SSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
Vol 3, Issue 4, April 2018

Synthesis of Stable ZnO Quantum Dots by a Simple Hydrolysis and Condensation Method

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***Abstract-* Herein, we report the preparation of ZnO quantum dots by hydrolysis and condensation method. These quantum dots are characterized by optical absorption, photoluminescence, and transmission electron microscopy, that suggest that the present method of synthesis gives stable, extremely small size particles with narrow size distribution and exhibit strong blue emission. The present method of synthesis of ZnO nanoparticles can used to fabricate low cost electronic devices for different applications.**

Key Words — ZnO nanoparticles, optical absorption, fluorescent, TEM, particle size.

I. INTRODUCTION

The engineering of materials of fundamental importance as size reduction and modification of shape allows tuning their fundamental properties. Semiconductor nanoparticles have attracted much interest because of their size-dependent optical and electronic properties [1]. Among various semiconductor nanocrystals, ZnO is an important functional material having bandgap of 3.37 eV [2] with broad range of applications including light-emitting devices [3], varistors [4], solar cells [5] and gas sensors [6]. Moreover, ZnO is a promising material for short wavelength optoelectronic devices, especially for ultraviolet (UV) light-emitting diodes (LEDs), and laser diodes (LDs), due to its large exciton binding energy of 60 meV [7, 8] at room temperature, which is larger than those of the widely used semiconductors GaN (26 meV) or ZnSe (20 meV) [9] and it is chemically and optically stable with less toxicity and biocompatible. Recently, there has been a growing interest in controllable synthesis of these nanoparticles with well defined morphologies, due to their novel electronic, optical and catalytic properties and potential applications in photonic, catalysts and electronic devices [10]. Recently, Ali et. al. have reported the growth of ZnO nanocrystals and their self-heating behaviour in ambient condition affects the properties and applications [11].

Various synthetic methods such as laser heating, sol-gel technique, spray pyrolysis, thermal decomposition of precursors, gas phase syntheses and colloidal solution routes have been used to prepare ZnO nanoparticles, among these colloidal method is more promising route to prepare ZnO nanoparticles. The literature survey reveals that the several routes are used to synthesis and growth kinetics of ZnO nanoparticles [12, 13] to control the size and has been studied and developed better routes. Herein, we report the preparation of ZnO quantum dots by hydrolysis and condensation of zinc acetate dihydrate and potassium hydroxide in methanol using the method of Pacholski [14]. The size of the nanoparticles is tuned by variations in the composition of precursor, temperature and time of reaction. The prepared nanoparticles are monodisperse, extremely small in size and better stability.

II. EXPERIMENTAL DETAILS

Chemicals: Zinc acetate dihydrate [Zn(CH3CO2)2. 2H2O], potassium hydroxide (KOH), methanol, chloroform, and n-Butylamine.

Synthesis of ZnO Nanoparticles: 0.15 M Zinc acetate dihydrate is dissolved in 75 ml methanol in the three neck flask and heated to 65 oC for 25 minutes using magnetic stirrer. In another flask, 0.725 M potassium hydroxide is dissolved in 25 ml methanol and added drop wise to the zinc acetate dihydrate solution over a period of 10-15 minutes. After 1-hour reaction, the solution is found to be cloudy. The heater and magnetic stirrer were switched off. After one hour, the supernatant was removed. The solution was washed with 60 ml of methanol to remove unwanted ionic species. One hour later, the supernatant was removed. Again fresh methanol was added and later supernatant was removed, this process is repeated two more times. By adding 10 ml of chloroform, a clear zinc oxide nanocrystal solution was obtained. By this process, the final yield of the nanocrystal is around 140 mg. In similar way different size quantum dots were prepared. Later, these nanoparticles are dissolved in n-butylamine. Various characterization techniques such as optical absorption spectroscopy (HITACHI U–3310 Spectrophotometer), fluorescence spectroscopy (Hitachi F-7000 Fluorescence Spectrophotometer) and transmission electron microscopy (TEM) (PHILIPS TECNAI – 20) were used to study the properties of ZnO quantum dots.

III. RESULTS AND DISCUSSION

The preparation of ZnO nanoparticles, with few modifications, followed by the procedure described by Pacholski [14]. Figure 1 shows the optical absorption spectrum of ZnO quantum dots. The prepared ZnO quantum dots are highly stable in nature. These spectra exhibit clear blue shift in their absorption edges as compared with the bulk ZnO (370 nm, Eg = 3.37 eV) indicating the existence of quantum size effect. The optical bandgap can be calculated using Tauc's equation. The estimated bandgap value is 4.28 eV respectively. It is known that the higher surface-to-volume ratio of quantum dots as compared to bulk material leads to a corresponding enhancement of surface related emission in the overall luminescence. The origin of enhanced visible emission from ZnO nanoparticles is usually attributed to oxygen vacancies located predominantly near the surface [15-16]. Figure 2 shows the photoluminescence spectrum of colloidal ZnO quantum dots. Strong band emission is observed at 380 nm, this clearly

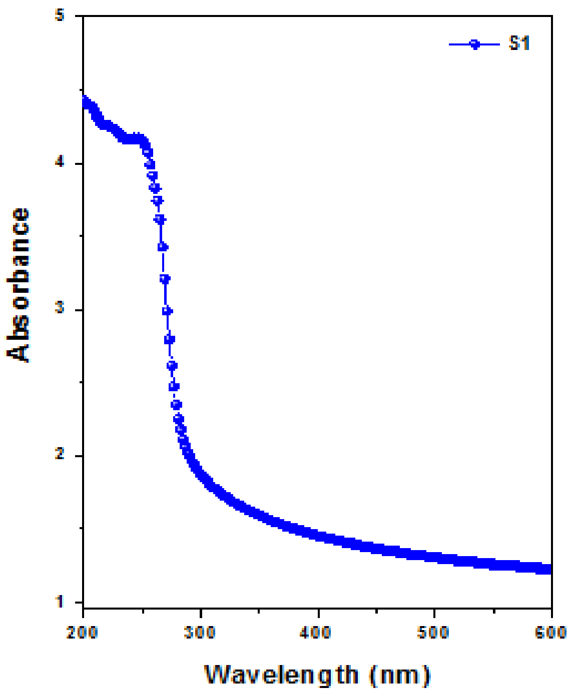

Figure 1: Optical absorption curve of ZnO quantum dots.

indicates that ZnO nanoparticles exhibit very strong blue emission and highly fluorescent. Blue emission can clearly seen under dark room condition, upon exposure to short UV.

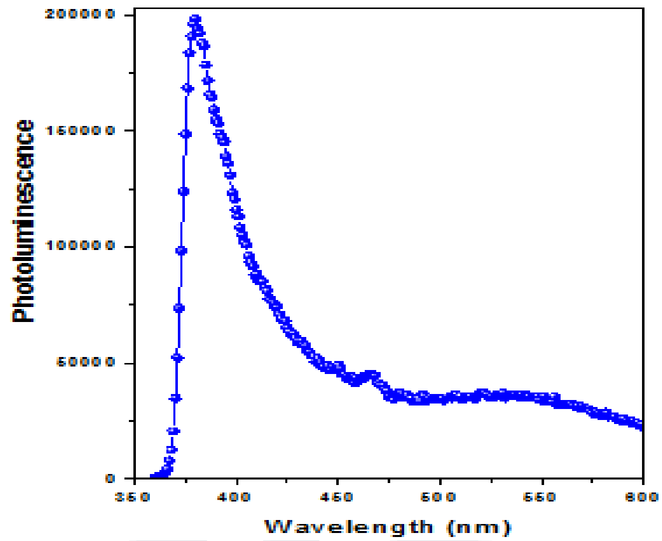

Figure 2: Photoluminescence of ZnO quantum dots.

In the literature, there are reports on Blue green and UV emitting ZnO nanoparticles [17-18]. The strong emission peak around 380 nm (3.26 eV) is attributed to the single exciton not due to the deep trap emission. TEM measurements were carried out on different size ZnO nanoparticles. Figure 3 shows the TEM micrograph of ZnO nanoparticles dissolved in n-butylamine. The average estimated particle size is in the range of 4-6 nm. This clearly shows that these nanoparticles are extremely small in size, spherical in shape and good homogeneity. The particle size is estimated from TEM is higher than the estimated from optical absorption edge measurement. Such a difference is commonly observed in the case of nanoparticles [20].

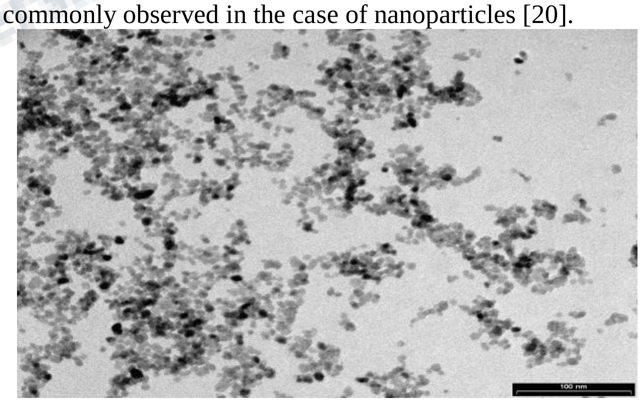

Figure 3: TEM picture of ZnO nanoparticles of sample 3

IV. CONCLUSIONS

In summary, stable, highly fluorescent ZnO quantum dots are prepared by hydrolysis and condensation of zinc acetate dihydrate and potassium hydroxide in methanol. The size of the quantum dots is controlled by varying the concentration of the precursor, time of reaction and temperature. Optical absorption, fluorescence and TEM measurements clearly confirm that these quantum dots are spherical in shape having narrow size distribution, monodisperse in nature and exhibit strong blue emission. The prepared nanoparticles are monodisperse, extremely small in size and better stability.

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