

Surfactant Mediated Synthesis and Characterization of Zinc Oxide Nanoparticles

A Dissertation

Submitted in partial fulfillment

FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy
National Institute of Technology, Rourkela



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CERTIFICATE

This is to satisfy that the thesis entitled “**Surfactant mediated synthesis and characterization of zinc oxide nanoparticles**” being submitted by Ms. Naubadini Sahoo (Roll No. – 412CY2022) for the partial fulfilment of the requirements for the award of M.Sc. degree in Chemistry at the National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of a degree or diploma.

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ACKNOWLEDGEMENTS

I owe this unique opportunity to place on record my deep sense of gratitude & indebtedness to **Dr. Aparna Mondal**, Department of Chemistry, N.I.T. Rourkela, for her scholastic guidance, prudent suggestions & persistent endeavor throughout the course of investigation.

I heartily owe my sincere gratitude & thankfulness to **Dr. N. Panda**, HOD of Department of Chemistry, NIT Rourkela for giving me the opportunity to do the project works in the institute.

My sincere gratitude is to **Amar** and **Bappaditya Bhai** for their overall guidance, immense help, valuable suggestions, constructive criticism & painstaking efforts in doing the experimental work & preparing the thesis.

Lastly, I express my abysmal adoration & heartfelt devotion to **my beloved parents** for their countless blessings, unmatched love, affection & incessant inspiration that has given me strength to fight all odds & shaped my life, career till today.

In the end I must record my special appreciation to **GOD** who has always been a source of my strength, inspiration & my achievements.

CONTENT

CHAPTER 1

INTRODUCTION	Page No
1.1 Crystal Structures of ZnO	6
1.2 Synthesis of Zinc Oxide:	7
1.3 Objective of present work	7

CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 Synthesis of ZnO nanostructure by precipitation Route	8
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CHAPTER 3

RESULT & DISCUSSION

3.1 Differential Scanning Calorimetry (TG-DSC)	8-9
3.2 X-Ray diffraction (XRD)	9-11
3.3 Fourier transforms Infrared Spectroscopy (FT-IR)	11-12
3.4 UV – Spectroscopy	12-13
3.5 Removal of Cr (VI) from aqueous solution	13-14

SUMMARY AND CONCLUSION	15
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REFERENCES	15-16
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ABSTRACT

ZnO nanoparticles were prepared synthesized by using wet chemical route directly from an aqueous solution of zinc acetate dehydrate and in the presence of sodium dodecyl sulfate (SDS) and sodium hydroxide. ZnO is an interesting semiconductor material due to its application on solar cells, gas sensors, ceramics, catalysts, cosmetics. The as-synthesized Zn(OH)₂ powders were calcined at various temperatures of 500°C, 650°C, 800°C and 1000°C. The materials prepared were characterized by DSC-TGA, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and UV-visible spectroscopy. From the thermal studies the mass loss was found to be only 19%. Results show that the calcinations temperature significantly affected the crystalline nature, and optical properties of the processed ZnO nanoparticles. The XRD spectra indicate that the ZnO crystal has a hexagonal wurtzite structure. Zinc oxide showed excellent UV absorption and transparency in the visible region.

CHAPTER 1

INTRODUCTION

Zinc oxide (ZnO) occurs naturally but most zinc oxide is produced synthetically. This semiconductor has several good properties such as good transparency, high electron mobility, wide band group, and strong room temperature luminescence, etc. ZnO has wide range of applications like transparent conducting electrode in flat panel displays and window layers in thin film hetero junction solar cells [1-6], due to its unique properties such as piezoelectric and transparent conducting properties, and optical transmittance in the visible region. ZnO has a wide band gap (3.37 eV) and a large excitation binding energy (60 meV). These properties are used in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes. A method for economical mass production and determination of conditions favorable for the synthesis of ZnO nanostructures would be very useful. That is why the study of synthesis and understanding of ZnO nanostructures is of great interest and technological important [1-7].

1.1. Crystal Structures of ZnO

ZnO is present in earth crust as a mineral zincite; however, most ZnO used commercially is synthesized synthetically. Zinc oxide mainly crystallizes in three forms: (i) hexagonal wurtzite, (ii) cubic zincblende, and the rarely observed (ii) cubic rocksalt. The most common structure is wurtzite, which is stable at ambient conditions. The zinc blende form can be stabilized by the growth of ZnO on substrates with cubic lattice structure. The zinc and oxide centers are tetrahedral in nature in both the cases. The rocksalt (NaCl-type) structure is observed only at relatively high pressure about 10 GPa.

There is no inversion symmetry in hexagonal and zinc blende polymorphs (reflection of a crystal relatively any given point does not transform it into itself). Wurtzite structure of ZnO is the most stable state, which has a hexagonal unit cell with lattice parameters $a = 0.329$, and $c = 0.520$ nm. This wurtzite structure has an ABAB hexagonal close packing (HCP) structure. The Zn cations and oxygen anions form a tetrahedral unit. The central symmetry lacks in the entire structure. The structure of ZnO can be described as a number of alternating planes composed of tetrahedral coordinated O^{2-} and Zn^{2+} ions, stacked alternatively along the c-axis.

1.2. Synthesis of Zinc Oxide

Recently, a great research interest has been given on synthesis of technologically important ZnO nanostructures [2-6]. ZnO is a direct band gap semiconductor with enormous potential applications in areas such as laser diode, optoelectronic devices and devices for solar energy conversion [8], ultraviolet optoelectronics, transparent electronics and powder generation etc. As the shape and size of the ZnO particles depends on the reaction conditions during their formation, different physical or chemical methods have been used to synthesize ZnO nanoparticles. For example, sol-gel, hydrothermal, thermal decomposition, thermolysis, spray pyrolysis, precipitation and co-precipitation. Among all these different methods the precipitation is one of the most important methods to prepare nanopowder. ZnO crystals and nanocrystals may also be prepared by methods including the use of templates, chemical vapour deposition (CVD), electrodeposition, pulsed laser ablation and solution based processes. Now a day, various wet chemical methods have been consolidated and are now fashionable for synthesizing ZnO nanoparticles because they provide a simple and electronic route as well as requiring low temperature. Indeed, a lot of efforts have been paid regarding the synthesis of ZnO nanoparticles using organometallic precursor as well as inorganic metal precursors of zinc. So, development of ZnO nanostructure in different morphologies through a simple and economical route would be very useful.

1.3. OBJECTIVE OF PRESENT WORK

- Preparation of the ZnO nanoparticles by precipitation method using inorganic precursor of zinc acetate dihydrate and sodium dodecyl sulfate as a surfactant.
- Effect of reaction conditions and calcination temperatures on crystal structure of ZnO nanomaterials.
- Structural characterization using TG-DSC, XRD, UV, IR analysis.
- Applications of synthesized materials for removal of toxic Cr(VI) from aqueous solution.

CHAPTER-2

EXPERIMENTAL PROCEDURES

2.1. Synthesis of ZnO nanostructure by precipitation Route

In this experiment all the chemicals used are of analytical grade and used without further purification. Nanostructure ZnO particles were synthesized through hydrolysis of zinc acetate dihydrate $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$ in the presence of sodium dodecyl sulfate $[(\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na})]$ acting as anionic surfactant in aqueous solution. In this procedure $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$ was dissolved in distilled water with continuous stirring. Then SDS was added to it. Finally, NaOH was added dropwise to the SDS modified $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$ solution until desired pH was achieved. Then the precipitate was heated to certain temperature, washed with distilled water and ethanol several times and then collected and dried. After drying, these precipitates were finally grounded to powder. The powder was calcined at different temperatures and studied using different characterization techniques. For comparison the samples were also synthesized without surfactant.

CHAPTER-3

RESULT & DISCUSSION

3.1 Differential Scanning Calorimetry (TG-DSC):

Figure 3.1 shows the thermal behavior of as-prepared powder heated up to 950°C. The first two weight losses between 100 to 145°C and 145 to 225°C regions are around 1.3% and 11.7 % respectively, and are ascribed due to the desorption of physisorbed and chemisorbed water from the hydroxide precursor. The third weight loss of 3 % between 225 to 750°C is due to the elimination of surfactant and decomposition of hydroxide precursor. So, it indicates that the major amount of the surfactant, which was added during the synthesis, was eliminated by simple washing. This was supported by the presence of one exothermic peak at 355°C in the DSC curve. The total mass loss was found to be 19%. Another exothermic peak at 505°C corresponds to the crystallization of ZnO nanoparticles.

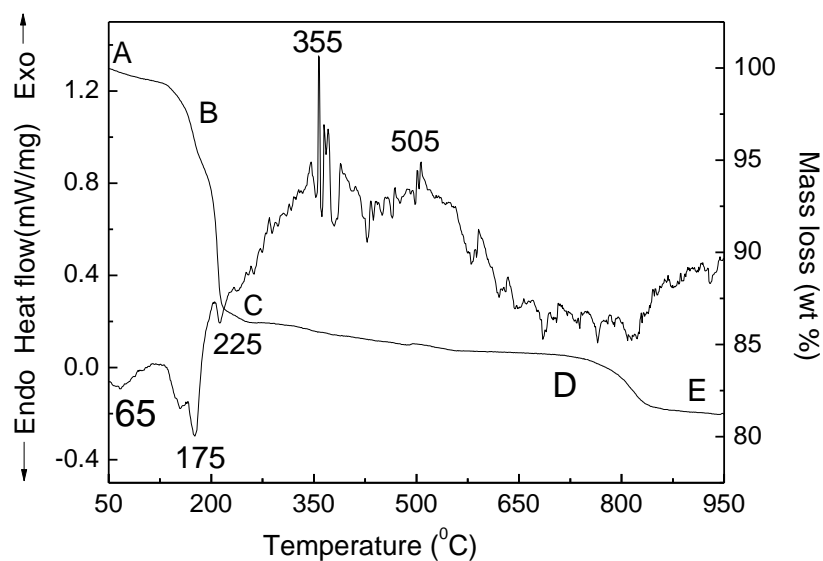


Fig. 3.1. DSC-TGA curves of as prepared powder using NaOH as precipitating agent.

3.2. X-Ray diffraction (XRD) Analysis:

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max – 2500 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Figure 3.2 shows the X-ray diffractograms of calcined ZnO nanopowders prepared with and without SDS by using $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ precursor and NaOH as precipitating agent. The XRD patterns of the powders calcined at 650°C are in good agreement with the hexagonal ZnO structure (JCPDS 36-1451). This figure shows well defined diffraction peaks at 2θ values of 31.95 , 34.6 , 36.45 , 47.7 , 56.6 , 62.6 , 68.16 , and 69.11 degrees corresponding to the reflections from the (100), (002), (101), (102), (110), (103), (112), and (201) planes are characteristics of single phase according to the (JCPDS file no: 36-1451). No impurity phase other than ZnO was observed in the XRD patterns of the powder calcined at 650°C for 2 h. It was also found that with increase in calcinations temperature to 1000°C , the peaks (in Fig. 3.3) become sharper due to increase in crystallite size. The diffraction peak intensities of the ZnO phase are also increased with the increasing calcinations temperatures.

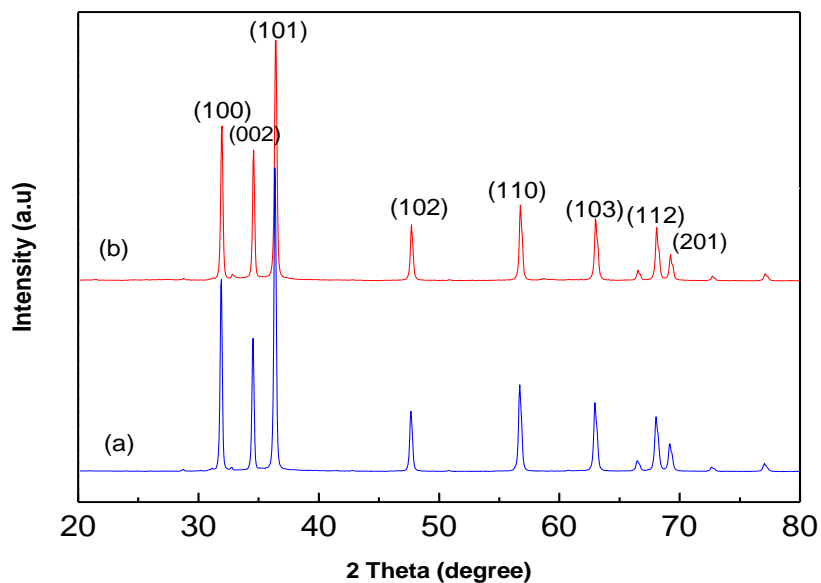


Fig. 3.2. X-ray diffractograms of ZnO nanopowders synthesized (a) with and (b) without surfactant and then calcined at 650°C for 2 h.

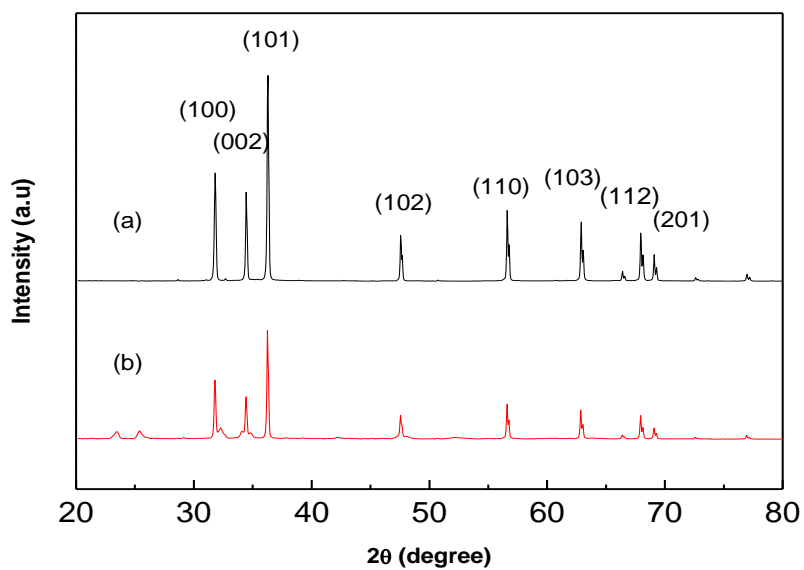


Fig. 3.3. X-ray diffractograms of ZnO nanopowders synthesized (a) with and (b) without surfactant and then calcined at 1000°C for 2 h.

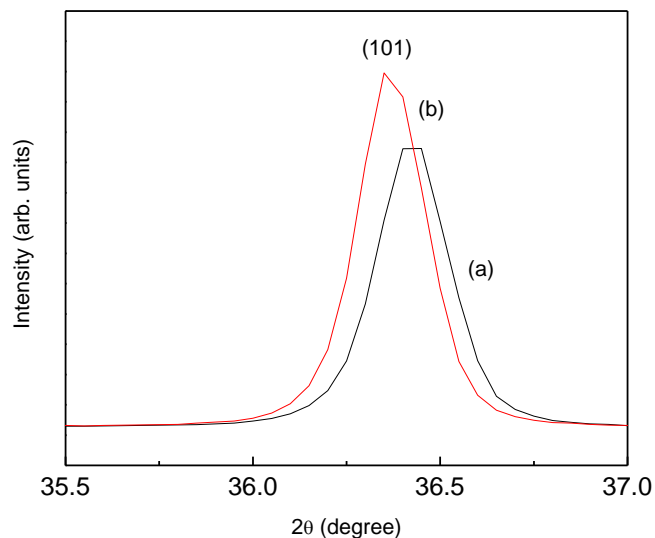


Fig. 3.4. X-ray diffractograms in (101) plane of ZnO nanopowders synthesized (a) with and (b) without surfactant and then calcined at 650°C for 2 h.

As can be seen from the Fig. 3.4, the peak width at half maxima is decreased in the sample synthesized with surfactant as compared to that of the sample synthesized without surfactant. So, it indicates that the surfactant plays important role in controlling the crystallite size in smaller dimension.

3.3. Fourier transforms Infrared Spectroscopy (FT-IR)

Figure 3.5 shows the IR spectrum of as prepared precursor synthesized using NaOH and SDS. From the graph the band at around 1235 cm^{-1} is assigned to an S=O stretching vibration of $-\text{SO}_4$ from the SDS molecule. The peaks at around 2925, 2865, 1235, and 1075 cm^{-1} are due to C-H stretching and bending which are absent in the calcined sample. A broadening peak at around 3504 cm^{-1} is proposed to be due to -OH stretching. The peaks below 800 cm^{-1} are characteristics peaks of Zn-O vibrations. Figure 3.6 shows the IR spectra of the samples calcined at 650°C synthesized with and without surfactant SDS. The ZnO samples calcined at 650°C does not contain any impurity from surfactant implies that the samples are surfactant free.

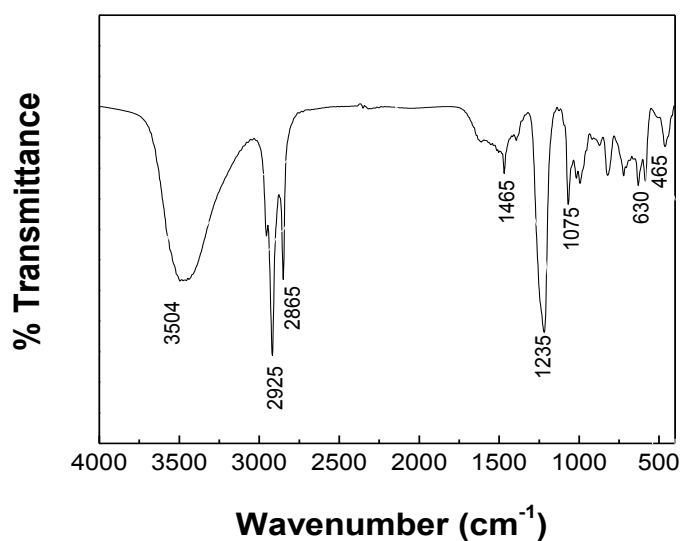


Fig. 3.5. FTIR spectrum of as prepared precursor synthesized using surfactant.

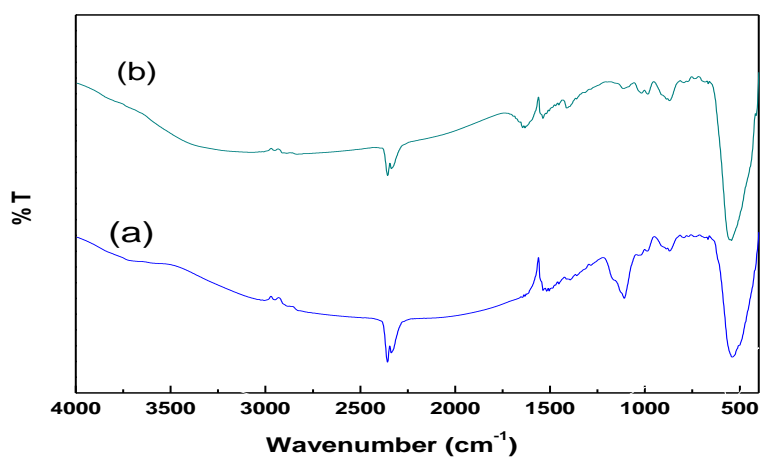


Fig. 3.6. FTIR spectra of ZnO nanopowders synthesized (a) without and (b) with surfactant and then calcined at 650°C for 2 h.

3.4. UV – Spectroscopy

Figure 3.7 shows the optical absorbance properties of as-prepared precursor and ZnO nanopowders calcined at 650 and 1000°C for 2 h prepared using SDS. The absorbance spectra the all the samples show high transparency or in other words no absorbance in a visible region above a 400 nm and high UV-shielding property below 400 nm. Therefore, it might be concluded that synthesized zinc-oxide synthesized using SDS and calcined at 650°C has very good UV-shielding property.

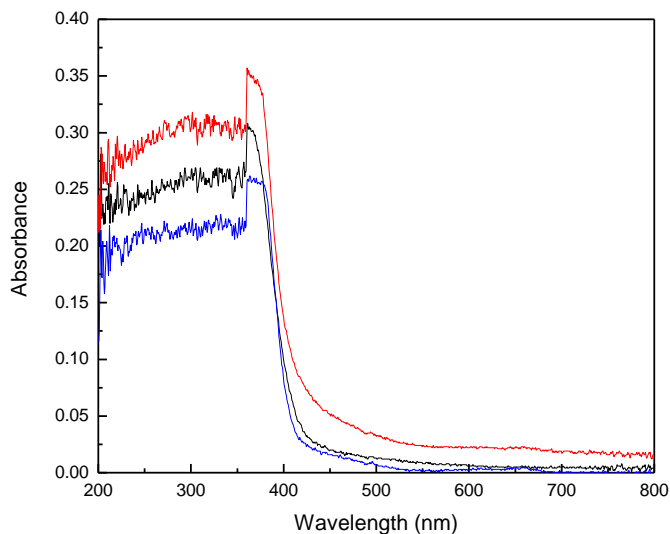


Fig. 3.7. DRS spectra of ZnO (a) as prepared and then calcined at (b) 650°C and (c) 1000°C.

APPLICATION

3.5. Removal of Cr (VI) from aqueous solution

Cr (VI) is one of the most toxic pollutants generated by the electroplating, metal finishing, leather tanning, photography, and dye and textile industries [9-12]. Cr exists both in trivalent Cr (III) and hexavalent Cr (VI) forms. Trivalent chromium is considered as a micronutrient for human, plant and animal metabolism. It is less toxic than hexavalent chromium which is extremely mobile in the environment and very toxic to living organism. The world Health organization (WHO) recommends the maximum allowable limit for the discharge of Cr (VI) in surface water is 0.1 mg/L, and in drinking water is 0.05 mg/L. So, Cr (VI) should be removed from aqueous solution to avoid the deleterious impact of the Cr(VI) on the human health.

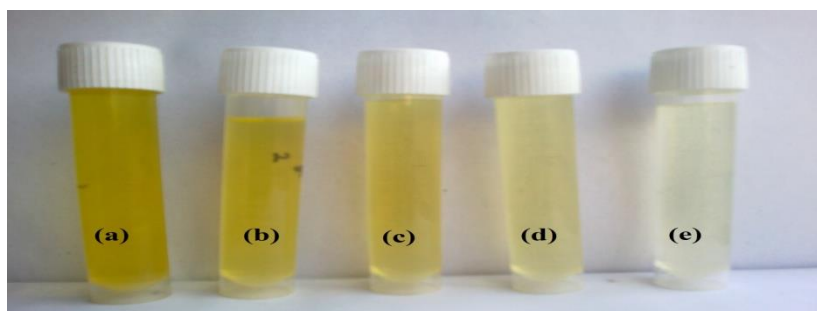


Fig. 3.8. Photographs of (a) pure Cr(VI) solution (yellow) with initial Cr(VI) concentration 298 mgL⁻¹ and solutions after (b) 1, (c) 2, (d) 3, and (e) 4 h (from left to right) of adsorption by ZnO.

All the adsorption experiments were carried out at room temperature. The Cr (VI) solutions with appropriate concentrations were prepared by diluting the stock solution (0.149 g/ 500ml). Typically, 0.6 g of sample (calcined at 650° C) was taken in a beaker with 60 ml stock solutions. The adsorption process was maintained on a shaker for 4h to realize adsorption equilibrium.

Contact time is one of the most important parameters in adsorption process. It can be visualized from Fig. 3.8 that a rapid uptake of Cr (VI) ions takes place. Equilibrium was reached within 4 h of contact time. During initial stage of adsorption, there is a rapid uptake of metal ions which slowed down after 2 h of contact time. Initially a large number of vacant surface sites are available for adsorption which gets saturated gradually thereby increasing competition between adsorbate molecules for vacant surface sites. The adsorption efficiency depends on surface area of adsorbent.

The adsorption amount was calculated according to the equation:

$$\% \text{ Removal} = (A_o - A_t)/A_o *100$$

Where A_o = Initial concentration of Cr (VI), A_t = solution concentration at different time interval.

Table 3.1. Amount of Cr(VI) removal with different contact time.

Time	% Removal
0	0
1h	56.25
2h	75.62
3h	78.12
4h	85.62

Table 3.1 shows that the with increasing the contact time from 1 h to 4 h, the percentage removal of chromium (VI) from water is increased nearly from 56 % to 86 %.

SUMMARY AND CONCLUSION

- ZnO nanopowders were synthesized by precipitation technique using inorganic salts of zinc acetate and NaOH as a precipitating agent and SDS as a surfactant.
- Characterization study was carried out using various techniques.
- FTIR results show that ZnO nanopowder heated at 650°C is free from surfactant.
- The crystal structure of synthesized ZnO was wurtzite type.
- All the samples show high UV-shielding property below 400 nm.
- The synthesized materials may have great potential application in heavy metal ion removal from aqueous solution.

REFERENCES

1. T. K. Subramanyam, B. S. Naidu, S. Uthana, Physical Properties of Zinc Oxide Films Prepared by DC Reactive Magnetron Sputtering at Different Sputtering Pressures, *Cryst. Res. Technol.* Vol. 34 (1999) (8), pp. 981–988.
2. Z. L. Wang, Zinc Oxide Nanostructures: Growth, Properties and Applications, *J. Phy. Cond. Mater.* Vol. 16 (2004), pp. 829- 858.
3. D. Wu, Z. Bai, K. Jiang, Temperature Induced Hierarchical Growth of ZnO Microcrystal, *Mater. Lett.* Vol. 63 (2009), pp. 1057–1060.
4. O. Yawong, S. Choopun, P. Mangkorntong, N. Mangkorntong, Zinc Oxide Nanostructure by Oxidization of Zinc Thin Films, *CMU, J.Spcl. Issue. Nanotechnol.* Vol. 4 (2005) (1), pp. 7-10.
5. S. Roy, S. Basu, Improved Zinc Oxide Film for Gas Sensor Applications, *Bull. Mater. Sci.* Vol. 25 (2002) (6), pp. 513–515.
6. T. K. Subramanyam, B. S. Naidu, S. Uthanna, Physical Properties of Zinc Oxide Films Prepared by DC Reactive Magnetron Sputtering at Different Sputtering Pressures, *Cryst. Res. Technol.* Vol. 35 (2000) (10), pp. 1194-1202.
7. Q. Shen, L. Jiang, H. Zhang, Q. Min, W. Hou, J.J. Zhu, Three-dimensional Dendritic Pt Nanostructures: Sonoelectrochemical Synthesis and Electrochemical Applications, *J PhysChem C*, 112 (2008): 16385-16392.
8. X. Gao, X. Li, W. Yu, Flowerlike ZnO Nanostructures via Hexamethylenetetramine-Assisted Thermolysis of Zinc-Ethylenediamine Complex, *J. Phys. Chem.* Vol.109 (2005), pp. 1155-1161.

9. M. H. Yu, *Environmental Toxicology: Biological and Health Effects of Pollutants*, CRC Press LLC, Boca Raton, FL, 2nd Edition, 2005.
10. A.K. Shanker, and B. Venkateswarlu, *Chromium: Environmental Pollution, Health Effects and Mode of Action*, *Encyclopedia of environmental health*, Elsevier, (2011) 650-659.
11. N. Kongsricharoern, and C. Polprasert, Chromium Removal by A Bipolar Electro-Chemical Precipitation Process, *Water Sci. Technol.*, 34 (1996) 109-116.
12. E.L. Hawley, R.A. Deeb, M.C. Kavanaugh, and J.J. Jacobs, Chromium(VI) Handbook, Chapter-8, Treatment Technologies For Chromium(VI), 275-310, CRC Press LLC, 2004.
13. C.R. Ramakrishnaiah, and B. Prathima, Hexavalent Chromium Removal From Industrial Wastewater By Chemical Precipitation Method, *Intern. J. Eng. Resea. Appl*, 2 (2012) 599-603.