Effect of Capping Agent Concentration on ZnO Nanoparticles

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Abstract – Zinc Oxide (ZnO) is a technological and promising material due to its unique physical and chemical properties. It is a II-VI semiconductor with wide band gap of 3.3 eV. It has potential applications in many areas such as optoelectronic devices, solar cells, chemical sensors, piezoelectric devices, spintronics etc. In the present work, ZnO nanoparticles with varying concentration of capping agent were prepared using chemical precipitation method. These particles were characterized using UV-Vis spectroscopy and absorption spectra have been obtained to determine the band gap. The obtained band gap values were in the range 3.405-3.433 eV. It was observed that particle size decreases with increasing capping agent concentration and the absorption edge shifts towards blue region as the capping agent concentration is increased. The effective band gap Eg increases with decreasing the particle size. This response is equivalent to size quantization effect owing to the small size of the particles. Using the effective mass approximation formula, the particle size of nanoparticles has been estimated.

Keywords: ZnO nanoparticle, UV-Vis Spectroscopy, Capping agent.

I. INTRODUCTION

Semiconductor nanomaterials have attracted growing interest during the last few decades due to their electrical, optical and chemical properties [1, 2]. The properties of nanomaterials can be different on a nanoscale due to two reasons i.e., quantum confinement effect and increased surface to volume ratio [3]. Among various semiconductor nanomaterials, ZnO is considered to be one of the best nanomaterials that can be used at a nanoscale. ZnO shows wurtzite structure and it has a large exciton binding energy of 60meV and a wide direct band gap of 3.3eV [4]. ZnO nanomaterials are of great importance to several technological applications such as UV light emitters, indicators gas sensors, coatings, cosmetics, biomedical field and photo therapy agents [5].

Synthesis of ZnO nanoparticles can be done by many methods including chemical precipitation method, pulsed laser deposition, chemical vapor deposition, sol-gel method, ball milling, molecular beam epitaxy and chemical precipitation. Among these, chemical precipitation method [6-8] has been popularly adopted to synthesize ZnO nanoparticles due to its low cost, superior uniformity and high yield of nanoparticles.

In the present paper, the objective is to study the effect of concentration of capping agent on the properties of ZnO nanoparticles.

II. CHEMICALS

In our work, chemicals used were AR grade Zinc Acetate dehydrate [(CH3COO) 2 Zn. 2H2O], Potassium hydroxide (KOH), Di-methylene sulfoxide (DMSO), thioglycerol, methanol and distilled water. Thioglycerol with different concentration was used as a capping agent for controlling the particle size.

III. SYNTHESIS OF ZNO NANOPARTICLES

ZnO nanoparticles were prepared using chemical precipitation method. 0.2 M of Zinc Acetate dehydrate was first dissolved in 20 ml DMSO and distilled water and magnetically stirred for 30 minutes. Then 1.2 M of KOH in 10 ml ethanol was drop wise added and stirred for 5 minutes. As a capping agent, we have used 0.12 ml of thioglycerol and magnetically stirred for one hour till the solution turns milky. The reaction was completed in a few hours and the nanoparticle was precipitated by centrifugation. Finally the solution was washed and dispersed in methanol for UV–Vis spectroscopy experiments.

For the study of effect of capping agent on ZnO nanoparticles, three different samples of nanoparticles ZnO (with thioglycerol 0.12ml as capping agent) A, ZnO (with thioglycerol 0.3ml as capping agent) B and ZnO (with thioglycerol 0.5ml as capping agent) C were prepared by changing the capping agent concentration.

In the final step, the obtained precipitate was filtered and dried in oven for 2 hours at 100oC. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle.

In the preparation of ZnO nanoparticles, the chemical reactions involved were:

$Zn\ (CH_3COO)_2 + KOH \rightarrow Zn\ (CH_3COO)\ (OH) + KCH_3COO$

$Zn\ (CH_3COO)\ OH + KOH \rightarrow ZnO + KCH_3COO + H_2O$

IV. CHARACTERIZATION

The optical absorption spectra of ZnO nanoparticles were determined using UV-Vis spectrophotometer as shown in Figure 2 and Figure 3. The absorption spectra have been recorded over the range 300 to 400 nm for determining the band gap values. The UV-Vis spectroscopy revealed that the material has turned into nanoparticle form showing a blue shift in the absorption peak. The band gap enhanced to ~3.4 eV, which is higher than the corresponding bulk ZnO. The particle size was calculated using effective mass approximation formula.

V. RESULTS AND DISCUSSION

The ZnO nanoparticles were successfully prepared by chemical precipitation method and it was characterized by the UV-Vis Spectroscopy. The average particle size (R) of nanoparticles was estimated using Effective Mass Approximation formula [9] as follows:

$$E = E_g + \frac{\hbar^2 \pi^2}{2R^2}\left\{\frac{1}{m_e} + \frac{1}{m_h}\right\} - \frac{1.8e^2}{\varepsilon R}$$

Where E= band gap of synthesized nanoparticle, Eg= bulk band gap of ZnO (3.3eV), R=radius of particle, m_h= effective mass of hole (for ZnO, it is 0.49 m_o), ε = dielectric constant of material (for ZnO, it is 9.1),m_e=effective mass of electron (for ZnO, it is 0.28m_o), and h is Planck's constant.

The values of particle size obtained from effective mass approximation formula for different concentration of capping agent are listed in Table 1. It was observed that as we increased the capping agent concentration, the particle size gets reduced and also the band gap is increased on increasing the concentration of capping agent. In this section author need to describe experimental/simulation results with graphs and appropriate tables.

TABLE 1: AVERAGE PARTICLE SIZE AND BAND GAP VARIATION OF ZNO NANOPARTICLES WITH DIFFERENT CONCENTRATION OF CAPPING AGENTS.

Sample	Concentration of Capping agent (ml)	Average Particle size (nm)	Band gap (Eg) eV
ZnO (A)	0.12	3.91	3.405
ZnO (B)	0.3	3.77	3.413
ZnO (C)	0.5	3.47	3.433

It is evident from the table the band gap values of ZnO nanoparticles changes from 3.40 to 3.43 eV by increasing the concentration of capping agent. These values exhibit a blue shift in band gap which is related to the size decrease of the particles and to the quantum confinement limit reaching of nanoparticles [10].

Figure 1 and Figure 2 shows the optical absorption spectra of ZnO nanoparticles. Absorption edge was obtained in UV region at wavelength 365nm, 362nm and 364.5nm for ZnO (A), ZnO (B) and ZnO (C) samples respectively.

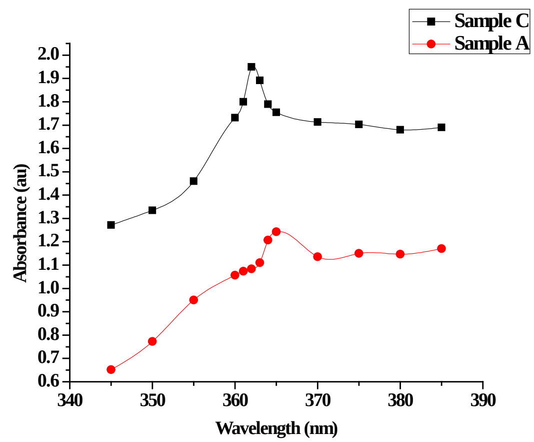

Fig. 1: UV of ZnO Nanoparticles prepared by 0.5ml (upper) and 0.12ml (lower) thioglycerol

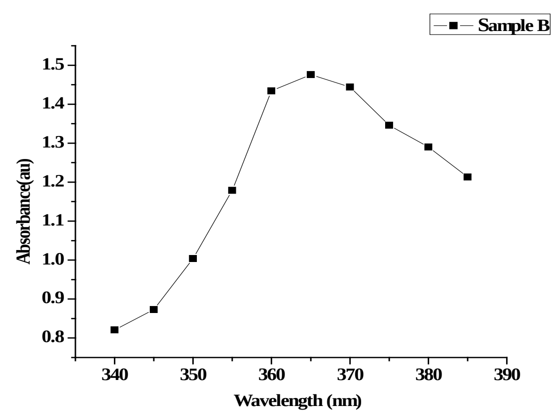

Fig.2: UV of ZnO Nanoparticles prepared by 0.3ml thioglycerol.

In the bulk material, the bands are actually comprised by the combination of adjacent energy levels of a huge number of atoms and molecules. The number of overlapping of orbitals or energy level gets decreases and the width of the band gets narrower, as the particle size reaches the nano scale, where every particle is comprised of a very small number of atoms or molecules, As a result, there is an increase in energy gap between the valence band and the conduction band. This describes the higher energy gap in nanoparticle than the corresponding bulk material. The band gap is the forbidden region for the electrons. When this forbidden region is larger, the restriction on the movement of electrons will be greater. Hence the nanoparticle exhibits the lower electrical conductivity than the bulk material from which they are prepared. So there is a shift of absorption spectrum toward lower wave length or blue region.

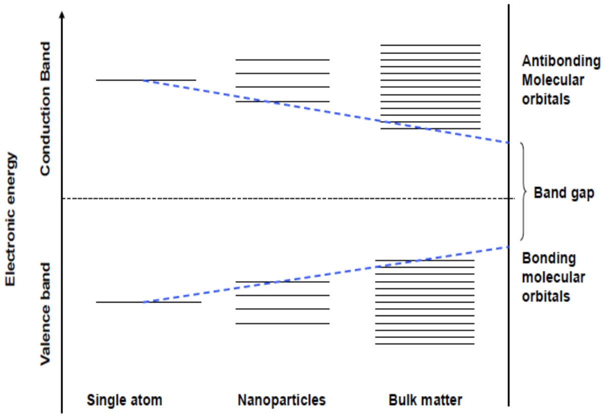

Fig.3: Diagram of band gap change in Nanoparticles

The formula will not be valid on further increasing the concentration of capping agent and also this would result in non-spherical geometry of the particles. This is the limit of increasing the concentration of capping agents.

The variation of band gap with particle size is shown in figure 4.

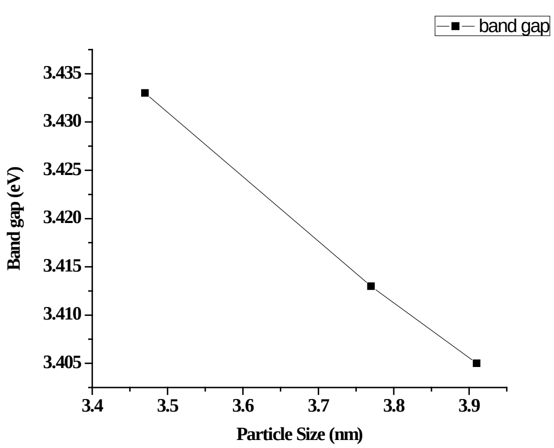

Fig. 4: Graph between particle size and band gap

The variation of band gap with capping agent concentration is shown in figure 5.

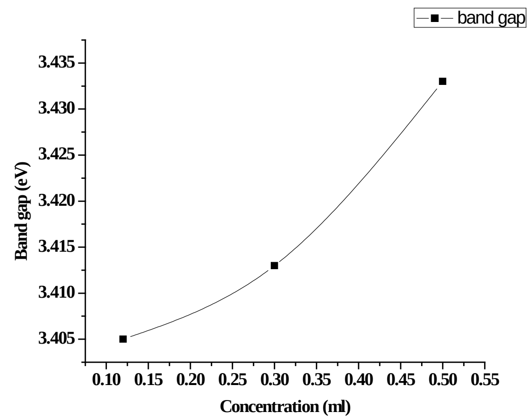

Fig.5: Graph between concentration and band gap.

The variation of particle size with capping agent concentration is shown in figure 6.

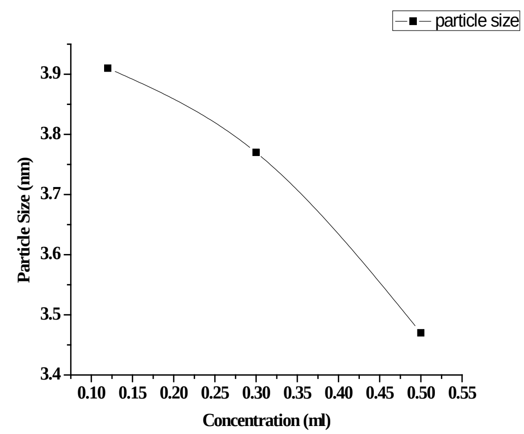

Fig.6: Graph between concentration and particle size.

VI. CONCLUSION

Using chemical precipitation method, different size of ZnO nanoparticles with different molar concentration of capping agent can be prepared [11]. The optical band gap data have been obtained to confirm nano-size of ZnO nanoparticles. The optical band gap values of ZnO nanoparticles changes from 3.405 to 3.433 eV by increasing the molar concentration of capping agent. These values exhibit a blue shift in band gap (Eg) which is related to the size decrease of the particles and to the quantum confinement effect. The particle size of ZnO nanoparticles was between 3.47 and 3.91 nm, depending on molar concentration of capping agent. The particle size depends on molar concentration of capping agent. This paper shows that capping agent restricts the growth of particles and by increasing its concentration, smaller particles can be obtained. The size of nanoparticles decreases almost linearly with the capping agent concentration as shown in figure 6.

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