was entrapped at an oxygen electrode using a dialysis membrane. They found that, as the glucose concentration was increasing the oxygen concentration was decreasing.^{15,16} According to the international union of pure and applied chemistry (IUPAC) nomenclature, “*a chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis into an analytically useful signal*”. The chemical information, mentioned above, may originate from a chemical reaction of an analyte or from a physical property of the system investigated.¹⁷ A chemical sensor (schematically shown in Figure 1a) is usually composed of two main parts; the first is the receptor part and the second is the transducer part. In some cases, a third part is included. This third part can be a membrane for selectivity tuning.

Today, membranes have become an important part of our daily life with constant advances in their preparation technology.^{18,19} Membranes are used in a wide range of applications *e.g.* for drinking water purification, in food and in drug industries and to separate a specific molecule or substances. Depending on their functional properties, membranes are used for specific application.¹⁸ It is very common that synthetic membranes are used in research laboratories and in the industry for separation processes, *i.e.* as a selective material. The selective part of the membrane can be made of polymeric material, ceramics, glass or made of metals. The pressure, concentration, electrical or chemical gradient across the membrane could be the driving force of the transport process. Polymeric membranes are usually made of polymers, function as a selective element that can only pass through a specific chemical species and block others. Hence, these polymeric membranes are a key part of potentiometric sensors.¹⁸⁻²⁰ In the receptor part or the selective layer of a sensor which may contains a biological element such as enzymes, antibodies or a chemically selective layer “membrane” that has two important characteristics *i.e.* semi permeability and the selectivity. Hence, the chemical information is converted to another energy form, which is then detected and measured by the transducer part of the sensor.

Figure 1.1: (a) Schematic diagram of a chemical sensor and (b) proposed ZnO nanorods based modified chemical electrode.

The transducer part has the capability of converting the chemical energy into another detectable analytical signal form.¹⁷ The principle operation of the transducer is usually used to define the class of the chemical sensor to be either optical, electrical or electrochemical etc.... However, the latter and specifically a certain subgroup from it would be considered in this thesis.

Electrochemical devices operate by transforming the interaction between the analyte in question and the electrode into measurable useful signal. This interaction may be stimulated by electric signal or could be due to spontaneous interaction at no stimulating current.¹⁷ Furthermore, electrochemical sensors can be categorized as, colorimetric, amperometric, conductometric or potentiometric sensors. One of the subgroups is the potentiometric sensor, where the built in potential of the working electrode *e.g.* ion selective electrode (ISE), a redox electrode or metal/metal oxide electrode, is measured versus a reference electrode, usually silver/silver chloride (Ag/AgCl) electrode.¹⁸⁻²³ It is worth to mention that, biosensors are not categorized as a separate class of sensors due to the fact that their working process is generally the same as that of chemical sensors.^{20,23} In principle the latter have a chemical or molecular target to be measured and biosensors target a biomolecule via receptor (biological sensing element) of interest for measurement.

1.2.1. Biosensors

Generally, there are two categories of biosensors,²³ the first is affinity biosensors while the second is catalytic biosensors. Affinity biosensors operation is based on the irreversible and non-catalytic binding of molecules by the receptor element. Biological analytes like antibodies, nucleic acids, dyes, cell membrane receptors and other specific biological binding elements are typical examples of bio-affinity agents. By utilizing affinity interactions, biosensors are able to separate individual or other selected compounds in any complex mixture of biomolecules and this separation can either be based on chemical or biological activity. The second class of biosensor, *i.e.* the catalytic biosensors are operating based on catalytic reactions. Here, for catalytic biosensors, biocatalysts such as enzyme, which is an element, that recognize and bind to the analyte in question. Then, this binding is followed by catalytic reactions, which then converts the undetectable signal to a detectable signal like *e.g.* electrical signal.

1.3. Chemically modified electrodes

Previously, metals and semiconductors have been used a lot as sensing layer. In 1952, Brattain and Bardeen reported that the potential of the semiconductor germanium (Ge) can be changed in different gaseous ambients.²⁴ Seyama *et al.*, used metal oxides such as zinc oxide (ZnO) in gas sensors for first time in 1962.²⁵ Later in 1967, Shaver demonstrated that the sensitivity of tungsten oxide (WO₃) could be enhanced by “activation” through the deposition of a small amount of platinum.²⁶ In 1969, also biosensors have witnessed a progress where Guibault and Montalvo reported the first sensing of urea using the potentiometric approach based on enzyme modification of the surface of Beckman cationic electrode, which is responsive to ammonium ions.²⁷ However, the term chemically modified electrodes (CMEs) was introduced by Moses *et al.*, in their published work in 1975 in which tin oxide (SnO₂) was modified by a functional group to be more chemically predictive electrode.^{28,29} The international union of pure and applied chemistry defined CMEs as “*the electrodes made of a conducting or semiconducting material which is coated with a selected monomolecular, multimolecular, ionic or polymeric film of a chemical modifier and that by means of faradaic (charge-transfer) reactions or interfacial potential differences (no net charge transfer) exhibits chemical, electrochemical and/or optical properties of the film*”.³⁰ Briefly, To suit a specific purpose of detection, CMEs surface is modified according to the needed purpose. Usually, for the direct oxidation to be achieved at bare electrode surfaces large over potentials are required.³¹ In addition to that, modification on the electrode surface may have fundamental demands that include selectivity and/or electron-transfer creation or catalysis of slow electrode reactions.³² Therefore, CMEs have been used in several applications such as electroanalysis,³³ molecular electronics,³⁴ electrochromic display devices,³⁵ chemical sensing³⁶ and solar energy conversion.³⁷

The sensor electrode size requirements make the CMEs a highly desirable option²³ that is being intensely pursued since 1940s. It is important to recall that, to detect and measure the concentration of oxygen in biological tissues, David and Brink have used microelectrodes during the 40s.³⁸ In fact, the fabrication of a thermodynamically stable electrochemical interface for a CME is a challenging task. Early studies, suggested the use of either incorporated redox-active component into the ISE membranes like lipophilic silver complex or involving a polymeric layer between the electrode and the ISE membranes that could provide a suitable electronic and ionic conductivity.³⁹ Metal oxide

nanostructures are playing an important role as the means to this end. The chemical structural and electronic surface composition of metal oxide nanostructures provide a suitable CMEs platform.⁴⁰

1.4. Metal oxide nanostructures

Metal oxide nanostructures are of interest as electrode materials for sensor applications (Fig. 1b) and energy conversion because of; (1) they provide large surface area to volume ratio that could carry high degree of the membrane molecules and exposing large surface for the oxidation of the analyte molecules on the surface of the modified electrodes. (2) provide biological activity on the electrode surface for enzymes immobilizing (biocompatibility) and relatively it is simple to coat different membrane on the electrode surface, and (3) provide fast electron transfer to catalyze slow electrode reactions (redox-active).

In general, there are two types of catalytic materials used in sensors technology. These are metals and semiconductor metal oxides. In the case of metals, the incomplete d-shell free electrons bear the responsibility of sensing. This is why metals like Pt, Pd, Rh, and Ir are commonly used as active catalysts since they possess incomplete d-shells. While metal oxide sensing mechanisms depend on a different mechanism for sensing. For metal oxides, the existence of specific lattice point defects allows a certain change of the electrical conductivity in the metal oxide. Although in metals, also, the conductivity is modified but this modification is relatively small and it is difficult to detect. Hence and due to this most of the gas sensors were fabricated using metal oxides.⁴¹ Nevertheless, the interaction of metal oxide and aqueous solutions is rather complex. Usually, metal oxide-aqueous interfaces are reactive due to the acid-base, ligand exchange and/or redox reactions involving protons (hydronium ions) and/or hydroxyl groups. The localization of these species at interfaces (adsorption) may result from electrostatic chemical reactions, and hydrophobic interactions between the surface and the sorbates.⁴²

Metal-oxides nanostructures are considered to be one of the most fascinating functional materials and have been widely deployed in various technological applications.⁴³ For sensing application using metal oxides microstructures, the first report was published in 1991 by Yamazoe where demonstrated that upon size reduction of SnO₂ the sensing characteristics can be improved.⁴⁴ After a decay in 2001, C. M. Lieber and co-workers reported a highly sensitive sensor based on boron-doped silicon nanowires.⁴⁵ They have demonstrated that semiconductors nanostructures are superior to their bulk

counterpart. Then, the interest among researchers working in nanoscience towards the synthesis or fabrication of nanostructures with desired dimensionality and size have been intensified.⁴⁶ In sensing technology, the higher sensitivity and lower limit of detection are driving force for new synthesizing morphologies and even new materials, *e.g.* composites. Thus, synthesis methods of metal oxide nanostructures are playing important role as the means to this end. Generally, there are two possible strategies: top down or bottom up approaches. At present time, since each approach has its own limitations, the most promising approach seems to be the combination of the bottom up growth methodologies with top down device fabrication technologies.⁴⁷ There are several experimental techniques to prepare metal oxide nanostructures such as the vapor-liquid-solid (VLS) that was discovered since 1960s by Wagner and Ellis for synthesis of Si whiskers or nanowires,⁴⁸ chemical vapor deposition and electrochemical deposition. All these are physical methods, while chemical methods also start to appear as promising methods. Among these chemical methods, the aqueous chemical growth (ACG). The ACG which can be considered to belong to “green chemistry”, is a low-temperature method for the synthesis of metal oxide nanostructures.⁴⁹ The ACG usually provides highly yield of the desired nanomaterial and facilitate scaling the nanodvices.⁵⁰ In addition to the low cost of this synthesis route, the ACG can be operated at sufficiently low-temperatures (< 100 °C) that allow the nanomaterials to be synthesized on any substrate *e.g.* plastic and paper. Furthermore, the simplicity to control the nanostructure morphology by different organic molecules is another advantage.⁵¹

1.5. Outline and goals

The goal of this thesis is to synthesis of metal oxide nanostructures by low cost wet chemical methods. Furthermore, these nanostructures are to be used for the development of CMEs with associated enhanced sensing and catalytic properties via doping with organic additives. The overall goal is pursued as follow:

First, potentiometric chemical sensors were utilized to selectively detect and quantify the amount of chosen analytes such as, dopamine, glucose or glutamate molecules. ZnO and Co₃O₄ nanostructures have been used as chemical sensors based CMEs to detect dopamine and glucose molecules while the glutamate molecules have been investigated by ZnO based CMEs. The second part of this thesis is to demonstrate visible

light-driven photoelectrochemical activities using BiZn_2VO_6 nanocompounds based CMEs.

Chapter 2 Properties of some metal oxides

In traditional metal oxide semiconductors, the sensing mechanism relies on the change to their surface potential at elevated temperature. Recently, the existence of nanomaterials have revolutionized the fabrication of chemical sensors without sophisticated steps. It is well established that, the addition of relatively small amount of impurities, can cause both the sensitivity as well as the selectivity of sensors to be enhanced. These added impurities usually act as donors (or acceptors). This will alter the doping concentration and hence the conductivity can be improved. These impurities can be realized by incorporating organic or inorganic additive materials to the metal oxide nanostructures. Among the metal oxides nanostructures, zinc oxide (ZnO), cobalt oxide (Co_3O_4) and bismuth zinc vanadate (BiZn_2VO_6) have attracted the attention of researchers in many laboratories for the development of different functional devices. Thus, have been considered in the present work. Organic additives that have been used in the present work are as follow: urea, sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), sodium p-toluenesulfonate (NaPTS), cetyl trimethyl ammonium bromide (CTAB) and polyethylene glycol (PEG). As mentioned above these organic additives were employed as dopants.

2.1. Zinc oxide (ZnO)

Zinc oxide is a promising metal oxide. It is unintentional n-type doped semiconductor material having a wurtzite structure under ambient condition.⁵²⁻⁵⁴ The wurtzite structure has hexagonal unit cell as shown in Figure 2.1a. Marino *et al.*, have shown that the crystal structure of ZnO is a hexagonal closed packing with Zn surrounded by four oxygen atoms and consequently has two polar surfaces.⁵³ The different surfaces of ZnO have different surface energies. The (0001) plane which is Zinc terminated possesses the maximum surface energy, while the (000 $\bar{1}$) plane which is oxygen terminated possesses the minimum energy. Due to this, and compared to other directions, the [0001] direction is the fastest growth direction (see Figure 2.1 b). Both the (0001) and (000 $\bar{1}$) are polar surfaces which are Zinc or Oxygen terminated, respectively. While other surfaces which are non-polar have equal numbers of O and Zn atoms.

Figure 2. 1: (a) The wurtzite crystal structure of ZnO and (b) the growth habit of the ZnO crystal.^{54,55}

2.1.1. Biological properties

ZnO is an important multifunctional material. However, for commercial industrial products in the near future, nanomaterials are expected to have a great impact. Therefore, here we deal with ZnO as a biological element; Zinc (Zn^{++}) itself, is a trace mineral that is second only to iron in the body. Unlike iron, where 80% of a total of about 3g in a human is in the heme group alone, similarly the total amounts of zinc in the human body spread among thousands of proteins. Zinc is essential for protein and DNA synthesis and maintenance. Furthermore, it is important for many physiological processes like wound healing, cell division and growth, stable proper sensation of the tasting and smelling. Zinc is also important for normal childhood growth in addition to a vital role in proper metabolism of carbohydrates and for adjusting proper sexual appetite. Since many decades ago, scientists know the role of zinc in the growth of microorganisms, plants and animals, but zinc role in humans was only known in 1963.⁵⁶

In recent past, it was discovered that Zn^{++} is released from ZnO nanostructure in uterine solution (biological solutions),⁵⁷ which is in agreement with the results of Z. L. Wang *et al.*,⁵⁸ They demonstrated that ZnO nanowires would be degraded into mineral

ions after immersion in horse blood. Moreover, zinc ion is expected to be transferred from the oxygen with lower stability constant to a ligand that has the higher stability.⁵⁹ However, there is consensus that zinc ion usually in cell biology is coupled with specific ligand (Cys and His) through tetrahedral coordination's fabricating what is so called zinc finger.⁶⁰ The number of the Cys and/or His is varying depending on the function of the finger. Nevertheless, it is important to note that, exposure to zinc oxide fumes from wedding can lead to metal fume fever.⁶¹

2.1.2. Zinc oxide based sensors

In addition to TiO₂⁶² and SnO₂⁶³ as being popular materials used to build gas sensors, ZnO with its attractive properties has been utilized for the same purpose. The principle of gas sensors operation is rely on the change of conductivity of a material as gas molecules are absorbed at its surface.²⁵ The exist of point defects on the surface of ZnO material, makes it very sensitive to gas detection as adsorbed gases can produce a large change in the surface conductivity. This change of the conductivity occurs at the grains due to charge transfer and band bending. The dominant defects identified in these surfaces as with other oxides are O vacancies. These surface defects do not produce any new filled electronic states in the bandgap *i.e.* not relying on the bulk properties.⁵² In the intrinsic range, ZnO is sensitive to O₂, O₃, H₂, CO, and simple hydrocarbons. Moreover, ZnO is known as a good sensing material to detect reducing gases such as H₂, CH₄, and CO.⁶⁴ Nevertheless, as a gas sensor material, ZnO is not a good candidate because it suffers from long terms stability and its selectivity can be poor if the ambient is changed.

Due to the relatively high surface area to volume ratio of ZnO nanostructures, they have become attractive as gas sensors with potential to overcome some fundamental limitations. Recently, and due to the polar and nonpolar surfaces, bio-safety (*antibacterial*), biocompatibility, low cost as well as the electronic and the optical characteristics of nanostructures that are superior to the bulk of this material, research on nanostructures of ZnO has intensified. As it is well known, the electronic and optical properties of ZnO nanocrystals depend on their size and morphology.⁶⁵ This can be attributed to the surface-to-volume ratio rather than to the quantum confinement.⁶⁶ ZnO nanostructures have received high interest due to their potential for opto-electronics and sensor devices. For instance in light-emitting diodes, solar cells, photo-catalysis and

biosensors. The interest for optoelectronic application is because, ZnO has a wide band gap of 3.37 eV and a relatively high exciton binding energy of 60 meV along with the defect emissions that covers the whole visible region.^{67,68} ZnO exhibits remarkable properties for sensing applications due to its biocompatibility and high isoelectric point (IEP) ~ 9.5 ⁶⁹ (The IEP is the pH value at which a molecule has no net surface electrical charge). These properties are suitable for the adsorption and immobilization of proteins or enzymes with relatively low IEP through electrostatic attraction, *e.g.*, cholesterol oxidase (COx) and glucose oxidase (GOx) with IEP value of ~ 4.6 and 4.2 respectively. Due to these properties, an enhanced direct electron transfers between the enzyme's active sites and the electrode can be achieved.⁷⁰ It is worth mentioning that, the physical and chemical properties of metal oxides can be tuned through adjusting and controlling their structure and morphology^{71,72} and therefore, issues related to ZnO morphology have been considered in this work.

2.2. Cobalt oxide (Co₃O₄)

Cobalt oxide has three well-known polymorphs:⁶¹ the cobalt monoxide (CoO), the dicobalt trioxide; (Co₂O₃) and the tricobalt tetraoxide (Co₃O₄). The latter, is the most functional material used for many applications including energy storage,⁷³ heterogeneous catalysts,⁷⁴ electrochromic devices,⁷⁵ sensors⁷⁶ and recently in overall water-splitting.⁷⁷ Due to its potentials as a robust solar selective absorber it has been employed for efficient water splitting.⁷⁸ As early as ancient times, Co₃O₄ has been used as agent for coloring glass, while during our modern time it has been used in pigments in glazing pottery and porcelain and for coloring of enamels. Also cobalt is a supplier of vitamin B12 for plants and animals. As a separate metal, cobalt was isolated in 1735 and confirmed as an element during 1780.⁶¹ In addition to low cost and environmentally benign nature, Co₃O₄ is a p-type semiconductor and has both direct and indirect band gap of 2.10 eV and 1.60 eV, respectively.⁷⁹ It crystallizes in a spinel structure with the Co³⁺ ions occupying the octahedral sites, and a Co²⁺ ions occupying tetrahedral sites with the oxygen ions forming a close-packed face centered cubic lattice.⁸⁰ This arrangement of ions leads to the fact that the Co₃O₄ has explicit surface features with different polar terminations.⁸¹ In addition, Co₃O₄ has a paramount electro-catalytic activity^{74,76,77 and 82} and relatively high IEP value of ~ 8 .⁸³

2.3. Bismuth zinc vanadate (BiZn_2VO_6)

Among the researched nanomaterials, bismuth zinc vanadate (BiZn_2VO_6) nano-compound has a new crystal structure type and belong to the mixed metal oxide structures family, usually denoted by BiM_2AO_6 ($\text{M} \equiv \text{Mg, Ca, Cd, Cu, Pb, Mn or Zn; A} \equiv \text{V, P or As}$). This family of metal oxide nanostructures possess a unique physical and chemical properties with interesting applications *e.g.* converting visible light to chemical energy and pollutant degradation.⁸⁴⁻⁸⁶ Typically, they are prepared by solid-state reactions that involves high-temperature ($> 700^\circ\text{C}$) which are considered to be expensive and environmentally unfavorable. Furthermore, the products may contain undesirable phases, which are usually inhomogeneous with regard to large particle size and can be characterized by low surface area that is unfavorable in the photocatalysis. Due to this, they have not been used frequently in these applications. However, recent advances in the wet chemical methods which could pave the way for these materials to be used in various applications. BiZn_2VO_6 compound with a band gap (E_g) experimentally measured and calculated to be ~ 2.4 ⁸⁵ and 1.6 eV,⁸⁷ respectively, makes it suitable for visible light driven water oxidation. In addition, it could merge both advantageous of its component parts (ZnO , and BiVO_4) materials. Note, ZnO ($E_g \sim 3.3$ eV) only utilize the ultraviolet component ($<5\%$) of the solar spectrum beside that it has also high recombination rate.⁸⁸ The same scenario is valid for the BiVO_4 . Although it is the most promising photocatalyst for water oxidation, poor photo-induced electron transportation, slow kinetics of oxygen evolution and a high charge recombination, are example of its limitations.⁸⁹ Thus, BiZn_2VO_6 compound is expected to combine the high electron mobility of ZnO to facilitate charge transport and the robust light absorption of BiVO_4 component.

2.4. Organic additives (surfactant)

Surfactants are used routinely in numerous industrial applications and products, like detergents, fabric softeners, emulsions soaps, paints, adhesives and inks. Surfactant molecules have both hydrophobic (water avoiding) and hydrophilic (water liking) portions in their structure (Figure 2.2a). Keeping in mind that the surfactants can be classified to anionic (-), cationic (+), amphoteric (- and +), or nonionic, depending on their hydrophilic part (the head group). Therefore, most important uses of surfactants are in lowering the surface or interfacial tension between two liquids. Due to this fact,

surfactant molecules are showing a crucial role in the growth process of metal oxide nanocrystals.⁹⁰ To the best of our knowledge, as one of the several methods for nanoscale material synthesis, surfactant based wet chemical processes has been very popular among researchers since the pioneering work by Pileni in 1993.⁹¹ Where he used reverse micelles to synthesize either well-defined nanosized crystallites or chemically modified enzymes. Although many researchers studied the effect of organic additives such as surfactants on the growth of metal oxide nanostructures, the full explanation has not been yet realized. However, the most practical explanation is that the surfactants or organic additives are considered as habit modifying additives that can tune the morphology.⁵⁵ The habit-modifying additives are usually adsorbed selectively on one face and hence inhibit further growth on this face. Therefore, there is a consensus that surfactants are usually used to tune the morphology of the grown nanostructures and improve the performance of an electrode. Inamdar *et al.* investigated the effect of the surfactant on the growth of ZnO film morphology and the associated their optical and photo-electrochemical performance.⁹² Wang *et al.* described that, the addition of surfactant has a dual effect; one in the morphology and the other is enhancing the sensitivity.⁹³ Among the many organic additives, sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), sodium *p*-toluenesulfonate (NaPTS), cetyl trimethyl ammonium bromide (CTAB), urea or polyethylene glycol (PEG) have been utilized for the presented research work.

Figure 2. 2: (a) The hydrophobic part is interacting more strongly with oil drop than with water and (b) PEG with abundant hydrogen.

In recent past, some authors have utilized PEG (Figure 2.2b) for growth of ZnO. Tian *et al.* reported that PEG was acting as a reaction media for the growth of the ZnO microspheres.⁹⁴ While Ghule *et al.* utilized the PEG as a stabilizing agent for ZnO nanorods,⁹⁵ and Inamdar *et al.* found that the PEG to be dominant in modifying the morphology of ZnO thin films.⁹² Long *et al.* synthesized ZnO by using hexamethylenetetramine (HMT) as precursors while adding different amounts of PEG as

the dispersant to grow flower-like structures,⁹⁶ and Teterycz *et al.* formed ZnO nanoballs by mixing zinc acetate and PEG.⁹⁷ Moreover, recently we have used PEG as growth template to synthesize cupric oxide (CuO) and cobalt oxide (Co₃O₄) nanostructures.^{98,99} In fact, the PEG is completely miscible with water and has found many applications in current technology as antifreeze when mixed with water.¹⁰⁰ This is probably due to its strong hydrogen bonding interaction in water with the hydroxyl oxygen atoms of PEG.¹⁰¹ Therefore, we assume that disruption of hydrogen bonding when dissolved in water is a hydrogenated-environment for growth of ZnO nanostructures (Figure 2.2b). Here, we show the successful experiments on the utilization of PEG as a hydrogen supplier for the growth of ZnO nanorods (NRs) using a wet chemical process.

Chapter 3 Synthesis and characterization of the CMEs

3.1. The fabrication and preparation of CEMs

In this thesis, chemically modified electrodes (CEMs) have been fabricated utilizing glass substrates coated with gold (Au) then followed by the growth of different metal oxide nanostructures by the aqueous chemical growth (ACG) method. Further, organic additives were chosen to tune the morphology and other properties of the grown metal oxide. Then, we have correlated the observed properties in sensing and photoelectrochemical (PEC) applications to the applied chemical modification.

First, a potentiometric chemical sensor was utilized to detect the presence and quantify the amount of some analytes in solutions, specifically, dopamine, glucose and glutamate molecules were the chosen analytes. ZnO and Co₃O₄ nanostructures have been involved in the chemical sensors based CMEs to detect dopamine and glucose molecules.^{102, 103, 51 and 104} and the glutamate molecules have been investigated by ZnO based CMEs.¹⁰⁵ The second part of this thesis we investigated the potential of BiZn₂VO₆ nano-compounds (NCs) based CMEs for PEC processes.¹⁰⁶

All reagents were of analytical grade and were used without being submitted to any additional purification. All the chemicals were purchased from Sigma-Aldrich (Stockholm, Sweden), below and in brief, the details of the preparation steps are given.

3.1.1. Substrate preparation

Usually we start with the substrate preparation step. This is important to avoid any possible contamination and any unwanted particles on the electrode. First, to fabricate CMEs, a 2 x 1 cm² glass substrates, were dipped in ultrasonic bath using isopropanol and acetone sequentially for 5-10 minutes. Then washed with deionized water and dried by a nitrogen gas. Secondly, the cleaning step was followed by the deposition of the Au thin layer on the glass substrate. In order to coat the glass by Au, they were affixed into the vacuum chamber of an evaporator instrument (Satis CR 725, Zurich, Switzerland) at the pressure of (2 × 10⁻⁶ mbar). After this, an adhesive layer of 20 nm of Titanium (Ti) was evaporated on the substrates and then a 100 nm thickness layer of Au thin film was evaporated.

3.1.2. Preparation of ZnO, Co₃O₄ and BiVO₄ seed solutions

In order to synthesize ZnO nanostructures, ZnO nanoparticles (seed-layer) were prepared by colloidal chemical techniques according to Henglein *et al.*, report with tiny modifications.¹⁰⁷ In a typical synthetic route, a 0.01M of zinc acetate dehydrate (274 mg) mixed with 125 ml of methanol absolute methanol (99%), kept at 60 °C under continuous stirring. Then, a 109 mg of potassium hydroxide (KOH) was dissolved in 65 ml of methanol (0.03M). Drop-wise from the later solution was added to the former solution under continuous stirring for 2 hours. These solutions were transferred into a Teflon glass bottle and kept at room temperature before it was spun coated on the Au coated glass substrate for several times to insure uniform spatial distribution. The main reason of this seed layer is to be as nucleation site that is initiating and directing the growth as well as to overcome the thermodynamic barrier between heterogeneous materials.¹⁰⁸ The expected average size of this ZnO nanoparticles in the seed layer solution is around 3-5 nm.¹⁰⁹ The same techniques have been applied for the preparation of Co₃O₄ and BiVO₄. However, a 0.01M cobalt acetate anhydrous in methanol was prepared and left for stirring at 60 °C for two hours. BiVO₄ samples were later used as control samples for x-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. The seed solution was prepared by using an equimolar concentration of 0.02 M of bismuth(III) nitrate pentahydrate and ammonium metavanadate in 25 ml methanol. This seed solution was either applied by dip- or spin coating on a cleaned Au coated glass substrates. The substrates containing the seed particles were then annealed at 120 °C for 5 min before dipping into the growth solution.¹⁰⁶

3.1.3. Synthesis of ZnO nanorods

The synthesis of the nanorods (NRs) have been accomplished by the ACG process under hydrothermal-like condition, that was developed by Vayssieres *et al.*¹¹⁰ The second step (see Figure 3.1), after the substrates seeded with zinc acetate dehydrate layer via spin coating technique at 1000 rpm for 20 s. The samples were annealed at a temperature of 120 °C for 5 min. Then after that, the substrates coated with ZnO seeds were introduced horizontally and upside-down to an equimolar concentration of 0.05 M of hexamethylenetetramine (C₆H₁₂N₄) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and kept in the preheated electric oven at 90 °C for 4-6 h.

Figure 3. 1:(a) Schematic diagram for the growth process of ZnO NRs and (b) optical photograph illustrating the substrates coated with ZnO seeds when introduced horizontally and upside-down in the growth solution in normal laboratory glass beaker.

The possible reactions involved in the synthesis of ZnO NRs are summarized below:¹¹¹

The HMT $((\text{CH}_2)_6\text{N}_4)$ plays a role as a buffer medium and supplies the ammonia (NH_3) during the growth. The NH_3 reacts with water and generates hydroxide (OH^-) ions and finally OH^- ions react with Zn^{2+} ion and yields $\text{Zn}(\text{OH})_2$. During growth the expected pH value might be between 6.5 and 7.¹¹¹ The produced $\text{Zn}(\text{OH})_2$ is thermodynamically unstable and it would be dehydrated when it is incorporated into the crystal, therefore could be referred as a growth unit.⁵⁵ Before the substrates were placed into the solution, and to prepare contact pads for the electrochemical measurements, a small part of the Au coated glass was covered. Finally, the samples were rinsed with deionized water for several times to avoid any residual salts on the surface of the nanostructures and then dried with flowing nitrogen gun.

For other doped ZnO nanostructures the only difference in the synthesis was that, the growth solutions were prepared separately then in each growth solution a certain amount of SDS, SDBS, NaPTS, CTAB, urea or PEG were added into the growth solution.

3.1.4. Synthesis of Co_3O_4 nanostructures

Figure 3. 2: SEM images of Co_3O_4 wire-like nanostructure synthesized with an equimolar concentration (0.1 M) urea and cobalt chloride in 100 mL deionized water.¹¹²

Usually the growth solution of the Co_3O_4 nanostructures is prepared by mixing an equimolar concentration (0.1 M) urea ($\text{CH}_4\text{N}_2\text{O}$) and cobalt chloride (CoCl_2) in 100 mL deionized water resulting in Co_3O_4 wire-like nanostructure. A scanning electron microscopy (SEM) image of the resulting Co_3O_4 nanowires is shown in Figure 3.2.¹¹² However, here in this thesis the concentration of the urea was varied in order to monitor the effect on the morphology of the synthesized Co_3O_4 nanostructures.

The amount of urea added in the growth solution was in the order of 0.23, 0.27, 0.3, and 0.4 M respectively, while the concentration of the cobalt chloride was kept constant at 0.1 M. The substrates containing Co_3O_4 nano-particles were fixed horizontally in the Teflon sample holder and dipped into the growth solution for 5 hours in a preheated electric oven at 90 °C. keeping in mind that, the seed solution was applied to the cleaned Au coated glass substrates by the dip coating method and then annealed at 120 °C for 5 minutes. After the completion of growth duration, the samples were cooled naturally at room temperature then washed with deionized water in order to remove any residual particles from the surface of the grown samples. The cobalt hydroxide nanostructures were annealed at 450 °C for 3 hours to convert the hydroxide phase to oxide phase. The

possible reactions involved in the synthesis of cobalt oxide nanostructures can be represented by the following equations:

3.1.5. Synthesis of the BiZn_2VO_6 nanocompounds

Figure 3. 3: (a) Scheme showing the growth process of the BiZn_2VO_6 NCs and, (b) SEM image of the BiZn_2VO_6 nanostructures grown for 4 h laying on the top of vertically aligned ordered ZnO nanostructure.¹⁰⁶

The mixed metal oxide BiZn_2VO_6 nanocompounds (NCs) was formed by BiVO_4 growth on top of the ZnO nanostructure, according to Zhou's and co-workers report with tinny modification at resulting in relatively shorter growth duration.¹¹³ In a typical

synthetic route, equimolar concentration of 0.02 M of bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and ammonium metavanadate (NH_4VO_3) were dissolved in 10 mL of nitric acid and a 70% (HNO_3) solution. 20 ml deionized water was added into this solution under vigorous stirring until the salts were completely dissolved. Then, ~12.8 g sodium hydrogen carbonate (NaHCO_3) was added to adjust the pH value to 6.5 until the formation of a yellow homogeneous solution. The as-grown ZnO NRs on the Au-coated glass were placed facing upwards in the bottom of this yellow solution. They were covered with aluminum foil and placed in the pre-heated oven for 4 or 10 h at 80 °C. The final products were washed with deionized water and then dried with blowing nitrogen gas. Finally they were dried at 80 °C for 10 h in a conventional laboratory oven (see Figure 3.3).¹⁰⁶

3.2. Membrane, enzymes and CMEs preparation

Figure 3. 4: Illustration of the fabrication of modified electrodes: spin coating of seed layer on Au coated glass, growth of the nanostructures, immobilization of polymeric membrane by deep coating and proposed mechanism of CME where a DA accumulated.¹⁰³

3.2.1. Dopamine membrane preparation and the buffer solution

Dopamine (DA, $\text{C}_6\text{H}_3(\text{OH})_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$) is a small and relatively simple molecule that performs diverse functions and in the 50s Carlsson has identified it as a

neurotransmitter in the brain.¹¹⁴ Many of the neurological processes like *e.g.* pleasure, cognition, learning and motivation have all found to be implicated by the DA. Neurologists found that DA exists with around 50 nmol/g in the caudate nucleus in the brain. Several neurological disorders have been found to be related to abnormal dopamine receptor signaling and in the dopaminergic nerve function. Parkinson disease patients have shown complete depletion of DA from the caudate nucleus in the brain.¹¹⁴ High levels are also known to be cardiotoxic leading to heart electrophysiology dysfunction. Usually, the concentration of DA in biological systems is in the range of 10^{-8} to 10^{-6} M.¹¹⁵

Therefore, the DA membrane¹¹⁶ (see Figure 3.4) and the buffer solution were prepared using powdered polyvinyl chloride (PVC) (0.18 g) as a plasticized polymer which was dissolved in tetrahydrofuran (6 mL) and mixed with β -cyclodextrin (β -CD) used as ionophore (0.04 g), potassium tetrakis (4-chlorophenyl) borate as ionic additive (0.01 g) and 2-fluorophenyl 2-nitrodiphenyl ether (0.4 g). A stock solution as a buffer containing dopamine hydrochloride (1.89 g) in deionized water (100 mL) was prepared and later diluted with a 100 mM sodium acetate-acetic acid (pH 5.5). The as grown nanostructures were dipped three times into the membrane solution. After that, all the electrodes were left to dry in a fume hood at room temperature for one night. All the functionalized CMEs were kept in a free water vapor moisture environment at room temperature when not in use.

3.2.2. Immobilization of glucose oxidase on ZnO and Co₃O₄ nanostructures

It is known that, glucose detection is a necessary test for all patients having diabetes. A glucose oxidase (GOx) solution was prepared by dissolving 30 mg of enzyme in 3 mL of 10 mM phosphate buffered saline (PBS) of pH = 7.3 and 300 μ L of Glutaraldehyde.^{51, 104} Then, using the drop casting process, the GOx was physically adsorbed on the ZnO nanostructures surfaces through electrostatic attraction and the samples were left to dry in a fume hood at room temperature for 3 hours. A 100 mM of glucose analyte was prepared in 10 mM PBS having a pH of 7.3 and the low concentrations of glucose were prepared in PBS by dilution.^{51,104}

3.2.3. Immobilization of ZnO NRs with L-glutamate oxidase (GluOx, EC 1.4.3.11)

L-glutamate acid (Glu) is an important amino acid that is usually applied to food items for improving/enhancing the taste. For the vertebrate central nervous system, Glu

is a major excitatory neurotransmitter.^{117,118} It is reported that abnormal concentrations of Glu may indicate disorder such as trauma, stroke, epilepsy and hypoglycemia.¹¹⁸ A 20 μL of L-glutamate oxidase (GluOx) solution was added to a 200 μL PBS solution (pH = 7.3) (0.01 M). A 2.5 mg of bovine serum albumin (BSA) was used as an enzyme stabilizer and a 10 μL of glutaraldehyde solution was used as the cross linker¹¹⁹ and they were added to this solution and immobilized on the ZnO NRs through electrostatic physical adsorption process. After that, all the electrodes were left to dry in a fume hood at room temperature for one night. All the functionalized biosensor electrodes were kept in a dry Petri-plate at 4 °C when not in use. Before the insertion of the GluOx immobilized sensor electrode in the Glu solution, it was soaked in PBS in order to achieve a stable response as well as to remove the extra molecules of the GluOx that might be on the surface of the electrode. A stock solution of 10 mM of Glu was prepared in few drops of 0.01 M HCl¹²⁰ and finally mixed with 0.01 M PBS. Known low concentrations of Glu for testing and calibrating the sensor were obtained by dilution.

3.3. Characterization techniques

3.3.1. X-ray diffraction

X-ray is an electromagnetic radiation with very short wavelength of a round 1 Å (10⁻¹⁰ m). In 1912, the atoms in a single crystal of copper sulfate pentahydrate (CuSO₄·5H₂O) were detected with high precision that is enabled by the periodicity of the crystal lattice by means of X-ray diffraction (XRD).¹²¹ Since then, XRD technique has been used as a powerful structural characterization for crystal quality and investigation of the composition of the synthesized material.

In this work, the XRD patterns were carried out by a Phillips PW 1729 powder diffractometer equipped with CuK α radiation (λ =1.5418 Å) using a generator voltage of 40 kV and a current of 40 mA. Figure 3.5a shows a typical XRD patterns of ZnO NRs grown on Au coated glass substrate.¹⁰² All the diffraction peaks of the XRD pattern can be indexed to ZnO with hexagonal wurtzite structure and all peaks agreed well with the standard card (JCPDS NO 36-1451) of bulk ZnO (Figure 3.5b).¹²²

Figure 3. 5: (a) XRD pattern of ZnO NRs grown on Au-coated glass substrate and (b) the standard card of bulk ZnO.

3.3.2. Scanning electron microscope

Scanning electron microscope (SEM) is a powerful technique that utilizes a focused electron beam to obtain information by scanning over a sample surface. The high-resolution images produced by SEM provide topographical, morphological and compositional information that makes it invaluable in a variety of science and industry applications. An electron microscope works on the same basic principles as optical microscopes, but uses a focused beam of energetic electrons rather than photons in order to obtain a magnified image of an object. A variety of signals are observed when the beam of the energetic electrons interacted and decelerated by the sample, this interaction is due to the significant kinetic energy carried by the accelerated electrons. These signals include secondary electrons, backscattered electrons, diffracted backscattered electrons, that are used to determine crystal structures and orientations of minerals, characteristic X-rays (used for elemental analysis), photons (used in cathodoluminescence analysis) and heat radiation. For imaging the sample surface, both secondary and backscattered electrons are used. However, the secondary electrons are very useful for revealing the morphology and topography, while backscattered electrons are useful for providing information about the compositional contrast.¹²³ The morphological analysis in this work were performed by SEM instrument using a LEO 1550 Gemini field emission gun at 5 kV. Figure 3.6 shows the SEM facility at Linköping University.

Figure 3. 6: A digital photograph of the SEM at IFM Department at Linköping University, Sweden.

Figure 3. 7: (a) TEM image of a BiZn_2VO_6 and the inset shows the corresponding selected area electron diffraction (SAED) pattern. (b) EDX mapping showing the Bi, Zn, and V distributions.¹⁰⁶

3.3.3. Transmission electron microscopy

The transmission electron microscopy (TEM) is a microscopy technique and can also be used for imaging the grown materials. Furthermore, TEM can provide much more information such as discrimination between a single crystalline, polycrystalline and glassy or amorphous structure material. In addition to composition of the material estimations, one can characterize lattice parameter and the lattice distances. All these properties are due to fact that TEM uses high-energy electrons, which strike the specimen, and parts of it are transmitted depending upon the thickness and electron transparency of the specimen. However, the specimen preparation is an important step of the TEM

analysis. For the research work conducted within the present thesis, the TEM experiments were performed using a FEI Tecnai G2 TF20 UT field emission microscope operated at 200 kV. This microscope is also equipped with an energy dispersive x-ray spectrometer (EDX). Figure 3.7 shows typical TEM images of BiZn₂VO₆. In Figure 3.7a a well-defined diffraction spots indicating a polycrystalline nature of the BiZn₂VO₆ is shown. Furthermore, an EDX mapping in Figure 3.7b of the sample demonstrates that the Zn distribution overlaps with the Bi and V distributions.¹⁰⁶

3.3.4. Photoluminescence spectroscopy

Photoluminescence (PL) technique is a non-destructive helpful analysis. By using PL one can investigate and study the optical properties of semiconductor materials of different types *e.g.* bulk material, thin films or nanostructures. PL is the spontaneous emission of light from a material that occurs when excited by photons (often ultra-violet). Usually carriers aim to recombine when a beam of light excites the sample. This recombination is manifested as emission of a photon with energy close to the near band edge emission or alternatively the emission happens through transition due to deep levels.¹⁰⁶ Then, the PL spectrum can be collected and analyzed. By PL measurement, one can obtain a variety of material parameters such as the optical band gap determination, impurities and defect detection. In this work, the PL properties of the prepared ZnO and BiZn₂VO₆ nanostructures were studied at room temperature (300 K). A micro-photoluminescence setup was used to study the optical properties of some of the samples presented in this thesis. A Nd:YVO laser having a wavelength $\lambda = 266$ nm was used as the excitation source and the excited sample area was a circle having a diameter of around 1.5 μm . To collect the emitted luminesce, it was mirrored into a single monochromatic grating equipped with liquid nitrogen cooled Si-Charge coupled device (CCD) camera. Figure 3.8 shows typical PL spectra of the as-grown BiZn₂VO₆ and PEG-doped BiZn₂VO₆ NCs on Au coated glass.¹⁰⁶

Figure 3. 8: Room temperature PL spectra of BiZn_2VO_6 NCs grown on Au with and without the presences of PEG.¹⁰⁶

3.3.5. Ultraviolet-visible spectroscopy

Figure 3. 9: UV-Vis. absorption spectrum of BiZn_2VO_6 NCs, an absorption peak at around ~ 482 nm corresponds to an optical band gap of about 2.57 eV.¹⁰⁶

Ultraviolet-visible (UV-vis) Spectroscopy is absorption or reflectance spectroscopy in the UV and visible range of the electromagnetic spectrum. UV-vis is also used to study the optical properties of the grown materials. UV-vis provide indication about the optical band gap of the material by simply corresponding the absorption peak (see Figure 3.9) or by calculations using the Tauc model.¹²⁴ In PL we deal with the transitions from excited states to the lowest energy state. However, while in UV-vis spectroscopy one can deal with the transitions for lowest energy state to the higher energy state. Optical absorption spectra in this work was obtained by a PerkinElmer Lambda 900 UV-visible spectrophotometer. For the measurements, the different nanostructures were grown on glass substrate and a blank glass slide was used as a reference.

3.3.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful technique to study the surface chemistry (up to 10 nm of depth) of a material. Upon irradiating by X-rays some electrons released from the material surface, then the kinetic energy and the number of electrons can be measured (see Figure 3.10). Moreover, XPS can also be used to measure the elemental composition, the chemical state, electronic state and might be used to get more information about the elements within the material being analyzed.

Figure 3. 10: Basic principle of the XPS technique.

In this work, the surface chemical composition of the grown metal oxide nanostructures was investigated by XPS technique and measured by Scienta ESCA200 using a vacuum generator with a monochromatic Al (K α) radiation. Figure 3.11, shows typical XPS spectra indicating a Co₃O₄ nanostructure.¹⁰³ A wide and short XPS scans are shown in Figure 3.11 (a-c). Figure 3.11b represented Co 2p XPS spectrum of the product. The spin-orbital splitting peaks at ~780 eV and ~795 eV are assigned to the Co 2p_{2/3} and Co 2p_{1/2}, respectively. The decomposition of the Co 2p spectrum contains the contribution of Co³⁺ octahedral and of Co²⁺ tetrahedral. The peaks positions are in agreements with the reported data for pure Co₃O₄ crystals. The peak at ~770 eV is corresponding to the Auger peak of cobalt.¹²⁵ The peaks at ~789 eV and ~803 eV are attributed to 2p_{2/3} and 2p_{1/2} shake-up satellite of Co³⁺, respectively.¹²⁶ The O 1s XPS peaks (Figure 3.11c) at ~530 eV, which corresponds to the oxygen species in the Co₃O₄ phase and at ~531 eV might be due to the hydroxyl group and adsorbed water.^{126, 127}

Figure 3. 11: XPS spectra of the as grown Co₃O₄ nanostructures on Au (a) a wide scan, (b) Co 2p, and (c) O1s spectra.¹⁰³

3.3.7. Electrochemical and photoelectrochemical characterizations

The potentiometric sensor (see Figure 3.12a), in which the potential of the CMEs is measured against a Ag/AgCl as a reference electrode in 3M KCl at room temperature by a pH meter (Metrohm AG model 744, Herisau, Switzerland) and using an electrical instrument (Keithley 2400) to measure the response time of the CMEs. A three-electrode cell setup (see Figure 3.12b) was used for the PEC, the linear sweep voltammetry (LSV)), chronoamperometry and electrochemical impedance spectroscopy (EIS). The later was performed to study the Mott-Schottky analysis. Using an SP-200 potentiostat (Bio-Logic, Claix, France), a platinum sheet was used as the counter electrode and a Ag/AgCl was used as a reference electrode. The electrolyte used was 0.1 M Lithium perchlorate (LiClO₄) in propylene carbonate solution at a pH of 7 to avoid ZnO decomposition. The LSV was carried out at a scan rate of 0.1 V/s. Chronoamperometry *I-t* curves were tested at a bias voltage of 0.5 V (vs Ag/AgCl). All electrodes were illuminated from the front side of the samples by a solar simulator (LCS-100, Newport, model 94011A). The total area of the photoelectrode was 2cm x 1cm, while the light is illuminated on a 1cm x 1cm that was

immersed in the electrolyte. The solar simulator uses a 100 W ozone free xenon lamp and includes an AM1.5G air mass filter with output power of 1 Sun. The EIS was performed at an amplitude of 20 mV in a frequency range of 0.1 Hz-5 kHz and a potential range of -1.0 V to +1.0 V.

Figure 3. 12: (a) schematic diagram showing a typical potentiometric glucose biosensor and (b) a photograph of the three-electrode cell setup using a metal oxide nanostructure based CMEs.

Chapter 4 Findings and summary

This thesis is concerned with synthesis of some metal oxide nanostructures (ZnO, Co_3O_4 , BiZn_2VO_6) by the low-temperature wet chemical approach and the effects of organic additives on structural, sensing and catalytic properties. Briefly, this research work is described as follow; the ZnO and Co_3O_4 nanostructures were used for chemical and bio-sensing applications and the BiZn_2VO_6 NCs was used for PEC activity. Here, in this chapter a summary of the findings from the six included papers are presented and discussed.

Incorporating β -cyclodextrin with ZnO nanorods: A potentiometric strategy for selectivity and detection of dopamine (paper I)

Figure 4. 1:SEM images of ZnO NRs, (a) as grown and before membrane immobilization, (b) high magnification showing the relatively large aspect ratio of the grown ZnO NRs, (c) after polymer membrane immobilization and (d) after measurements.¹⁰²

ZnO NRs based CMEs were grown on the Au coated glass substrate by the low temperature aqueous chemical growth (ACG) method. Due to the affinity of ZnO towards the dopamine molecule to form a strong electronic coupling (metal-ligand bond) between

the ZnO and the enediol, we expect good electrostatic interaction.¹²⁸ This is a ligand hybrid system that comes from the interaction of hydroxyl groups with Zn⁺⁺ ion. Therefore, we have prepared perm-selective membrane coated on ZnO NRs as CMEs to endow the electrode with the property of a selective transport of dopamine molecules. A polymeric membrane (see Figure 4.1c and d) was immobilized on the ZnO NRs surface through electrostatic adsorption process. Figure 4.1a and b are SEM images that show the ZnO nanostructures grown densely with a rod shape like with a hexagonal cross section and having diameters between 100 and 200 nm with an average length of around 1.5 μm . To test the sensitivity of our constructed chemical sensors we performed measurements while changing the dopamine molecule concentration from 1 μM to 100 mM in a buffer solution. Figure 4.2a shows that the electromotive force is changing when the composition of the test electrolyte is modified by different concentrations of the dopamine. This observation can be understood in term of the metal-ligand bond that would be formed through a β -CD ionophore and hence the charge could be transferred into the buffer solution. The actual cell diagram that creates the electrochemical potential is:

The obtained results revealed that the proposed sensor possesses a good linearity and sensitivity of 49 mV/decade in a concentration range of 1×10^{-6} and up to 1×10^{-1} M at room temperature. In addition, a response time of less than 10 s was observed as shown in Figure 4.2b. The high sensitivity and fast response time could be attributed to the high surface to volume ratio of the ZnO NRs, which are firmly coupled with the dopamine molecules.

Figure 4. 2: (a) The calibration curve for the presented dopamine chemical sensor giving the linear calibration equation as: $y = 49.857x + 246.6$ and (b) the response time measured in 0.01 mM concentration of dopamine.¹⁰²

Habit-modifying additives and their morphological consequences on photoluminescence and glucose sensing properties of ZnO nanostructures, grown via aqueous chemical synthesis (paper II)

Different surfactants (SDS, SDBS, NaPTS and CTAB) have been used in this work. They have been added into the growth solution to act as a source of impurities and as habit modifying additives that would yield a desired morphology of the ZnO nanostructured.⁵¹ It is worth to mention that, the morphology of the ZnO nanostructures is sensitive to the external conditions such as the solution pH value, the choice of the catalyst and the surfactant. It has been believed that, one or more of different parameters can influence the anisotropic shape of an inorganic nanocrystal. Examples of these parameters are the kinetic energy barrier, the temperature, the time and the nature of the capping molecules.¹²⁹ Here, the capping molecule is the only investigated parameter. However, the surfactant access with the existence of HMT might be producing a complex surrounding the nanostructures environment and thus modulating the kinetic energy is accompanied. The results of the morphology, crystal quality and the PL properties of the ZnO nanostructures are summarized below. Moreover, the grown ZnO nanostructures were used to fabricate low cost efficient glucose biosensor.

The crystal quality was found be the same for all the samples as described below. Figure 4.3 shows the XRD patterns of the ZnO with and without the surfactant-assisted growth of the ZnO nanostructures. All the X-ray spectra shows well-defined peak at 34.4° that corresponds to (002) plane, which indicates that the growth orientation is along the c-axis. All the other peaks can be assigned to hexagonal wurtzite structure of ZnO. However, the morphology was observed to be altered by the use of the different surfactants. The growth processes with the SDBS and the SDS have resulted in nano-wurtzite structures and nano-foam-like structures as shown in Figure 4.4a and Figure 4.4b respectively. Meanwhile, an interconnected and stacked spiral nano-hexagonal-like structures are shown in Figure 4.4c and Figure 4.4d, when the CTAB and the NaPTS are incorporated in the growth solutions, respectively. Several interfacial phenomena can be considered in the growth mechanism of these structures *e.g.*, adsorption, surface tension, and the critical micelle concentration.⁹⁰ This is because the surfactant molecules have both hydrophobic and hydrophilic portions in their structures. However, the adsorption phenomenon is more decisive factor for the capping molecules.

Figure 4. 3: XRD spectra of the ZnO nanostructures grown with and without the different surfactants.⁵¹

The adsorption of surfactant molecules on the high-energy face of crystals is in the order NaPTS > CTAB > SDS > SDBS.¹³⁰ In the first two cases the capping molecules strongly inhibited the usual growth habit of ZnO NRs *i.e.*, along the *c*-axis which is a well-known direction that have the higher growth velocity compared to the other growth directions. Whereas for the case of the SDBS and from the SEM image that is shown in Figure 4.4a, it is clear that this surfactant has an equal dimensional contribution on the planes. While the SDS has the same contributions but has longer chain length of the hydrophobic part and this fact makes the morphology to have a foam shape like structure.¹³¹ Briefly, with a certain amount of the head group (cationic or anionic) of the surfactant *e.g.*, CTAB would be dissociated in water into CTA⁺ and Br⁻.¹³² The electrostatic attraction between CTA⁺ and Zn(OH)₂ endows the surfactant capability to act as an ionic carrier resulting in a kinetic inhibition of growth along the [0001] direction. From Figure 4.5a, the ZnO:CTAB has shown wider range of detection “1x10⁻⁶ – 1x 10⁻² M” as compared to the others surfactants. The sensor sensitivity was 66 mV/decade. This sensing property is attributed to the fact that CTAB is cationic surfactant while the rest vary between anionic surfactants

and neutral molecules. Furthermore, we can also conclude that these adsorbed molecules have direct contributions on the optical band gap of ZnO. The PL properties of the prepared ZnO nanostructures at room temperature showed a paramount UV peak and the “green-yellow” is to some extent suppressed as shown in Figure 4.5f. The UV intensity and shape are depending on the surfactants that are absorbed by the surface of the ZnO and might be considered as impurities. Table I shows the PL peak position in the UV region and the full width at half maxima (FWHM).

Figure 4. 4: SEM images of the as-grown ZnO nanostructures after adding the surfactants (a) ZnO:SDBS nano-wurtzite structure, (b) ZnO:SDS nano-foam-like structure, (c) ZnO:NaPTS nano-hexagonal-like structure and (d) ZnO:CTAB interconnected nano-disk-like structure.⁵¹

Table I: Summary of the PL properties of ZnO nanostructures grown with and without surfactants.⁵¹

Type of Materials	UV peak position (nm)	FWHM (nm)	UV peak position (eV)	FWHM (eV)
ZnO	381.35	13.87826	3.253	0.11888
ZnO:CTAB	379.52	17.97788	3.269	0.15564
ZnO:NaPTS	379.83	17.68345	3.266	0.15282
ZnO:SDBS	380.21	15.58057	3.263	0.13436
ZnO:SDS	380.097	16.83327	3.264	0.14519

Figure 4. 5: Calibration curve for enzymatic glucose sensors where the ZnO nanostructures grown with assistance of: (a) CTAB, (b) NaPTS, (c) SDBS, (d) SDS and (e) ZnO NRs with the standard growth condition *i.e.* without surfactants. The insets proposed Fermi level position at ZnO surfaces and (f) Room temperature PL spectra of the product of ZnO nanostructures.⁵¹

Effect of urea on the morphology of Co_3O_4 nanostructures and their application for potentiometric glucose biosensor (paper III)

In this work, we investigated the effect of urea concentration on the morphology of the Co_3O_4 nanostructures. The amount of urea added in the growth solution was in the -

Figure 4. 6: SEM images of Co_3O_4 nano-flowers comprised on nanowires fabricated on the Au coated glass substrate using different concentrations of urea with a low and high magnification.¹⁰⁴

order of 0.23, 0.27, 0.3 and 0.4 M respectively, while the concentration of the cobalt chloride was kept constant at 0.1 M. Then after the Co_3O_4 nanostructures were successfully grown, they were used for the development of a sensitive glucose biosensor.¹⁰⁴ The majority of available data reveals that the Co_3O_4 nanostructures have been used as the main catalytic part. Here, we have used a heterogeneous catalysis of Co_3O_4 and GOx enzyme, we believe that, the properties of each component can be retained due to the compatibility of Co_3O_4 . Beside the fact that, the potentiometric measurements which is to some extent benign to GOx and can even be used to acquire improved properties due to a synergistic effect.

The SEM images of the Co_3O_4 nanostructures synthesized using different concentrations of urea (with low and high magnifications) are shown in Figure 4.6 (a-h). The Co_3O_4 nanostructures were highly dense on the substrate and exhibit morphology of flowers like and have been grown on the nanowires like structures *i.e.* new morphology has been grown on top of the nanowires when increasing the concentration of the urea. That might be due to the change in the pH of the growth solution with the change of the concentration of the urea.¹³³ With more amount of urea the solution becomes more basic *i.e.*, with higher pH, and that will affect the morphology.

Figure 4. 7: (a) Calibration curve of the fabricated GOx/ C_3O_4 nanoflowers/Au electrode to detect glucose molecules for the concentrations from $1\mu\text{M}$ to 10 mM with a linear calibration equation is: $y = -56,9x - 213,7$ and (b) the selective response of the CMEs in the presence of common interferences at concentrations of 100 μL of 100 mM copper, ascorbic acid, uric acid or urea, respectively.¹⁰⁴

Furthermore, the GOx was immobilized on the nanoflowers of Co_3O_4 in order to be used as CME for sensing of glucose molecules using the potentiometric method. The GOx

immobilized Co₃O₄ nanoflowers based electrode detected a wide range of the glucose concentrations from 1 μM to 10 mM with a sensitivity of -56.85 mV/decade as shown in Figure 4.7a. The high sensitivity of the presented glucose sensor based on the nanoflowers of Co₃O₄ could be attributed to their relatively large surface area to volume ratio, which can carry high degree of the GOx molecules and exposed large surface for the oxidation of the glucose molecules on the surface of the enzyme immobilized Co₃O₄ nanoflowers. The selectivity of the presented glucose biosensor was measured with a 50 μM of the glucose and a 0.5 mM of the copper ion, ascorbic acid, uric acid and urea, respectively and the observed response is shown in Figure 4.7b. The presented GOx/Co₃O₄ nanoflowers/Au based sensor is very selective in the detection of glucose due to the favorable oxidation offered by the GOx for only the glucose molecules using the potentiometric method.

Dopamine wide range detection sensor based on modified Co₃O₄ nanowires electrode (paper IV)

After we successfully demonstrated that, the ZnO NRs based CMEs has wide linear dynamic concentration range 1×10^{-6} to 1×10^{-1} M for the detection of dopamine molecules with a fast response time. However, the lower detection limit needs to be improved because the concentration of dopamine in biological systems is in the range of 10^{-8} to 10^{-6} M. Moreover, the effect of the organic additives on modifying the morphology and their associated effect on the sensing and even on the electronic structures, as demonstrated in paper I, II and III, it was appealing to seek a more sensitive sensor. In the present paper,¹⁰³ an anionic SDBS surfactant was used to achieve assisted growth procedure. After the SDBS-doped Co₃O₄ nanowires were successfully grown on Au coated glass substrates by the ACG method, the same polymeric membrane used in paper I was used here as well.

SEM images at low and high magnification for Co₃O₄ nanowires grown at relatively high concentration 2.8 mM (0.1 g in 100 ml) of the SDBS are shown in Figure 4.8a and b respectively. Further, the Co₃O₄ nanowires achieved with 1.4 mM (0.05 g) of the SDBS are shown Figure 4.8c and d. Relatively thin Co₃O₄ nanowires grown with a diameter of around 50 nm are shown. We believed that the SDBS in the growth solution would initiate the growth by the formation of an electrical double layer at the interface. Since the whole system has been subjected to ~ 90 °C there would be an aggregation of the SDBS molecules on the substrate.¹³⁴ This aggregates that is in the form of micelles have a crucial effect into

the thermodynamics of the system and hence in controlling and forming a template for the growth of Co_3O_4 nanowires.

Figure 4. 8: SEM images show the morphology of the Co_3O_4 nanostructures grown with a different amount of SDBS (a) 0.1 and (b) 0.05 g with high and low magnifications and both of them are dense with a high aspect ratio.¹⁰³

In order to describe the crystal structure, the XRD pattern of the annealed sample of Co_3O_4 nanostructures is shown in Figure 4.9. All of the five diffraction peaks could be indexed to cubic crystalline Co_3O_4 , and these peaks position is consistent with the values reported in the JCPDS NO 42-1467. However, the peaks are less intense, as compared to the Au peak.

The developed CME can be described by polymeric membrane/SDBS-doped Co_3O_4 nanowires/Au. It was studied by a potentiometric method where the system has employed the Co_3O_4 CMEs as the indicator electrodes versus Ag/AgCl as a reference electrode. In Figure 4.10 upon changing the dopamine molecule concentration from 1 nM to 10 mM in the buffer solution the electromotive force is changed. The wide range of detection of the SDBS-doped Co_3O_4 based CMEs was first attributed to the high surface-

Figure 4. 9: XRD pattern of the Co_3O_4 nanostructures on Au coated glass.¹⁰³

Figure 4. 10: Calibration curve showing the sensitivity and the linear response range of our constructed CMEs.¹⁰³

area to volume ratio of the nanowires and their better electro-catalytic properties. Secondly, these results might be connected to the presence of the surfactant that has a dual effect; one in modifying the morphology and the other is by enhancing the sensitivity via point defects, upon dehydration of the cobalt hydroxide phase is existed. Since it is known that defects have a significant impact on the surfaces of metal oxides and would enhance the catalytic activity of the Co_3O_4 .¹³⁵

Furthermore, to obtain information about the electronic structure and the transition from point defects, UV-Vis. spectroscopy was used. As shown in Figure 4.11a, the absorption spectra for three Co_3O_4 nanostructures grown with 0, 1.4 and 2.8 mM on glass substrate is displayed. Two absorption peaks were observed at ~ 2.35 eV and 1.57 eV. The first peak can be attributed to charge transfer from $\text{O}^{2-} \rightarrow \text{Co}^{+2}$, and the second one from $\text{O}^{2-} \rightarrow \text{Co}^{+3}$.¹³⁶ To determine the photon energy “optical band gap”, we plot $(\alpha E)^2$ versus E in Figure 4.11b for all three Co_3O_4 nanostructures, where α and E are the absorption coefficient and photon energy, respectively. The linear extrapolation of $(\alpha E)^2$ give two band gap values of each Co_3O_4 nanostructure ~ 3.65 eV – 2.05 eV for the structure grown without SDBS, ~ 3.95 eV – 2.09 eV for Co_3O_4 grown using 1.4 mM SDBS and finally ~ 4 eV – 2.29 eV for Co_3O_4 grown with a 2.8 mM SDBS. It is well established that the band gap of bulk materials can largely be increased when compared with counterparts of the nanomaterial.¹³⁷ These results confirmed that, SDBS as impurities may be dominant and have a direct influence on the electronic energy states within the band gap of the Co_3O_4 nanostructure.¹³⁵

Figure 4. 11: (a) UV-Vis absorption spectra and (b) plot of $(\alpha E)^2$ versus photon energy for the Co_3O_4 nanostructures.¹⁰³

Efficient donor impurities in ZnO nanorods by polyethylene glycol for enhanced optical and glutamate sensing properties (paper V)

Now it is clear that low dimensional (LD) nanostructures such as NRs, nanowires are the most reliable in term of the electron transport based CMEs. In this work, polyethylene glycol (PEG)-doped ZnO NRs was found to efficiently improve the optical and chemical sensing characteristics toward glutamate.¹⁰⁵ From the results, the PEG is

suggested to be used as an efficient donor impurities for ZnO NRs with preserving the favorable LD NRs morphology structure.

Figure 4.12a–d shows that all the ZnO NRs were dense, vertically aligned and with diameters in the range of 200–400 nm. However, ZnO NRs doped with 0.1% (w/v) of PEG exhibited low-density distribution compared to the other NRs (Figure 4.12c). In the experiment, water equimolar zinc nitrate hexahydrate and HMT of 0.05 M were mixed with different concentrations of PEG. However, as the PEG concentration is increased from 0 to 0.05, 0.1 or 0.15% (w/v) of PEG solution, the morphology is preserved as ZnO NRs that are usually grown when using HMT as a buffer medium.⁵¹

Figure 4. 12: SEM images of the ZnO NRs obtained with different concentrations of the PEG.¹⁰⁵

Many researchers have also incorporated organic additives to the ZnO material, and their exclusive results were demonstrated by introducing new morphology. Accordingly, some characteristics *e.g.* optical, electrical and catalytic have been modulated.^{92,138} In contrast, the incorporation of inorganic material into ZnO NRs with a certain concentration has no role on the morphology, but the aforementioned characteristics were notably modified.^{139,140} Note that the PEG is completely miscible with water and has found many applications in current technology as antifreeze when mixed with water.¹⁰⁰

Figure 4. 13: Schematic represent the four H sites in ZnO.¹⁴¹

This is probably due to its strong hydrogen bonding interaction in water.¹⁰¹ Therefore, we believe that the disruption of hydrogen bonding when dissolved in water, provides a rich hydrogenated environment for the growth of ZnO NRs. It is important also to note that, hydrogen is relatively very small in volume and the possibility of the incorporation inside the ZnO NRs structure is highly expected. Limpijumnong *et al.*, and E.V. Lavrov *et al.*,^{141,142} have investigated the configuration of hydrogen when incorporated into ZnO under hydrostatic pressure and they reported that, the hydrogen has four possible locations to reside in ZnO *i.e.* it might be a shallow donor or might not be a shallow donor (Figure 4.13). Lavrov *et al.*, have also reported that hydrogen related shallow donor in ZnO were studied by photoconductivity and infrared absorption spectroscopy.¹⁴³

For ZnO, the intrinsic optical transitions between carriers from the conduction band (electrons) and the valence band (holes) results in a sharp UV luminescence. In addition to the UV luminescence; there is the defect-related transitions called the “visible luminescence”, and appears as a wide band emission. Both emissions can clearly be seen in Figure 4.14.¹⁴⁴ The photoluminescence intensity (UV in this case) is explicitly increased. However, this dependence observed, except of the cases with PEG exceeding 0.1% (w/v). This observation is also in agreement with Tsirapas *et al.*¹⁴⁵ They correlated the best results for Schottky diodes to a certain amount (33.3%) of hydrogen. Therefore, one can infer that, a low amount of PEG introduces hydrogen, which acts as impurities and lead to increase the passivation of nonradioactive defect.¹⁴⁶⁻¹⁴⁸

Figure 4. 14: Room temperature PL spectra of ZnO NRs grown on Au coated glass with and without presences of PEG showing a sharp UV peak accompanied by two broad visible emission peaks.¹⁰⁵

Figure 4.15a shows that all the absorbance spectra for the ZnO NRs grown with various amounts of PEG exhibited spectral features and are very similar to those reported for pure ZnO. The absorption peaks for the PEG grown with 0, 0.1, 0.15% (w/v) of the PEG was observed at ~ 2.82 eV, 2.66 eV and 2.62 eV, respectively. It can be seen that the absorption edge moves towards a higher wavelength with increased PEG concentration. Next, we plotted $(ah\nu)^2$ versus E in Figure 4.15b for all three ZnO NRs. The linear extrapolation of $(ah\nu)^2$ gives the optical band gap value of each ZnO NRs. For the pristine ZnO NRs the obtained value was ~ 3.16 eV. While for the NRs grown with addition of 0.1, and 0.15% (w/v) of PEG, the corresponding values were ~ 2.95 eV and 2.67 eV, respectively. It is also worth mentioning that, in semiconductor nanocrystals the dimension of the nanostructures impurities and defects concentration can affect the physics of the band gap.^{54,149} That means the band gap of bulk materials can be larger when compared with nanomaterial forms and can be decreased or increased depending on the dopant nature. Therefore, the decrease in the optical band gap as the PEG concentration is increased could be ascribed to the PEG impurities that could act as shallow donors into the band gap of ZnO.

Now let us look on the electronic structure that has been investigated using oxygen 1s (O 1s) and zinc 2p (Zn 2p) XPS spectra of pristine and 0.1% w/v PEG-doped ZnO NRs. From Figure 14.16a the spin-orbital splitting peaks at ~ 1022.5 eV and ~ 1045.8 eV, are assigned to the Zn 2p_{3/2} and the Zn 2p_{1/2}, respectively. However, from the O1s spectra (see Figure 14.16b) a pronounced peak in the case of the pristine ZnO NRs at ~ 532 eV is-

Figure 4.15: (a) UV-Vis absorption spectra of ZnO NRs grown on glass with different amount of PEG and (b) the plot of $(\alpha E)^2$ versus photon energy.¹⁰⁵

Figure 4.16: XPS study of the as grown pristine ZnO NRs (solid line) and 0.1% w/v PEG doped ZnO NRs with 0.1% w/v PEG on Au (a) O 1s and, (b) Zn 2p spectra.¹⁰⁵

observed. While for the 0.1% (w/v) PEG-doped ZnO NRs this peak appears as a weak shoulder, indicated that the OH bonding could be incorporated inside the ZnO structure. The later result is in a good agreement with Van de Walle work in Ref.,¹⁵⁰ where he suggested that, the addition of a proton turning the oxygen into an element behaving much like fluorine and hence, it may appears as a weak shoulder compared to the case of the pristine ZnO NRs. As it is well known that, the electrical and optical properties of semiconductors could be affected with some impurities and small concentrations of native point defects. Accordingly, a shift of ~ 0.4 eV to the lower binding energy was observed in the core level of the O1s for PEG-doped ZnO NRs as shown in Figure 4.16b, which could be explained as an enhancement to the n-type conductivity of ZnO material.

Figure 4. 17:(a) Mott-Schottky plots of the pristine and PEG-doped ZnO NRs with different amount in 0.1 M LiClO₄ and (b) shows the increases of the capacitances upon the increase of the PEG amount.¹⁰⁵

Moreover, from the Mott-Schottky method, the doping density (N_d) into ZnO NRs was estimated. The Mott-Schottky plot of $1/C^2 = \frac{2}{N_d e \epsilon_s} [(V - V_{fb}) - kT/e]$ versus the voltage is shown in Figure 4.17a. Where C is the capacitance, V is the electrode potential, K is the Boltzmann constant, T is the temperature, e is the electron charge, and $\epsilon_s = 10$ is the dielectric constant of ZnO. From Figure 4.17a, the N_d from the slope of the straight line can be calculated and the flat band voltage (V_{fb}) could also be obtained from the intercept.¹⁵¹ All the obtained results for N_d and V_{fb} at the selected frequency (around 1.5 kHz) are summarized in Table II. Note in Table II the free carrier concentration for the 1.5% (w/v) PEG-doped ZnO NRs is less than the 0.1% w/v PEG-doped ZnO NRs.

Table II: Effect of doping on the flat band voltage (V_{fb}) and the doping density (N_d).

ZnO NRs	V_{fb} (V)	N_d (cm ⁻³)
Pristine	-1.09	2.81×10^{19}
+0.05% (w/v) PEG	-1.1	5.37×10^{19}
+0.1% (w/v) PEG	-0.87	1.39×10^{20}
+0.15% (w/v) PEG	-0.82	7.58×10^{19}

Furthermore, the capacitances increased when the amount of the doping increases. In Figure 4.17b at 0.1% (w/v) PEG the capacitance reached a value around 325 $\mu\text{F}^2/\text{cm}^4$ while it was 75 $\mu\text{F}^2/\text{cm}^4$ for the pristine ZnO NRs. This capacitance reached a value of ~ 200 $C^2 \mu\text{F}^2/\text{cm}^4$ for an amount of 0.1% (w/v) of the PEG as compared to the pristine sample that showed a maximum capacitance of ~60 $C^2 \mu\text{F}^2/\text{cm}^4$. However, at an amount of 0.15% (w/v) of PEG the capacitance has reached around 175 $\mu\text{F}^2/\text{cm}^4$. This behavior

can usually be observed for II–VI semiconductors and is called self-compensation mechanism.¹⁵² Self-compensation mechanism is a recombination of free carriers from dopant with opposite charge native point defects (vacancies, interstitials. *etc.*).

Now it is clear that from XPS and Mott Schottky investigations the most suitable amount of ZnO doping by PEG is a 0.1% w/v PEG, since the n-type conductivity has been significantly modified. Moreover, 0.1% w/v PEG-doped ZnO NRs based CMEs were compared with the pristine ZnO for the detection of glutamate (Glu) molecules. Figure 4.18a and b shows a comparison calibration curves between the PEG-doped ZnO NRs and the pristine ZnO NRs. As can be seen that from Figure 4.18 b, the GluOx/PEG-doped ZnO NRs/Au electrode was showed a wider range of detection for the Glu concentration with a superior sensitivity of 91.15 mV/decade and the lower limit of detection was found to be 0.05×10^{-6} M. Furthermore, some properties of the present chemical sensors like response time and the selectivity were studied by a potentiometric method. The response time is plotted in Figure 4.18c shows a value less than 10 s is the time needed for the CME to reach the saturation mode, which was measured in 1 mM of Glu. A wide range of detection and a good sensitivity of the GluOx/PEG-doped ZnO NRs/Au electrode and the fast response time are all due to the enhancement of the electro-catalytic property that is dictated by the existence of PEG beside the high surface area-to-volume ratio. In order to evaluate the GluOx selectivity, a 100 μ L of 100 mM glucose, ascorbic acid urea or Cu^{2+} ion respectively were added to a 0.1 mM Glu solution. Figure 4.18d shows that the interference is not significantly affecting the Glu signal intensity even with a very sharp signal of urea. This urea signal can be explained according to previously reported work.¹⁵³ During the interaction of the urea with a water molecule, two products are released in the reaction vessel including ammonia and carbon dioxide. The ammonia and the α xoglutarate are converted to glutamate in a reaction catalyzed by the GluOx. Mostly the specificity may be attributed to the existence of GluOx.¹⁵⁴

Figure 4. 18: Different properties of a potentiometric chemical sensor using ZnO NRs based CMEs to detect glutamate molecules (a) and (b) shows a comparison calibration curve between the pristine and the PEG-doped ZnO NRs, respectively, (c) the response time and (d) the selective response in the presence of 100 μ L of 100 mM of common interferents.¹⁰⁵

Low-temperature growth of polyethylene glycol-doped BiZn₂VO₆ nano-compounds with enhanced photoelectrochemical properties (paper VI)

In this part of the research work, the BiZn₂VO₆ NCs that have been prepared by a low temperature (80-90 °C) using BiVO₄ growth on ZnO NBs. Then, the NCs were doped with PEG to tune the electronic structure of the materials. Furthermore, the PEC activity of the prepared materials were investigated in 0.1 M lithium perchlorate in carbonate propylene under a simulated solar irradiation (AM1.5G).¹⁰⁶ The results of this work are discussed below;

Figure 4. 19: SEM of (a) PEG-doped ZnO NRs, (b) PEG-doped ZnO nanobelts, (c) PEG-doped BiZn₂VO₆ NC grown in 4 h and (d) side view of (c).¹⁰⁶

The starting ZnO nanostructures in this work were ZnO NRs, which were converted into NB structures during the BiZn₂VO₆ growth. In order to obtain the same morphology for the ZnO nanostructure part of all samples, also the control ZnO samples were converted into ZnO NBs. To achieve this, the as-prepared ZnO NRs electrodes were immersed into a solution containing 10 mL of Nitric acid, 70% HNO₃, and 20 ml de-ionized water. Sodium hydrogen carbonate (NaHCO₃) was added to adjust the pH value to 6.5. Then this beaker placed in an oven for 4 hours at 80 °C. Figure 4.19a and b show SEM images that indicating the etching effect and the clear tuning of the ZnO morphology from NRs to NBs. This expected behavior shows that the ZnO can be etched by the lower pH of the BiVO₄ growth solution (pH ≈ 6.0–6.5). BiZn₂VO₆ exhibited a morphology of rice-like nanostructures is shown in Figure 4.19c and d. In this work, different growth durations were investigated. However, long growth durations were resulted in the denser morphologies and larger width of the BiZn₂VO₆ structures.

Figure 4.20a shows the XRD patterns of the as prepared ZnO, BiVO₄ and BiZn₂VO₆ grown by the low-temperature ACG with 4 and 10 h growth durations. In the XRD patterns, the hexagonal wurtzite structure of the pristine and the doped ZnO NBs were -

Figure 4. 20: (a) XRD patterns of ZnO NBs, PEG-doped ZnO NBs, BiVO₄, and PEG-doped BiZn₂VO₆ NCs grown by the low-temperature aqueous solutions hydrothermal synthesis for 4 and 10h, (b) TEM image of a BiZn₂VO₆ and the inset shows the corresponding SAED pattern and (c) EDX mapping.¹⁰⁶

confirmed by comparing the experimental data with the literature data (JCPDS NO 36-1451). The XRD patterns of BiVO₄ agrees well with the characteristic pattern arising from a monoclinic scheelite phase of BiVO₄ (JCPDS NO 74-4894). However, the XRD patterns of the BiZn₂VO₆ NCs samples exhibited orthorhombic unit cells that is usually observed for mixed metal oxides.⁸⁷ One can also note that the XRD patterns for the BiZn₂VO₆ and the PEG-doped BiZn₂VO₆ grown for 4 h and 10 h are identical. Thus 4 h is a suitable growth time for the BiZn₂VO₆ NCs, which is an improvement compared to previous published results on the growth of BiM₂AO₆ by solid-state reactions using high-temperature and relatively longer growth durations (≥ 700 °C, up to 30 h).^{84,85,87 and 155} Furthermore, the existence of a mixed metal oxide (BiZn₂VO₆) was confirmed by a TEM as is shown in Figure 4.20b and c. Figure 4.20b represents the selective area electron diffraction (SAED) pattern that shows the polycrystalline nature of the product. Figure 4.20c shows the energy dispersive X-ray spectroscopy (EDX) mapping and demonstrates that all the Zn, Bi and V has an equal distribution.

Figure 4. 21: XPS spectra of (a) and (b) O1s and V2p of the as grown BiVO₄ and BiZn₂VO₆ NCs on Au coated glass, respectively, (c) Bi4f for both the BiVO₄ and the BiZn₂VO₆ and (d) Zn 2p spectrum for BiZn₂VO₆ NCs.¹⁰⁶

The XPS was also used to analyze the BiVO₄ control sample and the PEG-doped BiZn₂VO₆ sample. The XPS peaks at ~530 eV and ~516.8 eV in Figure 4.21a correspond to oxygen species in the metal oxide and vanadium oxide phase, respectively.¹⁵⁶ The hydroxyl group from adsorbed water has appeared as a shoulder at ~ 532 eV for the BiVO₄. While for doped BiZn₂VO₆ NCs in Figure 4.21b, the hydroxyl group and adsorbed water at ~ 532 eV is the dominant feature and the feature related to O1s spectrum now appears as a tail in the lower binding energy (marked by a circle in Figure 4.21b). Moreover, one can notice that the V2p_{3/2} XPS peak for the BiVO₄ control sample is located at around ~ 517 eV and for doped the BiZn₂VO₆ NCs is located at around ~ 517.5 eV *i.e.* shifts slightly to a higher binding energy. The same scenario is true for the peak positions of Bi4 can be noticed in Figure 4.21c. According to the literature, the unit cell of the monoclinic BiVO₄ has $a \sim 7.2 \text{ \AA}$, $b \sim 11.7 \text{ \AA}$ and $c \sim 5.1 \text{ \AA}$,¹⁵⁷ while for mixed metal oxides

(BiM₂AO₆) which is orthorhombic and possesses a unit cell with $a \sim 11.5 \text{ \AA}$, $b \sim 5.5 \text{ \AA}$ and $c \sim 8.5 \text{ \AA}$.⁸⁷ Thus, this shift in the binding energies can be attributed to the incorporation of ZnO element into the BiVO₄ structure because the bonding length and the band structure is expected to be different for BiVO₄ and BiZn₂VO₆. The Zn2p XPS spectra of the BiZn₂VO₆ is shown in Figure 4.21d, where the spin-orbital splitting peaks at $\sim 1022.3 \text{ eV}$ and $\sim 1045.4 \text{ eV}$ are assigned to the Zn2p_{3/2} and Zn2p_{1/2}, respectively.¹⁰⁶

Moreover, UV-Vis. spectroscopy indicates an optical band gap at around 2.57 eV as shown in Figure 4.22a. This is larger than previously reported data⁸⁵ by 0.17 eV. However, it is still a narrow band gap that can be used for visible light-based applications. The room temperature PL spectra in Figure 4.22b shows the UV peak that is originate from free excitonic emission and the so-called green-yellow band that is caused by deep level emissions. As can be seen that the PEG has a crucial role in quenching the PL emission. This role comes from the fact that the PEG has many hydrogen bonds which can modulate the PL characteristic as reported elsewhere.¹⁵⁸ This decrease in the PL intensity can be refereed as lower recombination rate which corresponds to higher PEC activity and vice versa.¹⁵⁹ Therefore, the PEC activity for the PEG-doped BiZn₂VO₆ is investigated. Figure 4.23a shows linear sweep voltammetry for ZnO NBs, PEG-doped ZnO NBs, BiZn₂VO₆, and the PEG-doped BiZn₂VO₆ electrodes under simulated solar light at dark conditions (dashed lines) and under light irradiation (full curves). The observed photocurrent density was 0.35 mA cm⁻² and 0.59 mA cm⁻² for the undoped and the PEG-doped ZnO NBs at 1.23 V (vs Ag/AgCl), respectively. In comparison, the photocurrent density was 1.25 mA cm⁻² at 1.23 V (vs Ag/AgCl) for the undoped BiZn₂VO₆ NCs. Hence, the photocurrent density of the BiZn₂VO₆ NCs, when compared with pristine and PEG-doped ZnO NBs, increases significantly, which can be assigned to efficient electro-catalytic surface activity of the BiZn₂VO₆ NCs under visible light irradiation.⁸⁵ PEG-doped BiZn₂VO₆ NCs reached a values of 2 mA cm⁻² at 1.23 V vs Ag/AgCl. Which corresponds to an improvement over 60% compared to pristine BiZn₂VO₆ NCs. This improvement in the charge collection efficiency of the electrode surface is attributed and explained for couple of reasons; firstly, the electron communications processes on the electrode surface were efficient due to the heterogeneous catalysis effect at the BiZn₂VO₆/ZnO NBs interfaces.

Figure 4. 22: (a) UV-Vis absorption spectrum of the BiZn₂VO₆ grown on glass with the same procedure as that used for the Au coated glass (b) PL intensities normalized for the 380nm peak of the as-grown BiZn₂VO₆ and PEG-doped BiZn₂VO₆ NCs.¹⁰⁶

Figure 4. 23: (a) Linear sweep voltammetry of the ZnO NBs, PEG-doped ZnO NBs, BiZn₂VO₆ and PEG-doped BiZn₂VO₆ NCs electrodes in dark and under solar illumination (AM 1.5G) and (b) Chronoamperometry I-t curves of all electrodes at an applied voltage of +0.5 V with 50 s light on/off cycles.¹⁰⁶

Secondly, PEG impurities that act as shallow donor and enhance the n-type conductivity as it has been suggested in our previous work.¹⁰⁵ These results are also consistent with previous published studies,¹⁶⁰⁻¹⁶² where the authors argued that the doping plays distinct role in enhancing the photoactivity of semiconductor materials. Figure 4.23b shows the response time of the pristine and doped electrodes in the dark and under simulated solar light at an applied voltage of +0.5 V. The stationary photocurrent density was 0.09 mA cm⁻², 0.13 mA cm⁻², 0.14 mA cm⁻² and 0.2 mA cm⁻² for the pristine ZnO NB, PEG-doped ZnO NB, pristine BiZn₂VO₆ and PEG-doped BiZn₂VO₆, respectively. These results confirm that the PEG-doped BiZn₂VO₆ NCs based electrode exhibited the highest current density, with a good reproducibility and stability.

Chapter 5 Conclusion and future prospects

The presented work is concerned with synthesis of ZnO, Co₃O₄ and BiZn₂VO₆ based modified electrodes by the low-temperature wet chemical process and the effects of organic additives on structural, sensing and catalytic properties. Briefly, this research work can be divided into; (1) A potentiometric chemical sensors were used to determine the analytical concentration of dopamine, glucose and glutamate molecules in solution. ZnO and Co₃O₄ nanostructures have been involved in the chemical sensors based CMEs to detect dopamine and glucose molecules. The glutamate molecules have been investigated using ZnO based CMEs. (2) The BiZn₂VO₆ NCs based CMEs were used for visible light-driven PEC activities.

Dopamine sensor was studied by the potentiometric method using pristine ZnO NRs based CMEs in paper I. In this research work the proposed sensor showed good linearity in a concentration range of 1×10^{-6} and up to 1×10^{-1} M. However, the concentration of dopamine in biological systems is in the range of 10^{-8} to 10^{-6} M. In paper II different surfactants (SDS, SDBS, NaPTS, and CTAB) have been used into the growth solution to be acted as the source of impurities and as habit-modifying additives that would yield a desired morphology of the ZnO nanostructured. The results showed that the surfactant was affecting both the morphology and the photoluminescence characteristics and can tailor the sensing properties. However, no surfactants dependence was observed to modify the crystallographic structure. The findings in this paper indicated the importance of the use of controlled nanostructures morphology for developing efficient functional materials. Furthermore, the effect of different concentrations of urea on the morphology of Co₃O₄ nanostructures based CMEs was investigated in paper III. The Co₃O₄ nanostructures exhibit morphology of flowers-like and have comprised on nanowires due to the increasing amount of urea. Accordingly, the presented glucose biosensor detected a wide range of glucose concentrations from 1×10^{-6} M to 1×10^{-2} M with a sensitivity of -56.85 mV/decade and indicated a fast response time of less than 10 s. This performance is attributed to the heterogeneous catalysis effect at glucose oxidase enzyme, nano-flowers, and nanowires interfaces that have enhanced the electron transfer process on the electrode surface. An anionic surfactant, namely sodium dodecylbenzenesulfonate (SDBS), was used to achieve assisted growth procedure. After the successful growth of the

SDBS-doped Co₃O₄ nanowires on Au coated glass substrates by the ACG method the same polymeric membrane for dopamine molecules used in paper IV. The results also showed that, the morphologies of the Co₃O₄ nanostructures were readily tunable by changing the concentration of SDBS as an additive in the growth solution. Furthermore, the proposed SDBS-doped Co₃O₄ CMEs based dopamine sensor showed a lower LOD and a wider range of detection ranging from 10⁻⁹ M and up to 10⁻² M compared to that previously reported in paper I. Paper V focused on the use of PEG-doped ZnO NRs based modified electrodes to further increase the sensitivity towards Glutamine. PEG was used as the impurity that would yield a desired modulation into the electronic structures and preserving the ZnO NRs morphology. A slight increase in the carrier concentrations from ~10¹⁹ for pristine ZnO NRs to 10²⁰ cm⁻³ for the ZnO NRs formed with 0.1% (w/v) of PEG was extracted using the Mott-Schottky analysis at the ZnO NRs/electrolyte interface. Therefore, the enhancement of the sensing properties was attributed to the electro-catalytic properties that was triggered by the PEG addition to the growth procedure along with high surface area-to-volume ratio of the ZnO NRs.

In paper VI, we demonstrated that for the first time BiZn₂VO₆ nano-compounds (NCs) have been prepared by low temperature (80-90 °C) by using BiVO₄ growth on ZnO nanobelts (NBs). Then, the NCs were doped with polyethylene glycol (PEG) to tune the electronic structure of the materials. Furthermore, the photo-electrochemical activity of the prepared materials were investigated in 0.1 M lithium perchlorate in carbonate propylene under a simulated solar irradiation (AM1.5G). The results showed that, 4 h is already a suitable growth time for the BiZn₂VO₆ NCs. The BiZn₂VO₆ nanostructures exhibit morphology of rice-like grown in 4 h lying at the top of vertically aligned ordered ZnO NBs. The photocurrent density of the PEG-doped BiZn₂VO₆ NCs were substantially improved. The PEG-doped BiZn₂VO₆ NCs reached a value of 2 mA cm⁻² at 1.23 V vs Ag/AgCl which corresponds to an improvement over 60% compared to pristine BiZn₂VO₆ NCs. These results indicate that, the PEG assists the photo-excited electrons and holes to overcome the energy barrier (*e.g.*, the binding energy) and enhances the charge separation/migration processes of the BiZn₂VO₆ NCs electrode. The improved charge collection efficiency of the electrode surface can be attributed to: (1) the heterogeneous catalysis effect at the BiZn₂VO₆/ZnO NBs interfaces that was enhanced. Which has led to an efficient electron communications processes at the electrode surface, and (2) the PEG

impurities that act as shallow donors and enhance the n-type conductivity as it has been suggested in paper V.

Due to the green chemistry aspect and the relatively low cost of the aqueous chemical growth (ACG) method, I plan to continue my research using the ACG approach reported in this thesis to synthesize further other mixed metal oxide nanostructures. I have already started a research project to utilize and avail the grown BiZn_2VO_6 for water splitting using sun visible radiation as cheap means to produce efficiently hydrogen as a clean energy source.

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