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Research Article

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A Synthetic Approach on ZnO Quantum Dot

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ABSTRACT

In recent existence, ZnO quantum dots (QD) have fascinated awareness as awfully hopeful candidates for optoelectronic, electronic, and biological applications. Low toxicity, low cost, and biocompatibility makes them excellent candidates for in vivo bio-imaging, gene/drug delivery and cancer detection. This QD have too promised momentous burst through an examine for sterile agents, and in exposure of imperative antigens and allergens because of their high isoeletric points. The ZnO Quantum dots were synthesized. The quantum dots are characterized by using UV-Visible spectroscopy, Fluorescence Spectrophotometer, X-ray diffraction studies, Transmission Electron Microscope and Electron dispersive spectroscopy are found to be having a particle in the range from 2 nm to 5 nm. This study shows that lowest grain size and highest band gap influences the optical properties by reducing the size. Due to excellent optical properties such as size tunable fluorescence and a narrow and symmetric emission profile a broad excitation range II-IV fluorescent Quantum dots have undergone intensive investigation as a new type of biolabling over a recent years and also proven to be superior to conventional dyes. The ease of processing and good photoluminescence property of ZnO quantum dots provides practical and economical approach signal-target imaging application.

Keywords: ZnO; Quantum dot; Synthesis; X-ray diffraction

INTRODUCTION

The integration of nanotechnology with biotechnology is an attractive trend as nanotechnology provides the analytical tools and platforms for the investigation of biological systems. As a powerful fluorescent probe, quantum dots have been used for imaging of biological targets, disease diagnoses and prognoses, tracking cell/protein interactions and cell vitality, etc. Traditional organic dyes are limited by their narrow excitation range, low fluorescence intensity and short lifetime. On the contrary, QDs have broad excitation but narrow, strong and tunable emission spectra [1-3]. Which allow the simultaneous observation of multiple probes with different fluorescent colors using a single light source [4], with bright emission and extraordinary photo stability [5]. QDs make the long-term real-time monitoring and tracking of molecules and cells more feasible. For example, researchers were able to observe QDs in lymph nodes of mice for more than 4 months [6]. The improved photo stability of quantum dots also allows the acquisition of many consecutive focal-plane images that can be reconstructed into a high-resolution three-dimensional image. Furthermore, QDs have the fluorescence lifetime significantly longer than that of organic dyes or auto-fluorescent flavin proteins [7]. Therefore, combined with pulsed laser and time-gated detection, the use of QDs label can produce images with greatly reduced background noise [8].

Traditionally, most colloidal quantum dots are synthesized through an organometallic method, which involves hazardous precursors, high temperature reaction, and organic solvents. Although there are some efforts to make the QDs water-soluble, many complicated post-synthesis steps have to be taken to exchange the solvent and to achieve the strong emission. There is a considerable need for a simple, economic and environment-friendly aqueous route to produce biocompatible QDs with strong emission and good stability.

Another remaining issue with quantum dot probes is their *in vivo* toxicity. So far most QDs contain toxic elements, such as cadmium (Cd), lead (Pb), mercury (Hg) and arsenic (As), etc. It was reported that [9,10]. A variety of synthesis, storage, and coating strategies have been proposed. But the toxicity of QDs can only be reduced to some extent, rather than being eliminated completely. The need for understanding the potentially harmful side effects of QDs becomes clear and must be carefully examined. More important, the nontoxic QDs are extremely desirable and the biocompatibility of QDs is crucial before the quantum dot applications can be approved for human clinical use.

Along with the booming nanotechnology, quantum dots are a novel and outstanding nanomaterial with various promising applications and advantages over other materials. However, there is still a lack of an environmentally friendly synthesis of water soluble QDs that are nontoxic and can be directly conjugated for misapplications. The overall goal of this research work is to develop such an aqueous synthesis method to produce the nontoxic quantum dots with strong emission and good stability, suitable for biomedical imaging applications.

In the present work, the ZnO QDs was synthesized in a convenient and safe route, which were isolated and redispersed in water based solvents, without losing any of the properties. The prepared QDs were characterized by UV-Vis Spectroscopy, Fluorescence spectrophotometry, XRD, TEM, EDX and Cyclic voltammetry. The UV-Vis Spectroscopy and Fluorescence spectrophotometry has shown that the ZnO QDs has good absorption as well as good luminescent properties in the visible region. In order to determine the size and shape of the particle the synthesized QDs were characterized by XRD analysis and TEM images. Also, EDX analysis confirms the presence of Zn and O element. The ZnO QDs was also characterized electrochemically using gold electrode by cyclic voltammetry. Also as the QDs has the good photoluminescence property it can be used for the biological application such as cell imaging, therapeutics, diagnostics, cancer therapy, etc., and also used in optoelectronic devices.

EXPERIMENTAL SECTION

Materials

The salt of Zn $(CH_3COOH)_2.2H_2O]$ [(99.9%) (Merck chemical Ind. Ltd, India) is used to prepare ZnO solution (methanol solvent). 0.2 mm of L-cysteine solution was make up with distilled water (Merck).

Synthesis Method

A solution of 0.2 mm L-cysteine and ZnO thus obtained was ultrasonic at 60°C for 120 min to get a clear solution. The prepared sol was transparent and found to be stable with no precipitate or turbidity. Sodium hydroxide (NaOH) was added drop by drop to get the desired pH it. This was ultrasonicated for 60 min at room temperature. There transparent sol was kept for one week to complete the gelatin and hydrolysis process. During this period white precipitates of L-cysteine capped ZnO crystallized and settled down. The final product was filtered and washed with excess methanol to eliminate the preliminary resources and dehydrated at 500°C for 1 h. The products are then trodden delicately to give zinc oxide quantum dots [11].

Electrode Fabrication for Electrochemical Characterization

The gold electrode was surface modified with the above synthesized quantum dots by dipping the gold electrode in ZnO QDs solution for a period of 24 hours. Then the gold electrode modified with QDs thoroughly washed in DD water. As modified, electrode was characterized with cyclic voltammetry.

RESULTS AND DISCUSSION

UV-Visible Absorption Spectra

Figure 1 shows the typical absorption spectra of ZnO QDs. The absorption spectra of ZnO quantum dots were found to be at 305 nm.

The absorption peak of as prepared ZnO QDs exhibits the lattice absorption at around 305 nm. This peak corresponds to a band gap of 4.0 eV. A comparison with the value of bulk ZnO (1.76 eV) shows that the band edge is blue shifted which are indicative of quantum confinement in ZnO quantum dots.

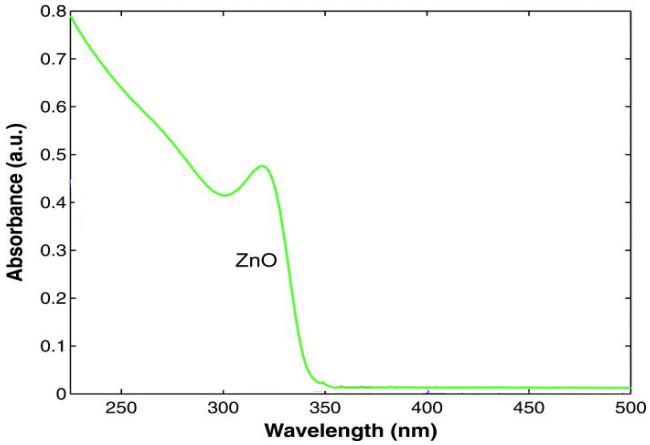

Figure 1: Absorbance spectra of ZnO QDs

Photoluminescence Spectra

Surface passivation leads to the quenching of surface traps hence improving the quality of quantum dots. The emission spectrum in the Figure 2 displays that the emission peak is at 464 nm and this spectrum characterized by good symmetry and narrow spectral width. The sharp peaks show a blue shift in energy when the size of quantum dot decreases. The energy shift in photoluminescence has shown with good correlation with the result obtained from others techniques such as UV-Visible absorption spectroscopy, and X-Ray diffraction (XRD) pattern which will be discussed in the next section. The sharp excitonic peak in the absorption spectra and the narrow PL spectra shows that the quality of as-prepared is very good.

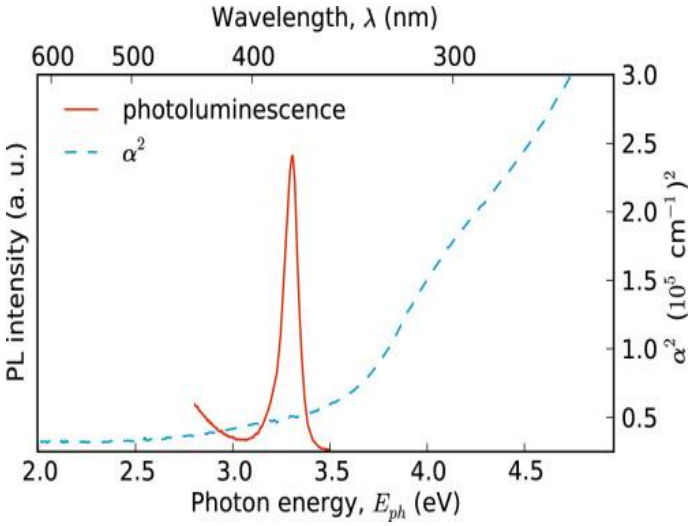

Figure 2: Photoluminescence spectra of ZnO QDs

XRD Analysis

Figure 3 represents the XRD pattern of L-cysteine capped ZnO quantum dots. The considerably broadened XRD patterns are due to the quantum size effect [12]. From XRD pattern analysis it is found that the crystal structure of all samples is cubic [13]. The (110), (112), (100,101) planes are clearly distinguishable in the pattern (JCPDS). It is evident from the figure that the maximum of the 100% peak occurs at 25.5° which corresponds to the 100% of the cubic phase. Therefore, the crystal structure of as-prepared ZnO sample is assumed to be pure cubic (Zinc blend structure) phase. The average size of ZnO quantum dots are in the range 1.6 nm, which was obtained from the width of the (110) peak using the Debye-Scherrer's formula.

$$d=0.9\lambda/\beta\cos\theta$$

where, d is the diameter of the nanoparticle, λ is the wavelength of the x-rays used, β is the full width at half maximum of the 100% XRD peak and θ is Bragg angle.

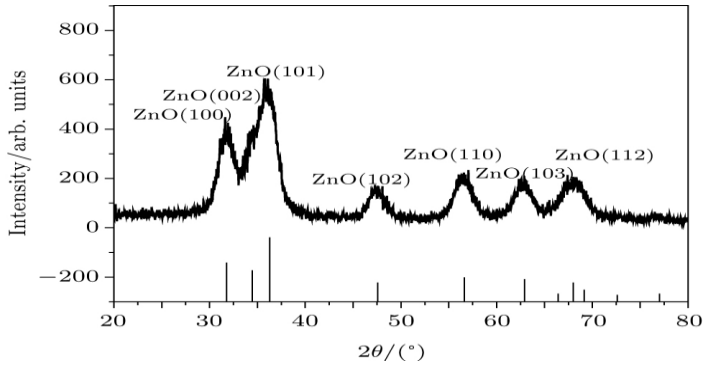

Figure 3: XRD patterns of 2-ME capped ZnO quantum dots

This is in close agreement with the size calculated from the UV-Visible absorption edge. It is important to note that the smallest grain size (1.6 nm). The surface structure and size of the nanoparticles at any instant of time depends on the rate at which matter joins the surface or leaves it and mobility of the surface atoms. All these process are highly influenced by surface coating that have the ability to control the size and shape of the nanoparticles through charge transfer and lowering of the surface tension.

To estimate the band gap energy, the effective mass model is used. The blue shift of band gap energy with the decrease in the diameter of QDs is described by the following equation:

$$Egeff=Eg+\hbar 2\pi 2/2\mu R2$$

Where, R is the radius of the particle (calculated from XRD pattern), □□is the effective reduced mass, Egis the bulk band gap energy (1.76 eV), Egeff is the effective band gap energy, and ħ=h/2π, h being plank's constant. As the effective mass of the electrons is much smaller than that of the holes (me*=0.2, mh*0.8), the charge carrier confinement mainly affects the energetic level of the electrons. Thus by using the estimated particle size from the XRD data, the effective band gap of ZnO QDs found to be greater than 1.76 eV, which agrees well with the confinement regime.

TEM Images of ZnO Quantum Dots

In order to determine the size and shape of the quantum dots, TEM images of the ZnO quantum dots were taken. 2 µl of the sample was placed on the copper grid and it was allowed to air dry. The Figure 4 shows a typical image of ZnO quantum dots. The TEM images show that the particles are monodisperse in shape and size. Under the TEM images, the ZnO nanoparticles appeared as spherical particles with crystalline with that calculated from the absorption spectrum and XRD analysis. On average, the size distribution is around 10% without any size selective treatment. The synthesized ZnO QDs shows the particles with a size of 5 nm.

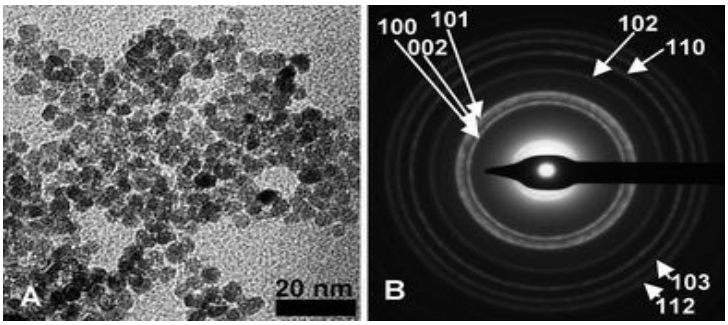

Figure 4: TEM images of a ZnO Quantum dots

The ZnO nanoparticles were uniform in size and remain suspended in the solution without any aggregation. They were stable and were strongly photoluminescence and the size of the particle remained the same for weeks together. These particles are water soluble in nature and can be directly used for biological imaging purposes. They can also be used for drug loading and drug delivery.

EDAX Characterization of ZnO Quantum Dots

It is analytical technique used for elemental analysis of a sample. EDAX studies were done with the ZnO quantum a dots and EDS spectrum is shown in the Figure 5. The characteristic peaks for Zn, is observed.

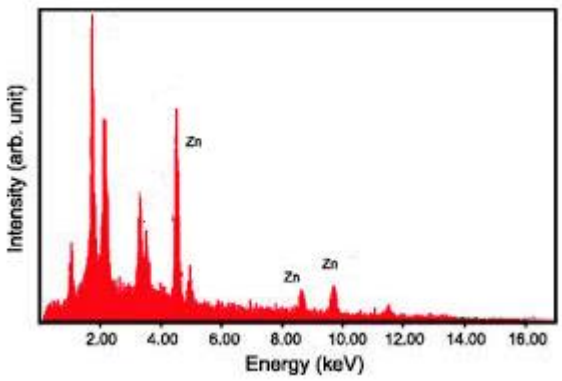

Figure 5: EDAX spectra of ZnO quantum dots

Cyclic Voltammetry

The effect of scan rate was investigated for the proposed QDs modified Au electrode. From the Figure 6, it is understood that the peak current of the modified electrode seems to increase linearly with increase in scan rate. A calibrated plot was taken for peak current vs. square root of the scan rate, which exhibits a linear response with R2=0.9976 [3.7 (b)]. So hence it is justified that the QDs modified gold electrode follows a diffusion controlled phenomena.

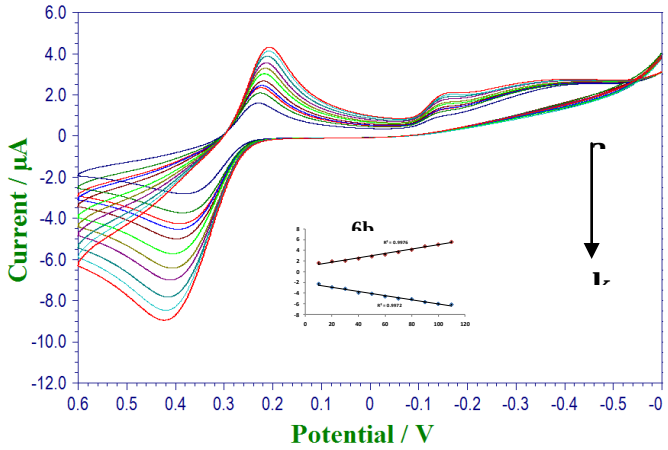

Figure 6(a): The electro chemical behaviour of QDs modified gold electrode in 0.1M PBS at the different scan rates: (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 (f) 60 (g) 70 (h) 80 (i) 90 (j) 100 (k) 110 mV per second. Figure 6(b): Dependence of the peak current on the scan rate.

CONCLUSION

QDs have revolutionized the field of medicine. ZnO quantum dots have been gaining attention as promising alternatives to the more widely studied but toxic cadmium based quantum dots. Still, there is an urgent need to study the effect of different surface modifiers on ZnO quantum dots for increased quantum efficiency and better fluorescence stability, which will enable their applications as more sensitive, qualitative and quantitative tools for imaging, diagnosis and better targeting such as drug delivery. The forthcoming years would see their potential applications in different fields such as molecular probes against various biological markers such as free antigens, cell surface markers/antigens, bacteria, viruses and tissue.

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