NiO QDs /ZnO nanorods composite structure for catalytic reduction of Cr^{6+}

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In

Chemistry

By

Imtiaz Ahmed

Supervisor

Dr. K.K Haldar

Centre for Chemical Sciences

School of basic and applied sciences

Central University of Punjab Bathinda -151001

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DECLARATION

I declare that the thesis entitled, **NiO QDs /ZnO Nanorods Composite Structure for Catalytic Reduction of Cr^{6+}** has been prepared by me under the guidance of Dr. K.K Halder Centre of Shemical Science School of Basic and Applied Sciences Central university of Punjab. No part of this dessertation has formed the basia for the award of any degree or fellowship previously.

Name and signature of supervisor

Centre for chemical sciences

School of Basic and Applied Sciences

Central University of Punjab Bathinda -151001

Date:

Imtiaz Ahmed

CERTIFICATE

I certify that Mr. Imtiaz Ahmed has prepared his thesis entittled **NiO QDs /ZnO Nanorods Composite Structure for Catalytic Reduction of Cr^{6+}** for the award of M.sc degree of the Central University of Punjab under my guidance .He has carried out this work at the centre of chemical sciences School of Basics and Applied Science Central University of Punjab Bathinda.

Name and signature of supervisor

Centre for chemical sciences

School of Basic and Applied Sciences

Central University of Punjab Bathinda -151001

Date:

Imtiaz Ahmed

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LIST OF FIGURE

LIST OF ABBREVIATION

S.No	Full form	Abbreviation
1	Nanoparticles	NPs
2	Metallic nanoparticles	MNPs
3	Ultraviolet – visible spectroscopy	UV-Vis
4	Scanning electron microscope	SEM
5	Transmission electron microscope	TEM
6	Face centred cubic	FCC
7	Body centred cubic	BCC
8	Nickel nanoparticles	NiNPs
9	Zinc nanoparticles	ZnNPs
10	Photoluminescence	PL
11	High-resulation transmission electron microscope	HRTEM
12	Zero ,one,two,three, dimensions	0D,1D,2D,3D
13	Quantum Dots	QDs

14	**Potassium dichromate**	**$K_2Cr_2O_7$**
15	**X-ray deffraction**	**X-RD**
16	**Electrochemical impedance Spectroscopic studies**	**ESI**
17	**Nickel(III) oxide**	**Ni_2O_3**
18	**Nanometre**	**Nm**
19	**Tetraethyl orthosilicate**	**TEOS**
20	**Potential of hydride**	**P^H**

ABSTRACT:

NiO QDs /ZnO nanorods composite structures for catalytic reduction of Cr^{6+}.

Name of student:	Imtiaz Ahmed
Registration number:	16mscchm11
Degree for which submitted:	Masters in Chemisrty
Name of supervisor:	Dr.K.K Haldar
Name of Department:	Chemical Sciences
Name of School:	School of Basic and Applied Sciences

Keywords: NiO/ZnO composite; decorated, heterostructure; photocurrents; Cr (VI);Photoreduction.

Infront of the emerging interest and talent to search for new materials, we have synthesized Nickel oxide (NiO) nanoparticles decorated Zinc oxide (ZnO) nanorods composite (NiO/ZnO) nanostructure. By the X-ray powder diffraction and high-resolution transmission electron microscopy (HRTEM) the NiO/ZnO heterostructure formation was confirmed. The fabricated environmental affable NiO/ZnO composite nanostructure under UV-lights shows a well-defined photoreduction characteristic of hexavalent Chromium (Cr) (VI) to tri-valent Chromium (Cr) (III). Photoluminescence (PL) spectroscopy, photocurrent study, and electrochemical impedance spectroscopy, proved that the superior photoreduction property is ascribed due to the decreased electron-hole recombination process. In addition to the photocatalytic activity rate of the NiO decorated ZnO nanorods was much higher than that of exposed ZnO nanorods dfv for the reduction of chromium (VI) and their rate of activity is found to be 0.306 min^{-1}. All results have demonstrates that in the development of high-performance photocatalyst the suitable surface engineering may open up new opportunities.

DEDICATION

This work is dedicated to my whole family specially my loving parents for their love, kindness, inspiration,patience and supports.

.

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This work was carried out from 1st of january onword .I owe my deepest gratitude to my supervioser Dr. K.K Haldar, without his continuous optimism, concerning this work enthusiasm, encouragement and support this study would heardly have been submitted.His guidance help me in all the time of research and writing of this thesis. I could not have imagined having better advisor and mentor for my M.Sc. study. I am grateful to **Dr.K.K. Haldar** for enlightening the first research paper and first glance of reaserch.

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Last, but not least, I would like to thanks my parents first to my mother a strong and gentle personality who teach me to trust in almighty Allah, and believe in hard work and to my father for earning an honest living for me and for supporting and encouragement to believe in myself and to my preety sister and my brothers for supporting me everytime.

Imtiaz Ahmed

CHAPTER I

Introduction:

High amount of heavy metals ions are detected from aquatic stream in minning operations, tanneries, petrochemical industries, electroplanting and also in textile industries and these useful high amounts of metals ions are cobalt, copper, nickel chromium, zinc, cadmium, mercury and arsenic (Patterson, 1987) etc. According to the Agency for Toxic Substances and Disease Registry (ATSDR), Cr (III) salts shows less mobility the of Cr (VI) and Cr(VI) shows higher mobility and are much toxic for human life .In aqueous solution, Cr^{6+} exist in the form chromate (CrO_2^{4-}), dichromate ($(Cr_2O_7)^-$) (Sharma & Forster, 1995). Hydrogen chromate ($HCrO_4$) which is of great concern due to its toxicity which is 500 time toxic then trivalent one.According to the WHO , the suggested limit of Cr^{6+} in potable water is only 0.5mg/l (Selvaraj, Manonmani, & Pattabhi, 2003). It causes lungs cancer, skin irritation and also harms kidney and liver (Gupta, Rastogi, & Nayak, 2010). Chromium exposure also affects the aquatic animals such as Whales. Recently, it has been reported that Free-ranging North Atlantic Sperm Whales and Right Whales are highly influenced by the Chromium (Chen et al., 2009)

For the remediation of chromium there is several chemical and physical technique using a low cost fertilizer industry (Qin, McGuire, Blute, Seidel, & Fong, 2005), (S. Lee, Lee, Chon, & Lee, 2008) waste material (Kratochvil, Pimentel, & Volesky, 1998) Seaweed Biosorbent,(Mohan & Pittman Jr, 2006) Membrane Filtration, using sphagnum moss peat(Sharma & Forster, 1993) Montmorillonite-supported magnetite nanoparticles, ,(Yuan et al., 2009) nanofiltration (Hafiane, Lemordant, & Dhahbi, 2000). UV irradiation in presence of TiO2 etc.VIA photo-catalytic reduction (Ku & Jung, 2001) of Cr(VI) to Cr (III)has been also achieved and are effectively used to remidate other heavy metal ions like Cd(II)(Nguyen, Amal, & Beydoun, 2003), Hg(II) and As (V) (H. Lee & Choi, 2002).From all these material, the much attracted intrest in particular NiO/ZnO heterostructural nanomaterial,because of NiO has p-type semiconductor (3.5e.V) low lattice mismatch with ZnO and high hole mobility which is highly beneficial for the formation of p-n heterojunction with ZnO.

As compared to other wide band gap oxides ZnO shows higher electron mobility property (Ko et al., 2011),(Klingshirn, 2007),(Dai et al., 2014) While ZnO and NiO nanostructures individually have been studiedextensively, the composite structure of NiO/ZnO nanocrystals has not been widely explored (Chrissanthopoulos et al., 2011), (Y.-M. Lee, Nung, & Lai, 2010) (Abbasi, Ibupoto, Khan, Nur, & Willander, 2013; Xu et al., 2012). So before discussing my result/work details a gliempse of nanomaterials are presented here..

Nano: The word ‘Nano, is a Greek word which mean ‘dwarf, and nano is prefix which is extremely small

Nanometerial: Nanoparticles may b defined as objects having range from 1-100nm this is only due to the size of nps may differ from the bulk material.Nps is used for chemical as well as biological purpose. The characterstic properties of nanostructure are highlighted to b result of side effect, classical and quantum ones, internally and externally that arise in zero dimensional quantum dots, one dimensional wire, and two dimensional layers. They have several applications which includes microlasers , photonic layers and probe microscopy etc.(Pokropivny, Lohmus, Hussainova, Pokropivny, & Vlassov, 2007)Systematic classification of nanostructural material: On the basis of their controlled manipulation of their microstructure on the atomic level it may be classified into different types, briefly they are discussed with example as under:

- 0-D System: e.g nano pores and nano particles, such as Fullerene
- 1-D System: It is confined only in one dimensional e.g layer or laminate type structure like Carbon nanotubes.
- 2-D System: Confined only in two dimension,e.g filament type structure where the length is greater then the cross-sectional dimensions such as grapheme or cone sheet.
- 3-D System: It is confined in three dimensions;e.g it is most typical structure composed of consolidated equiaxed crystallites such as graphite or nano-cone.

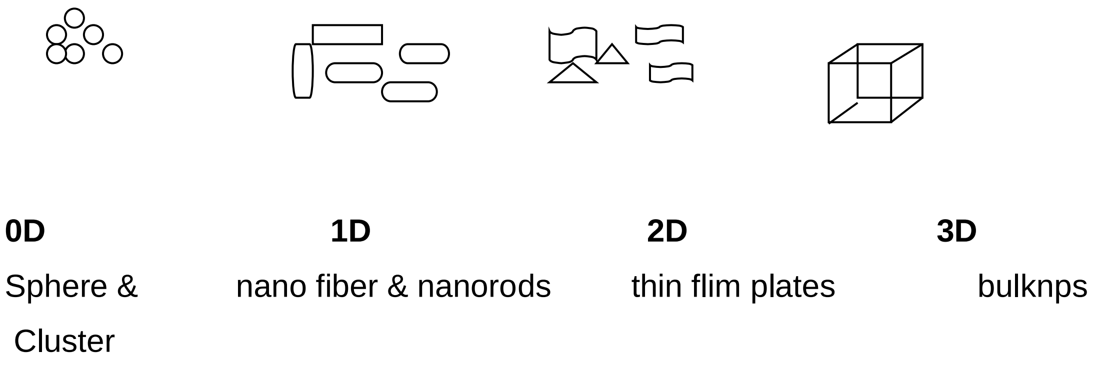

Figure 1. 0D,1D, 2D,3D structure of nanomaterial.

CHAPTER II

REVIEW LITRATURE:

Semiconductor nanocrystals:

On the nanometer scale these nanocrystal are very small light emmiting particles. Many researchers are studies all these semiconductor nanocrystals deeply and are devolped them for broad applications in molecular and cellular imaging solar energy conversion optoelectronic device and altrasensiative detection. The spatial enclosure within the nanocrystal of the electronic charge carriers is leaded by the most voital feature of the nanocrystal which is confinement effect. Nanocrystal having the typically dimensions in the range og 1-100nm, and are bridge the gaps between small molecule and large molecule showing separate electronic transitions of isolated atoms and molecules.bulk semiconductors are considered by the composition dependent band gap energy which requires the minimum energy to excite the electrons from the ground state valence energy band into the vacant conduction energy band.

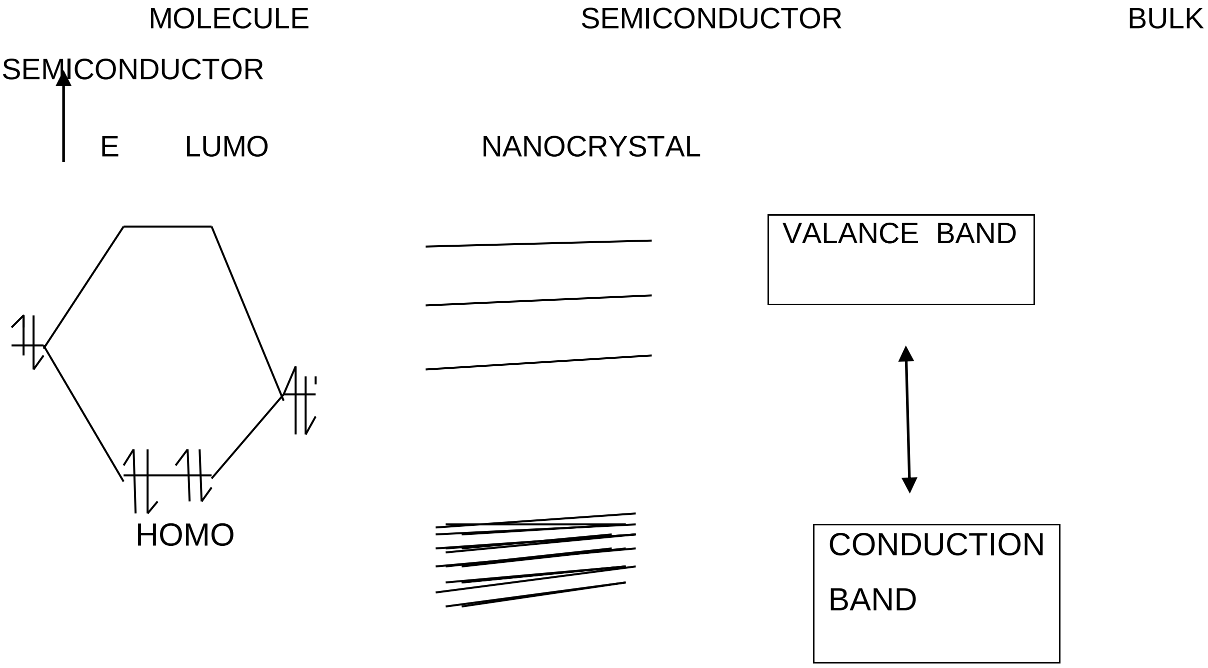

Figure 2. Semiconductors showing excitation of electron from valence energy band to thre vacant conduction energy band.

The crystal become smaller, the number of atoms will increase on the surfaces which undergo the impact on the optical properties. Within the crystal lattice the atom on the surface of the crystals incompletely bonded.

Metals nanocrystals: Nanocrystal is a material having atleast one dimensional less then 100nm and metals having small crystals are known as metals nanocrystals nanocrystal are lead to be the creation of new material with innovatory properties and function.

OXIDES:

It may be defined as the chemical compound which contain atleast one oxygen atom and another element from its chemical formula. E.g silver oxides ,ZnO ,Co2 and many more metals. The oxides are classified into fallowing types based on their nature and properties exhibited by the campound.

- Acidic oxides
- Basic oxides
- Amphoteric oxides
- Neutral oxides

- **Metal Oxides and their synthesis :**

The compounds which are mattalic in nature and are formed with metal and oxygen in the form of oxide ions (O^{2-}) are known as metal oxides. (examples) potassium oxide, magnesium oxide, sodium oxide, aluminium oxide, zinc oxide,lead oxides, nickel oxides, iron(III) oxide, and copper(II) oxide etc.

Generally metal oxide are mostly insoluble in water so they produced salt with acids, thay are basic in nature and are often exist in solid form at room temperature .Some metal oxide are amphoteric in nature and form salt with base in neutralization reaction.e.g when NaOH react with AlO2 to for sodium aluminate. The oxides of metal which has two O-O bonds are known as peroxides.

Nickel oxide: The chemical formula of nickel oxide is NiO. The well characterized oxides of nickel are Ni_2O_3 and NiO2. The nickel oxide is synthesized by various methods .The nps of the nickel oxided with the ZnO are discussed further.

Zinc Oxides:The chemical formula of the zinc oxide is ZnO. Zinc oxide is mostly used by the dermatologist for the treatment of skin.Nnostructure of the zinc oxide isis synthesized into a different morphologies which includes nanowires, nanorods, terapods, nanobelts, nanoflowers , nanoparticles.

The synthesis of zinc oxides are typically which are carried out at temperature of 90 C degree. In human and environment risk there are gap in understanding that manufactured nps pose for consumers and for occupational exposed people. The nanoparticles life cycle, the human exposure routes, the behavior of nps in the body, and the risk for workers which is a need for assessing the health and environmental impacts(Karthikeyan et al., 2017). Inhalation, absorption through the skin or digestive tract, injection, and absorption or implantation for drugs delivery systems for possible routes of entry into the body. ZnO are largely present in most of the sunscreen formulation to protect against UV-induced skin damage. It is represented to alternative to chemical agent because it does not undergo any chemical decomposition.

Actually, in many formulations ZnO are incorporated as nanosized particles because in this form they are apparent and more esthetically acceptable to the consumers. Two different formulations of 26–30 nm ZnO particles and one placebo cream base formulation containing no ZnO nanoparticles were compared.

Various synthetic methods for the synthesis of Nanoparticles (or) Synthesis of nanomaterials:

- Top-Down Procedures (Physical methods)
- Bottom-Up Procedures (Chemical Methods)
- Laser Ablation Sol-Gel method
- Chemical Vapour Spray pyrolysis Deposition
- Thermolysis Electro Deposition Micro Emulsion

With the help of liquid phase synthesis we can also synthesize the nanoparticles methods such as:

- Colloidal method
- Sol-gel processing
- Water oil microemulision method
- Hydrothermal method
- Polyol method

The most important method are discussed as under:

Colloidal method:

This method is easy and simple and well established wet precipitation methods mostly used in the chemistry in which ions of the different solution are are mixed under the countrolled pressure and temperature to form insoluble precipitates. The basic principle of the colloidal

prepration of the metal nanoparticles is known as antiquity.eg gould colloids are used to high quality red and purple stain glass.

Sol-gel technique:

Sol is the name colloidal solution which is made up of solid particles few hundred nm in diameter pendant in a liquid phase. Now **gel** is a solid macromolecule which absorbed in the solvent. Sol –gel technique consist of the transformation of the chemical of a liquid into a gel state and with subsequent post –treatment and transition into solid oxide material. The main banifits of the sol-gel processing are the high purity and uniform nanostructure produced at low temperature.

With the help of sol-gel method we can also synthesize the caremic material of high purity and homogeneity. The process occur by mean of liquid solution of organometallic precursors {Ti(IV)-Butoxides,TOMOS,TEOS, Zr(IV)propoxides} which undergo by mean of the hydrolysis and condensation lead to the formation of new phase{SOL}.

$M\text{-}O\text{-}R + H_2O \Longrightarrow M\text{-}O\text{-}H + R\text{-}O\text{-}H$ (hydrolysis)

$M\text{-}O\text{-}H + HO\text{-}M \Longrightarrow M\text{-}O\text{-}M + H_2O$ (water)

$$\mathrm{MO\text{-}O\text{-}R + HO\text{-}M} \Longrightarrow \mathrm{M\text{-}O\text{-}M + ROH}\ \text{(alcohol)}$$

M = Si,Zr, Ti,

Sol –gel is also used for couting under well defined controlled temperature and atmospheric temperature. It is used for making a thin coat on the flat substrate .this technique is used for high energy milling and mechanical milling.

Hydrothermal method:

This method is used under high temperature aquous solution at high vapour pressure. This method of synthesis is also used to synthesize single crystals that depend under high temperature on the solubility of minerial in hot water. The most important part of this hydrothermal synthesis is that method over the other type of crystal growth includes the ability to create the crystalline phase which is not stable at the melting points. This method is also suitable because the crystal formed during this synthesis have good crystal quality.

Quantum Dots:

The crystal of fluorescent semiconductor material having the diameter of as few as 10-100 atoms i.e 2-10 nm, are known as Quantum dots. They are resistance to photobleaching, brightness, fluorescence spectra, which are very narrow and are used to labels the imagae of the molecule. (QDs) are semiconductor nanocrystals consist of a colloidal core enclosed by one or more surface coatings that provide detailed description to this nanoparticles. These heterogeneous fluorescent nanoparticles have large potential for use as indicative and imaging agents in biomedicine and as semiconductors in the electronic industry.

In other word or in simple way the quantum dots are the semiconductors crystal having the nano meter dimensions with peculiar conductive properties which are determined by its size. These are made up of many of the same material as ordinary semiconductors .Qds is made with the help of two steps.

- Nucleation: This is initiated by heating a solvent at approximately 500 F and injucting a precursor such as cadmium and selenium, they chemically decompose amd recombine to form CdSe nanopareticles .

- Growth: The size of the nano crystal can be determined based upon the varying the length of time of reactions.

Specific physico-chemical properties of metal containing nanoparticles:

In relevant test of environments the physio-chemical properties of the particles should be thoroughly analyzed in order to understand the mechanism behinds the toxicity of Nps. The method that can be applied to characterized nps size, shape, crystal structure, aggregation, chemical composition surface properties, porosity and solubility and this in-depth overview is given by Bandyopadhyay et.al (2012) in the resent review. Joint nominators, Production and Differences in the physico-chemical characteristics of some metals such as Ag, CuO and ZnO NPs.

The joint nominators for Ag,CuO,and ZnO nps ist of all we have to notice the metallic elemental composition of all the three selected particles. Secondely, all the three nps are used to fight against the undesirable growth of microorganism in these three nps the CaO and ZnO are successfully used for biocides and silver nps are used most widely as antimicrobial.

The third joint nominator for the three NPs is their negative surface charge, which results from oxygen atoms in CuO and ZnO. The oxygen is not initially contain by the Ag nanoparticles, under most environmental condiation the surface of metallic Ag nps is oxidized and negatively charge oxo group and hydroxo group causes the negative surface charge of the particles.

Then toxicologically perhaps the most important joint property is that all the three NPs are soluble to some extent in aqueous media. As for as difference is concerned differences between Ag, CuO and ZnO there chemical composition is different so in similar particles size their toxicity is different. Furthermore copper is a redox element hacin common vale of 2 or 1.

Thus differently from Zn and Ag redox-active Cu ions may be involve in the electron transfer process. The surface of Ag nps but not CuO and ZnO is frequently functionilized with different couting PVP and creating most weidly used.

Last but not least, copper and zinc (but not silver) are necessary trace elementalmost all types of living cells, while silver has no known function in the living organisms.

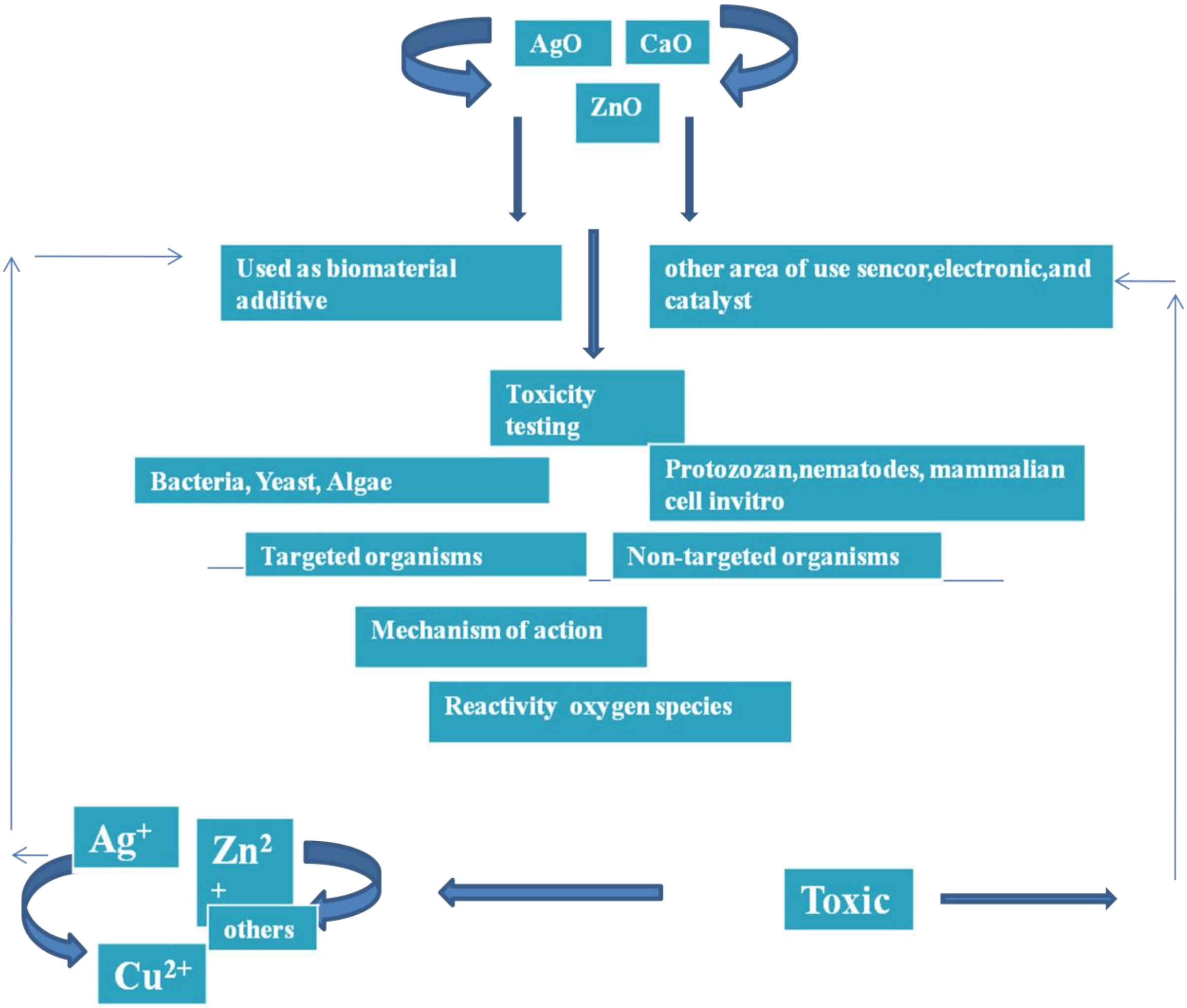

Figure 3 Representation of the production of ZnO,Ag,and CaO

Resent progress on NiO:

Nano-sized NiO metal or Ni-based alloy the coming out and quick development of nanotechnology has enable us to assemble nanostructures with a consistent size and morphological distribution helped by superficial synthetic procedures. For electrocatalysis, the considerably higher surface area afforded by the nanostructures can theatricalally improve the present density at the same overpotential by increasing the convenience of electrolytes to active surfaces. NiO nanostructures with high surface area can be synthesized using various methods, as well as bottom-up synthesis via the reduction of nickel salts as well as top-down template-based synthesis.

Because of the unique chemical and physical properties, the metallic and bimetallic nanoparticles with controlled size, density, morphology and composition is of great interest for their synthesis.. In general, a wide range of applications in several areas such as microelectronics, optoelectronics, catalysis, photocatalysis, biomedicine, information storage, among others have been proposed. NiO nad ZnO play vital role for forming the bimattelic compound. ZnO have wide direct band gap (3.5e.V) and is typically n-type semiconductor metal oxide whic h is another most important nanomaterials for UV photodetection for the photocatalytic applications. ZnO shows higher electron mobility property compared to other wide band gap oxides. While ZnO and NiO nanostructures individually have been studies broadly, the combine structure of NiO/ZnO nanocrystals has not been widely explored.

With the help of two method sol-gel process and microwave route a well designed composite nanostructure of NiO nanoparticles and decorated ZnO nanorods in aqueous solution These NiO nanoparticles decorated ZnO nanorods composite nanostructures visible excellent UV-visible light directed photocatalytic presentation for the photoreduction of toxic heavy metals of Cr (VI) to Cr (III).

Photocatalytic activity of ZnO/NiO: In combinatoion of light such as UV or Sunlight ability of some nano material (e,g TiO_2) which speet up a certain reaction i.e photoreaction, as an catalyst is known as photocatalytic activity. For the degradation of some organic dyes there is to much research groups used to study ZnO nps as photocatalyst and at last found that it show good photocatalytic activity.ZnO have various photocatalytic application and they are non toxic in nature. Pure ZnO shows n-type conductivity. ZnO nanoparticles have almost diverse application in all the fields, such as ceramics, piezoelectric chemical sensors,anti-UV additive ,photocatalyst and transducers (Nagaraju, Shivaraju, Banuprakash, & Rangappa, 2017). They attract much concentration in photoelectric fields such as UV-lights emitter. In case of NiO it exhibits high photocatalytic activites, the photogenerated electron can easily migrated from NiO to ZnO because conduction band of NiO is more negative than that of the conduction band of ZnO. The combine system of ZnO and NiO show good photocatalytic activites.

Experimental methods:

Chemical Used:

Nickel nitrate hexahydrate(Otto, 98%), Zinc nitrate hexahydrate (SDFCL, LR), potassium dichromate ($K_2Cr_2O_7$) (Loba Chemie, 99.9 %), ethylenediamine (SDFCL, AR), 1, 5 – diphenylcarbazide (Loba Chemie, 98%), Na2SO4 (Loba Chemie, 99 %),

NH_3 solution (Loba Chemie, 25%), sodium alginate (SDFCL, AR), sodium hydroxide(Loba Chemie, 98%), ethanol(AR, 99.9%), HCl (SDFCL, 85%),. Without any further purification all the above chemical are used for this work.

CHAPTER III

Methods:

For the production of NiO nanoparticles decorated ZnO nanorods composite nanostructure first of all ZnO nanorods were synthesized after that then NiO was deposited on ZnO nanorods . With slight modification the ZnO nanorods were prepared (Jia, Wang, Dong, Long, & Fu, 2009). For a short time in 50ml double distilled water 7.45g zinc nitrate hexahydrate and 20g NaOH (sodium hydroxide) were dissolved .Then 4ml of alkali solution of zinc was mixed with 3ml ethlenediamine and 15ml pure ethnol, followed by the sonication for atleast 30mins.

After that the mixture of the solution was transferred to a Teflon-lined autoclave for hydrothermal synthesis and then reaction were conducted at the temperature of 180 C degree in a electric hot air oven atleast 24hrs .after the reaction the method centrifuge is take place and the ZnO nanorods were collected by centrifugation a nd fallowed by frequent washing with ethnol and deionised water for NiO nanoparticles decoration. In a classical method NiO nanoparticles, 54 mg $Ni(NO_3)_2 \cdot 6H_2O$ and 50mg ZnO nanorods were dissolved in de ionized water (100 ml) and 0.1M sodium alginate was added to the solution to serve as stabilizing agent.

Next, the ammonia (NH_3) solution was added to maintain the pH below 6 which avoid the formation of $Ni(OH)_2$ and then place it for 30min.In a microwave oven for microwave irradiation. After that at 6000 rpm the solid gel like product was washed by centrifugation and for further characterization it re-dispersed in deionized water and at last the final product was to b found in blackish in colour.

CHAPTER IV

Instrumentation:

The obtaind crystalline phase of the ZnO nanorods and NiO/ZnO caompsite was studied by the X-Ray differaction pattern (Bruker's Eco D8 advance). By using a JEOL-TEM 2010 transmission electron microscope with an operating voltage of 200kV the transmission electron microscopy were taken. Absorption spectra were obtained with a UV-Vis spectrophotometer (Shimadzu) at room temperature .In Fluoro Max-P (HORIBA JOBIN YVON) Luminescence Spectrometer the emission spectra of all sample were recorded. In a cylindrical annular batch photoreactor fitted with a medium pressure mercury vapor lamp of 125W and lamp was surrounded with a double-walled borosilicate immersion well and cooled by circulating water constantly in which the the photoreduction of Cr(VI) was done. For the photoreduction study, 20ppm of potassium dichromate solution in 100ml and 30 mg of catalyst were taken in the reaction vessel. By using 0.1M HCl and 0.1M NaOH before starting the experiment, the pH of solution was maintained at some extent above 2. The solution was subjected to adsorption desorption equilibrium fot about 15min. under dark condition. During the photoreduction the aliquots were collected at regular time intervals. The analysis of Cr (VI) was carried out byforming a complex with 1, 5 - diphenylcarbazide

CHAPTER V

Results and discussion:

Electrons are transfer from NiO to ZnO increase the lifetime because of the improvement of photocurrent. The enhanced photoelectrochemical activities for the NiO decorated ZnO nanorods composites could be attributed to the larger surface area of NiO nanoparticles which can reduce quick. The powder X-ray diffraction (XRD) patterns of ZnO nanorods and NiO decorated ZnO nanorods composite structures are shown in Figure 4. The powder XRD patterns are well matched with the standard JCPDS Card. The XRD pattern (refer spectra ‘a’ of figure 4) clearly shows single crystalline phase and hexagonal structure of ZnO nanorods (JCPDS card no. 36- 1451).

However, in the case of NiO decorated ZnO nanorods composite samples, the XRD pattern exhibits patterns for both NiO and ZnO structures. The diffraction peaks at 36°, 43.1° and 63.5o (Figure 4b) are for NiO (JCPDS card no. 44-1159) and ZnO respectively, and the remaining peaks in the NiO decorated ZnO nanorods composite specimens are guided to be the hexagonal structure of ZnO. (Jia et al., 2009)

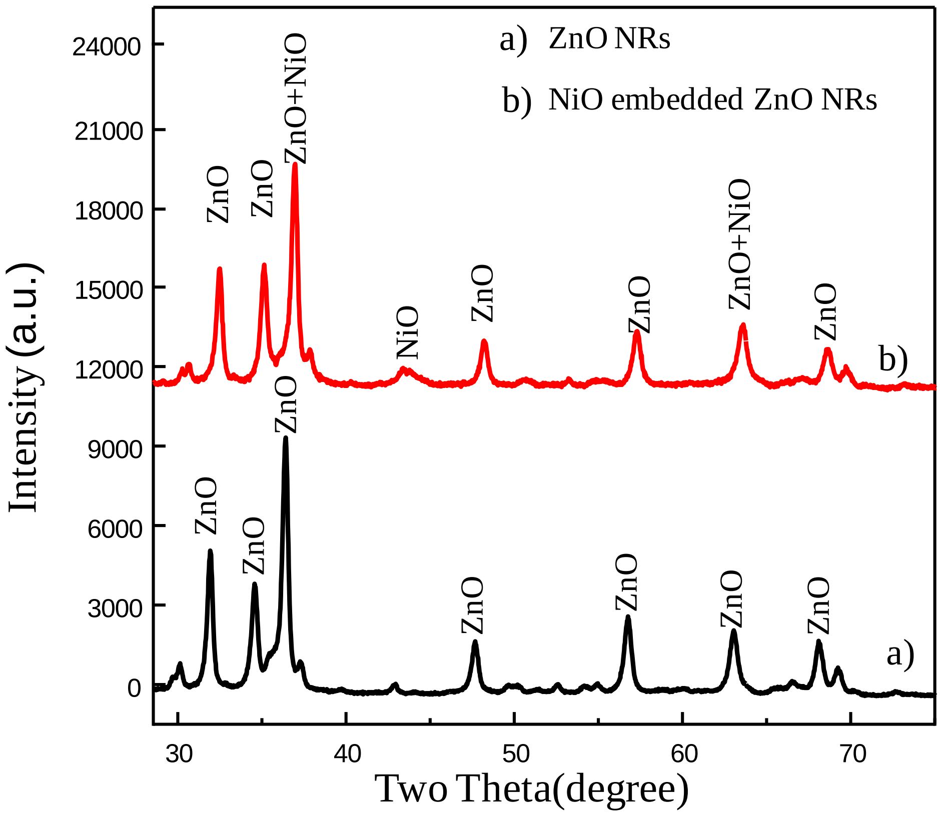

Figure 4. The powder X-ray diffraction (XRD) patterns of (a) ZnO nanorods and (b) NiO
Embedded ZnO nanorods composite structure

This result indicates that the precursor has completely transformed into NiO decorated ZnO nanorods composite structure. The hexagonal structure of ZnO nanorods was not modified by the decorating of NiO nanoparticles into the ZnO surface. The as-prepared NiO decorated ZnO nanorods composite structures were further characterized by transmission electron microscopy (TEM) and is shown in Figure 5. Figure 5a reveals a wide view of the TEM images showing NiO/ZnO nanorods. They could easily assemble together to form a 1D structure when dropped on the carbon-supported copper grid with an appropriate concentration. Without size sorting, the 1D structured nanocrystals obtained here showed good monodispersity with the existence of well-resolved lattice planes. The decorated ZnO nanorods composite structures possessed a highly crystalline structure. The NiO/ZnO heterostructures were further confirmed HRTEM analysis. Figure 5b shows a typical HRTEM image of a longitudinal of NiO/ZnO nanorods where both ZnO and NiO are visualized. This result clearly reveals that the favored growth directions of ZnO nanorods are along the [0001] direction. From the HRTEM, FFT, inverse FFT images, and line-scan height profile (Figure 5e-h), the dspacing was obtained as 2.81Å, which corresponds to the (100) planes of hexagonal ZnO. The typical dspacing was also calculated for NiO onto the ZnO nanorods and the value is 2.41Å corresponds to the (100) planes of NiO. From the lattice parameters, it is evident that the lattice mismatch between NiO and ZnO are very close, resulting in the difficulties in identifying the interface between NiO and ZnO both simultaneously. However, the NiO particle and ZnO nanorods combine together easily and form a heterojunction.

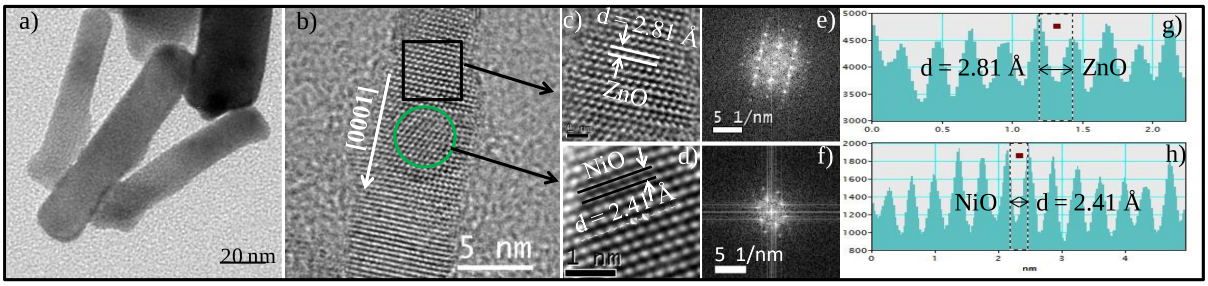

Figure 5. Represents the TEM images of (a) NiO decorated ZnO nanorods, (b) typical HRTEM images of NiO decorated ZnO nanorods where NiO (c) and ZnO (d) (e and f). Area are marked to achieve the FFT of the selected area. And (g and represents to corresponding d-profile of ZnO and NiO, respectively.

We have correlated the photocurrent response of ZnO nanorods and NiO decorated ZnO nanorods composite counterpart electrodes by inserting them in a photoelectrochemical cell to prove the effect of NiO decoration onto ZnO on the charge separation of ZnO for the present heterostructure. The photocurrent response of ZnO nanorods and NiO decorated ZnO nanorods composite structures are shown in Figure 6, under illumination of light irradiation. Both of them shows effective response towards the on/off cycle of light depicting the electron transfer process. From the Figure, it is clearly seen that photocurrent response of NiO decorated ZnO nanorods crystal is higher compared to ZnO nanorods.

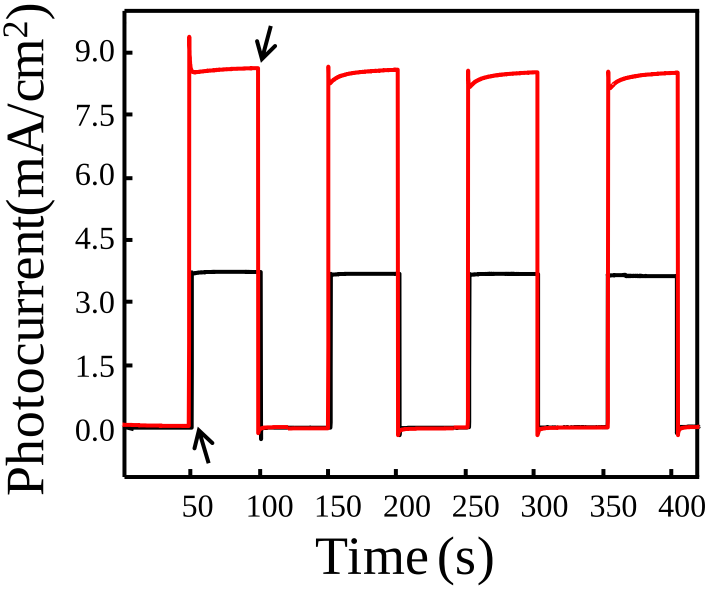

Figure 6 Photocurrent potential versus time scans for ZnO nanorods (black) and for NiO decorated ZnO nanorods (red). The upward arrow (↑) and downward arrow (↓) represent the switching on and off step of the illumination, respectively.

The following responses for charge recombination process in the ZnO films (Zheng et al., 2015) Thus, the enhancement of the photoresponse speed can widen the opportunity of exploiting NiO decorated ZnO nanorods heterostructures for superior photocatalytic activities. The photogenerated electron separation was further confirmed by comparing the photoluminescence (PL) spectra of the ZnO nanorods in absence and presence of NiO nanoparticles, respectively. Figure 7 represents the PL spectra of ZnO nanorods and NiO decorated ZnO nanorods, respectively. From the figure, it is found that the NiO decorated ZnO nanorods exhibited much lower emission intensity than ZnO nanorods, indicating that the recombination of the photogenerated charge carrier was greatly inhibited in presence of nanoparticles onto ZnO nanorods. At the same time, this commanding visible emission is associated with the increase of surface oxygen vacancy-related defects of ZnO NRs in the NiO decorated ZnO heterostructures.

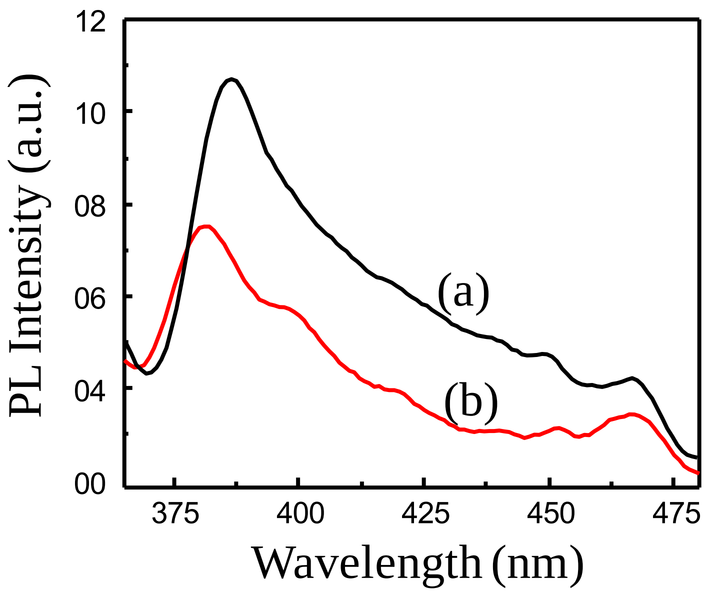

Figure 7. Photoluminescence (PL) spectra of (a) ZnO nanorods and (b) NiO decorated ZnO nanorods

The present result suggests a high separation efficiency of photogenerated electron-hole pairs for NiO decorated ZnO nanorods compared to bare ZnO nanorods (Zhang et al., 2010) For a better understanding the origin of the admirable photocatalytic performance of NiO decorated ZnO nanostructures, and to support Photoluminescence (PL) results, we utilized electrochemical impedance spectroscopy (EIS) studies. The Nyquist plots, a complex impedance plot has been presented here to figure out the different electrochemical characteristics of the electrode-electrolyte interface. Figure 8 shows the analysis of the impedance spectra of NiO decorated ZnO nanostructures and ZnO nanorods. A larger impedance semicircle radius in the high-frequency region is revealed for NiO decorated ZnO composite nanostructures compared to bare ZnO nanorods, which corresponds to a larger recombination {He, 2009 #50}]. It is well known that the recombination resistance is inversely proportional to the recombination rate of the photoinduced charge carriers {Kim, 2014 #51}. By the way, the NiO decorated ZnO composite nanostructures have a lower recombination rate of the photoinduced charge carriers over bare ZnO nanorods.

Thus, NiO deposition on ZnO nanorods significantly hindered the recombination rate of the photoinduced charge carriers which leads to an excellent visible light directed photocatalytic application of NiO decorated ZnO composite nanostructures. This indicates the persistent by our EIS results,which also consists of the photoluminescence analysis.

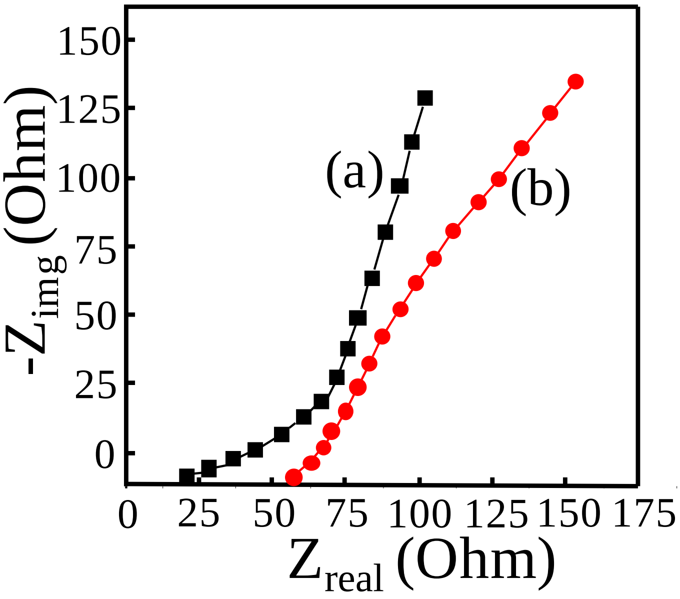

Figure 8 .The Nyquist plots of (a) NiO decorated ZnO nanorodsand (b) ZnO nanorods catalysts.

Finally, the photocatalytic activity of the NiO decorated ZnO nanorods composites (NiO/ ZnO)for the reduction of inorganic pollutants has been demonstrated by carrying out experiments ofthe photocatalytic reduction of Cr (VI) ion as a test reaction. Therefore photocatalytic reduction of Cr (VI) was explored by using both bare ZnO nanorods and NiO decorated ZnO nanorods composite heterostructure. Figure 9 shows the photoreduction of Cr (VI) in aerobic condition under UV light exposure against time and the concentration was measured at 356 nm at pH slightly above 2.

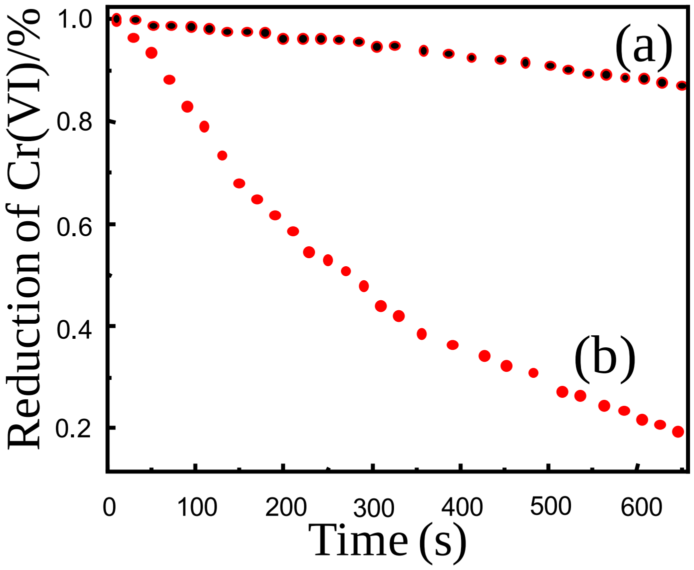

Figure 9. (i) Photoreduction of Cr (VI) to Cr (III) in presence of (a) ZnO and (b) NiO decorated ZnO nanorods heterostructures under UV light

The pH of the aqueous solution is crucial for the adsorption of Cr(VI) possibly because of the presence of various Cr(VI) species. Oxalic acid was used as a hole scavenger for the photoreduction studies. It is found that the absorbance is gradually reduced with increased UV irradiation time for the NiO decorated ZnO nanorods composite heterostructure. It clearly shows thatshows that the process is slower in the case of ZnO nanorods. Figure 10(i) represents the Cr (VI) reduction rate as a function of UV irradiation time. It is found that the absorbance of Cr (VI) is gradually reduced with increased duration of UV irradiation time for the NiO decorated ZnO nanorods composite heterostructure shown in above given (Figure 9. The ZnO and NiO decorated ZnO nanorods composite heterostructures were tested for 11 min under identical conditions. It is interesting to observe that 98.7% of Cr (VI) is reduced to Cr (III) by the NiO decorated ZnO nanorods composites after 11 min of UV irradiation, whereas 10.3% reduction is observed in the case of ZnO nanorods.

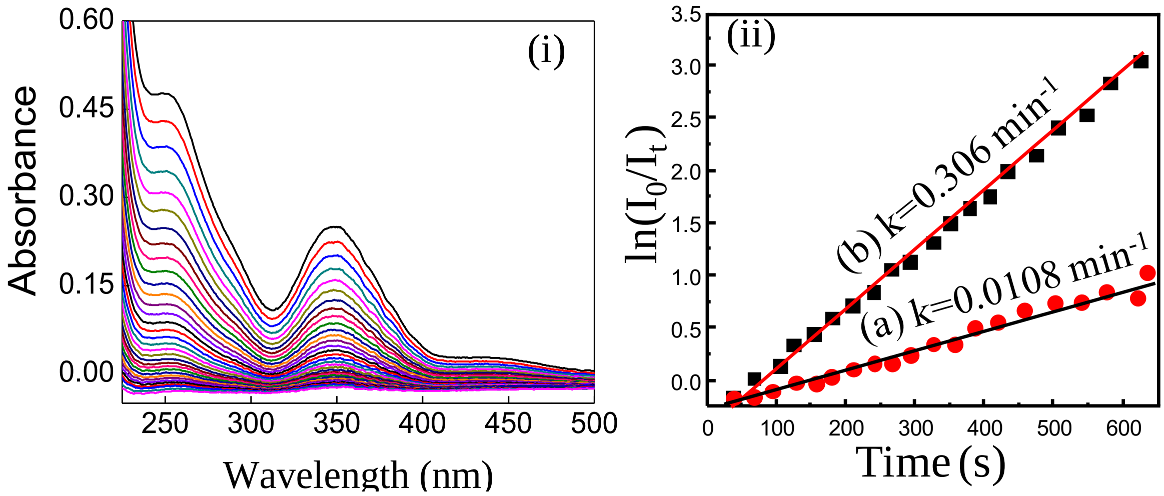

Figure 10 (i) The absorbance spectral changes of Cr(VI) solution in the presence NiO decorated ZnO nanorods heterostructures, and (ii) Photocatalytic reduction of Cr(VI) in presence of ZnO naorods (a) and presence NiO decorated ZnO nanorods heterostructures under UV light (b).

The photoreduction of Cr (III) under the same UV irradiation condition is negligible in the presence of NiO nanoparticles, and in absence of both ZnO nanorods and NiO decorated ZnO nanorods composites. Therefore, the large reduction efficiency of Cr (VI) to Cr (III) in the solution can be attributed to a photocatalytic effect that happens due to the presence of the NiO decorated ZnO nanorods composites. Degradation rate kD is calculated using following equation:

$$kD = (C0-C)/C \quad (1)$$

where C0 and C are the initial absorbance and the sample absorbance, respectively. The kinetic profiles of Cr (VI) to Cr (III) reduction under UV light are also investigated. The photoreduction of Cr (VI) to Cr (III) follows apparently first-order kinetics. Its kinetics can be expressed as

$$ln(I_0/I_t) = kt,$$

where k is the apparent reaction rate constant, I_0 is the concentration of Cr (VI) at

adsorption equilibrium, and It is the residual concentration of Cr (VI) at different illumination time intervals. To optimize the NiO decorated ZnO nanorods catalyst concentration, the effect of catalyst concentration on the Cr (VI) to Cr(III) photoreduction in aqueous solution

was investigated. The results are illustrated in Figure 11.

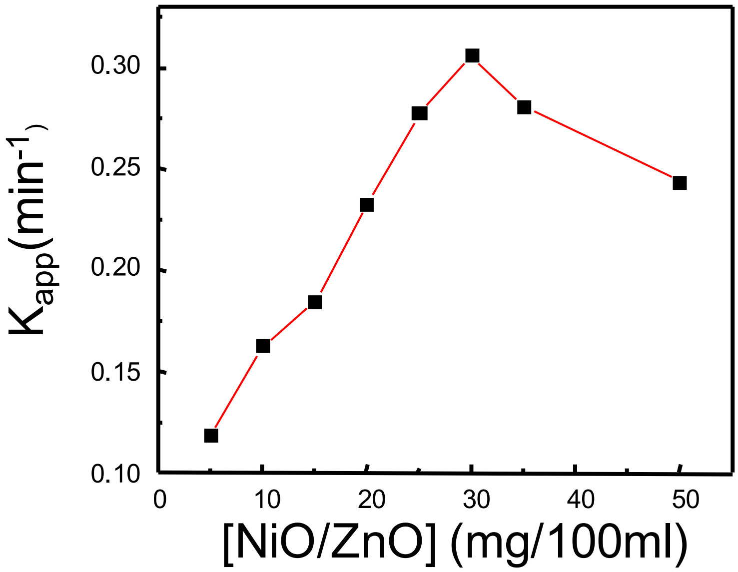

Figure 11. Optimization of photo catalyst loading on photocatalytic reduction of Cr (VI) to Cr (III) using NiO decorated ZnO composite nanorods.

The lifetime of a catalyst is an important parameter for any catalytic process because of its further use for a long span of time leading to a significant cost diminution. For this reason, the NiO decorated ZnO nanorods composites catalyst was recycled, which indicate a slowdown in efficiency only from 100% (first run) to 95.0% (sixth run) as shown in Figure 12. Figure 10(ii) shows a linear relationship between *ln(I0/It)* and reaction time (*t*), indicating that the photoreduction of Cr (VI) follows a first-order kinetics model.

The apparent rate constants as kinetic evidence for the samples are determined to be 0.0108 and 0.306 min-1 for ZnO nanorods and NiO decorated ZnO nanorods composite heterostructure, respectively. Thus, the photoreduction of Cr(VI) to Cr(III) enhances due to NiO decorated onto ZnO nanorods. This is because of the promotion of an electron from NiO to ZnO when UV-light was illuminated and is responsible for possible photoreduction Cr(VI) to Cr(III) . These results clearly demonstrate that NiO decorated ZnO nanorods composites have significantly improved photoreduction of Cr(VI) in comparison with bare ZnO nanorods. Thus, the

NiO decorated ZnO nanorods composite heterostructures improve the separation of photogenerated electron-hole pairs due to the potential energy differences between NiO and ZnO, thus enhancing the photoreduction activity of Cr(VI).

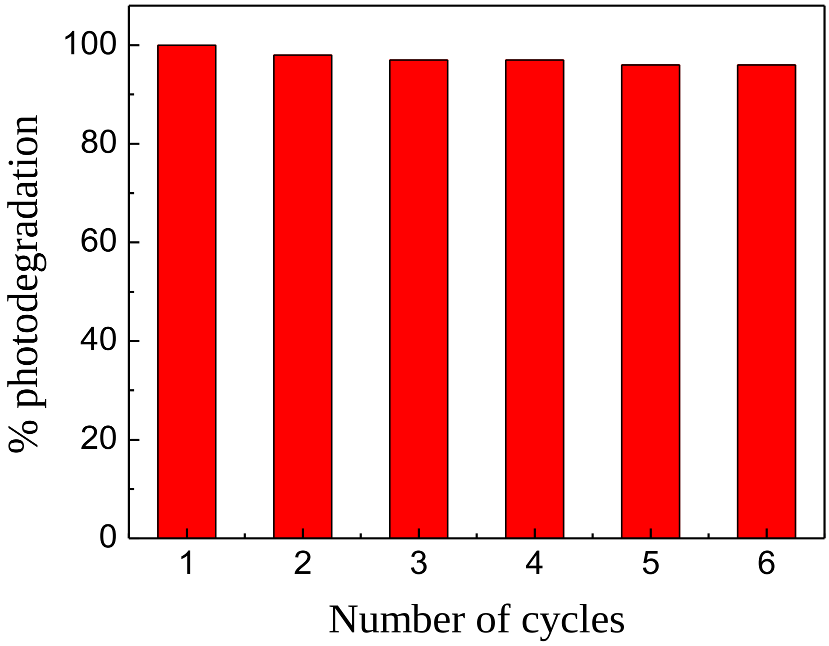

Figure 12. Recycling and reuse of NiO decorated ZnO nanorods photocatalyst for the photoreduction of Cr(VI) to Cr(III).

CHAPTER VI

4. Conclusion

In précis, by using a microwave technology and sol-gel process, NiO/ZnO nanorods composite structurewere profitably fabricated with NiO were decorated on the ZnO nanorod surface. The examination of photoreduction capability shows that the NiO nanoparticles decorated ZnO nanorods composite structure possess higher photoreduction ability than the bare ZnO nanorods for the reduction of Cr (VI) to Cr (III) under UV-light irradiation due to the enhanced separation efficiency of photogenerated electron-hole pairs and exhibited excellent stability (about 5% loss after six cycles). Furthermore, the photocatalytic activity rate of the NiO decorated ZnO nanorods for the reduction of chromium (VI) is much higher than that of bare ZnO nanorods and the rate is found to be 0.306 min-1. Comparing our results with literature, it is found that NiO decorated ZnO nanorods composite shows much better photoreduction of Cr(VI) to Cr(III) to most of the other photocatalyst reported by ref 8 and 18. These results have demonstrated that suitable surface engineering may open up new opportunities in the development of high-performance photocatalyst. This work will be carried out in our lab for developing new NiO/ZnO nanocomposite based photoanode for the photoelectrochemical cell.

References:

Abbasi, M. A., Ibupoto, Z. H., Khan, A., Nur, O., & Willander, M. (2013). Fabrication of UV photo-detector based on coral reef like p-NiO/n-ZnO nanocomposite structures. *Materials Letters, 108*, 149-152.

Chen, T. L., Wise, S. S., Holmes, A., Shaffiey, F., Wise Jr, J. P., Thompson, W. D., . . . Wise Sr, J. P. (2009). Cytotoxicity and genotoxicity of hexavalent chromium in human and North Atlantic right whale (Eubalaena glacialis) lung cells. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology, 150*(4), 487-494.

Chrissanthopoulos, A., Baskoutas, S., Bouropoulos, N., Dracopoulos, V., Poulopoulos, P., & Yannopoulos, S. (2011). Synthesis and characterization of ZnO/NiO p–n heterojunctions: ZnO nanorods grown on NiO thin film by thermal evaporation. *Photonics and Nanostructures-Fundamentals and Applications, 9*(2), 132-139.

Dai, W., Pan, X., Chen, S., Chen, C., Wen, Z., Zhang, H., & Ye, Z. (2014). Honeycomb-like NiO/ZnO heterostructured nanorods: photochemical synthesis, characterization, and enhanced UV detection performance. *Journal of Materials Chemistry C, 2*(23), 4606-4614.

Gupta, V. K., Rastogi, A., & Nayak, A. (2010). Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *Journal of Colloid and Interface Science, 342*(1), 135-141.

Hafiane, A., Lemordant, D., & Dhahbi, M. (2000). Removal of hexavalent chromium by nanofiltration. *Desalination, 130*(3), 305-312.

Jia, T., Wang, W., Dong, Y., Long, F., & Fu, Z. (2009). Controlling growth of ZnO nanostructures via a solution route. *Journal of Wuhan University of Technology-Mater. Sci. Ed., 24*(2), 249-253.

Karthikeyan, V., Padmanaban, A., Dhanasekaran, T., Kumar, S. P., Gnanamoorthy, G., & Narayanan, V. (2017). Synthesis and Characterization of ZnO/NiO and Its Photocatalytic Activity. *Mechanics, Materials Science & Engineering Journal, 9*.

Klingshirn, C. (2007). ZnO: From basics towards applications. *physica status solidi (b), 244*(9), 3027-3073.

Ko, S. H., Lee, D., Kang, H. W., Nam, K. H., Yeo, J. Y., Hong, S. J., . . . Sung, H. J. (2011). Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell. *Nano letters, 11*(2), 666-671.

Kratochvil, D., Pimentel, P., & Volesky, B. (1998). Removal of trivalent and hexavalent chromium by seaweed biosorbent. *Environmental science & technology, 32*(18), 2693-2698.

Ku, Y., & Jung, I.-L. (2001). Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. *Water Research, 35*(1), 135-142.

Lee, H., & Choi, W. (2002). Photocatalytic oxidation of arsenite in TiO2 suspension: kinetics and mechanisms. *Environmental science & technology, 36*(17), 3872-3878.

Lee, S., Lee, J.-U., Chon, H., & Lee, J. (2008). Reduction of Cr (VI) by indigenous bacteria in Cr-contaminated sediment under aerobic condition. *Journal of Geochemical Exploration, 96*(2-3), 144-147.

Lee, Y.-M., Nung, W.-M., & Lai, C.-H. (2010). Fabrication and characterization of ZnO branched nanorods and ZnO/NiO heterojunction electrodes by chemical solution method. *Physica E: Low-dimensional Systems and Nanostructures, 42*(9), 2289-2294.

Mohan, D., & Pittman Jr, C. U. (2006). Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of hazardous materials, 137*(2), 762-811.

Nagaraju, G., Shivaraju, G., Banuprakash, G., & Rangappa, D. (2017). Photocatalytic Activity of ZnO Nanoparticles: Synthesis via Solution Combustion Method. *Materials Today: Proceedings, 4*(11), 11700-11705.

Nguyen, V. N. H., Amal, R., & Beydoun, D. (2003). Effect of formate and methanol on photoreduction/removal of toxic cadmium ions using TiO2 semiconductor as photocatalyst. *Chemical engineering science, 58*(19), 4429-4439.

Patterson, J. W. (1987). *Metals speciation separation and recovery* (Vol. 1): CRC Press.

Pokropivny, V., Lohmus, R., Hussainova, I., Pokropivny, A., & Vlassov, S. (2007). *Introduction to nanomaterials and nanotechnology*: Tartu University Press Ukraine.

Qin, G., McGuire, M. J., Blute, N. K., Seidel, C., & Fong, L. (2005). Hexavalent chromium removal by reduction with ferrous sulfate, coagulation, and filtration: A pilot-scale study. *Environmental science & technology, 39*(16), 6321-6327.

Selvaraj, K., Manonmani, S., & Pattabhi, S. (2003). Removal of hexavalent chromium using distillery sludge. *Bioresource Technology, 89*(2), 207-211.

Sharma, D., & Forster, C. (1993). Removal of hexavalent chromium using sphagnum moss peat. *Water Research, 27*(7), 1201-1208.

Sharma, D., & Forster, C. (1995). Column studies into the adsorption of chromium (VI) using sphagnum moss peat. *Bioresource Technology, 52*(3), 261-267.

Xu, L., Zheng, R., Liu, S., Song, J., Chen, J., Dong, B., & Song, H. (2012). NiO@ ZnO heterostructured nanotubes: coelectrospinning fabrication, characterization, and highly enhanced gas sensing properties. *Inorganic chemistry, 51*(14), 7733-7740.

Yuan, P., Fan, M., Yang, D., He, H., Liu, D., Yuan, A., . . . Chen, T. (2009). Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium [Cr (VI)] from aqueous solutions. *Journal of hazardous materials, 166*(2-3), 821-829.

Zhang, Z., Shao, C., Li, X., Wang, C., Zhang, M., & Liu, Y. (2010). Electrospun nanofibers of p-type NiO/n-type ZnO heterojunctions with enhanced photocatalytic activity. *ACS applied materials & interfaces, 2*(10), 2915-2923.

Zheng, X., Yan, X., Sun, Y., Bai, Z., Zhang, G., Shen, Y., . . . Zhang, Y. (2015). Au-embedded ZnO/NiO hybrid with excellent electrochemical performance as advanced electrode materials for supercapacitor. *ACS applied materials & interfaces, 7*(4), 2480-2485.