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Green Synthesis of Glucose Capped ZnO: Fe Quantum Dots: A Study on Structural, Optical Properties and Application

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Abstract

In the present investigation, Fe doped and glucose capped zinc oxide (ZnO) quantum dots (QDs) were prepared by using simple green synthesis method under room temperature as it is an environmental friendly process. Then their structural and optical properties were examined by using X-ray diffraction (XRD), Transmission electron microscope (TEM), Ultraviolet (UV) and Photoluminescence (PL) techniques. During this study period, an interesting cubic-hexagonal crystal nature was confirmed through powder XRD technique and also a spherical shaped surface morphology was found from TEM images whose size is approximately 10 nm. The UV results have shown an enhanced absorption when compared with uncapped ZnO:Fe QDs. Further, an interesting strong blue emission was observed in the glucose capped ZnO:Fe QDs which was maximum at 465 nm because of formation of small size particles and broad emission band was also observed from violet to red region. This enhanced emission nature is highly suitable for all types of bio-applications. The results of the present study show the glucose capped ZnO:Fe QDs induced a better antibacterial activity when compare other QDs. In future, these QDs can be used for cancer cell targeting application.

Keywords: ZnO, glucose, green synthesis, structural and optical properties and antimicrobial activity.

Introduction

In general, semiconductor metal oxide nanoparticles are of great importance because of their multifunctional properties, especially its high photostability and biocompatible properties which are used for various applications[1-2]. ZnO is one of the well-known semiconducting materials, was synthesized and characterized by using various routes in producing nanostructures[3-6]. It can be used in physical, chemical and biological applications due to its potential properties[7-10]. In this case, the metal doped ZnO nanostructure plays a dual role of optical and magnetic behaviors which are of greater importance[11]. In human, the microorganisms are playing a vital role in producing different types of diseases which cause many health related problems even it leads to death in a short period of time. Therefore, now a day, the researchers are trying to develop a new application in the form of nanostructures for the anti-microbial activity and to overcome the problems caused by the microorganisms[12]. In this connection, the present study was aimed to synthesis and characterizes ZnO nanostructures to anti-microbial activity. In this present study, we prepared a Fe doped ZnO and Fe doped-glucose capped ZnO QDs (ZnO:Fe/Glucose QDs) using green synthesis technique. Because the natural organic molecule glucose is one of the most important biocompatible material and stabilizing agent, and it can easily afford the production needs of cheap and renewable raw materials[13]. Hence, we found that this way is mild, energy efficient and environment friendly route to produce ZnO QDs.

Methodology

The QD samples were prepared using green synthesis technique under room temperature. For the preparation of ZnO:Fe QD sample, initially zinc acetate ($Zn(CH_3COO)_2$) was dissolved in double distilled water (DDW) and stirred well. Then the dopant ferric chloride ($FeCl_2$) was dissolved in DDW and added into $Zn(CH_3COO)_2$ solution. To this mixture, freshly prepared sodium hydroxide (NaOH) solution was added in drops till the pH becomes 10 to form ZnO crystal. Further, a white colloidal precipitate was formed and this solution was kept under ultrasonic condition to stabilize the particles. Finally, this solution was washed several times to remove the unreacted compounds and then centrifuged, and the obtained product was annealed to get ZnO QD. Similarly for the preparation of ZnO:Fe/Glucose QD sample, the capping agent of glucose was introduced after the addition of dopant but before the change of pH value. Finally, all the prepared samples were sent for various characterizations to know the structural and optical properties.

Results and Discussion

Structural analysis: Figure-1a shows the powder XRD patterns of ZnO:Fe and ZnO:Fe/Glucose QD samples. In this, the diffraction peaks from the prepared samples were corresponding to the hexagonal crystal structure in ZnO:Fe QDs, and a mixed cubic-hexagonal crystal structure[14] in ZnO:Fe/Glucose QDs (JCPDS 65-2880, 80-0075) with fine crystallinity. The peak broadening clearly indicates the formation of small size particles. Finally, Debye-Sherrer's formula was used to estimate the crystalline size (D) of both the samples and their size were ±10 nm.

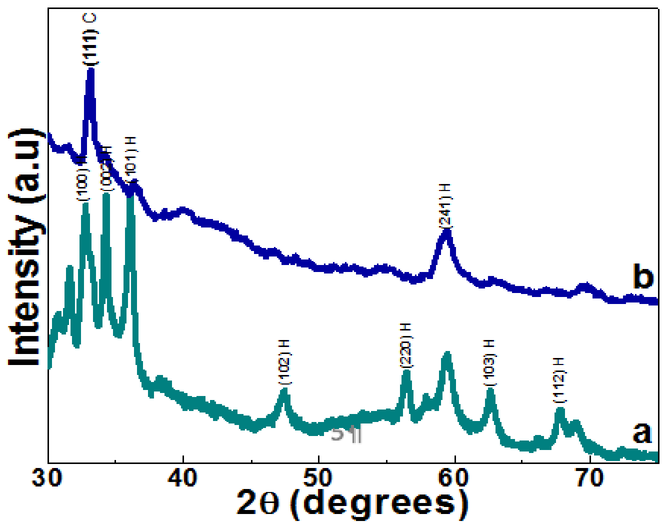
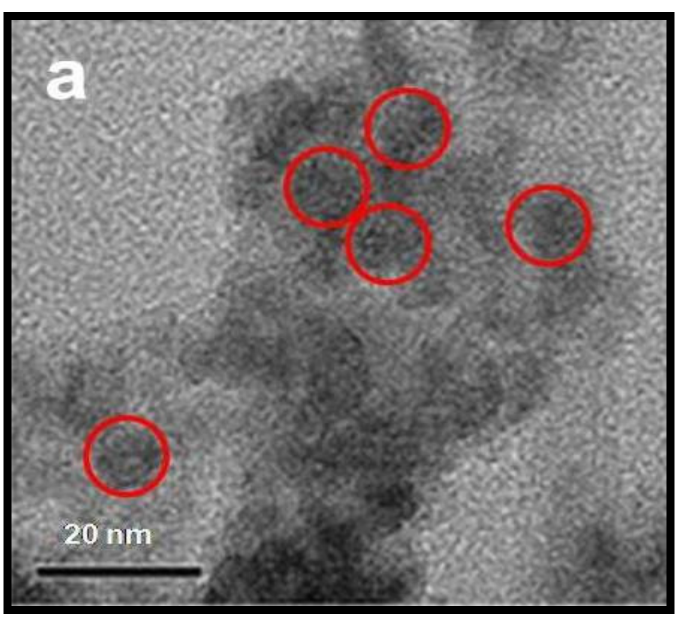


Figure-1
XRD pattern of ZnO:Fe(a) and ZnO:Fe/Glucose (b) QD samples

The TEM images of ZnO:Fe and ZnO:Fe/Glucose QD samples were shown in the figure-2 (a) and (b) respectively. A spherical shaped particle nature was observed in the both uncapped and capped QD samples but a cluster like morphology was noted in the ZnO:Fe/Glucose QD sample as QDs were formed inside the glucose matrix, and has shown an embedded nature. The size of the particles was ±10 nm.



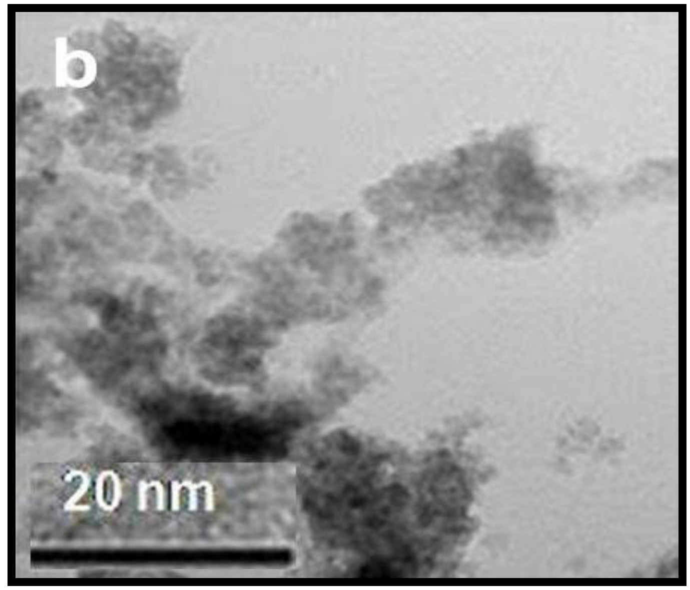


Figure-2
TEM images of ZnO:Fe(a) and ZnO:Fe/Glucose (b) QD samples

Optical analysis: Figure-3 (a) and (b) shows the UV absorption spectrum of ZnO:Fe and ZnO:Fe/Glucose QDs and their corresponding bandgap energy values were 3.65 eV and 3.54 eV, respectively. Further a little red-shift was found in the ZnO:Fe/Glucose QDs which may be due to the surface capping effect of glucose on ZnO crystal.

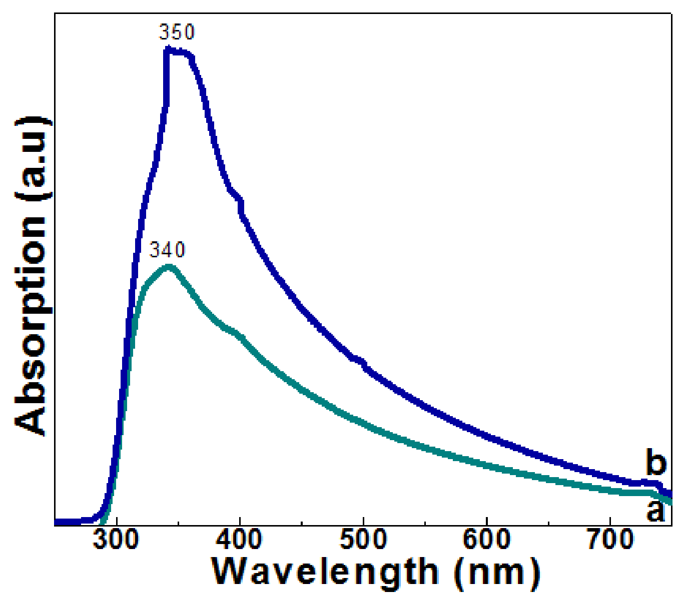


Figure-3
UV absorption spectrum of ZnO:Fe(a) and ZnO:Fe/Glucose (b) QD samples

The PL emission spectrum of ZnO:Fe and ZnO:Fe/Glucose QD samples were given in figure-4 (a) and (b), respectively. ZnO:Fe QDs shows a strong green emission peak which was appeared around 550 nm, and band-edge related UV emission was strongly quenched. Therefore, we believed that this quenching effect due to the entering of Fe ions into the ZnO crystal lattice and then the transition was occurred between the energy levels of Fe ions which are responsible for the quenching of UV emission. Hence, we have concluded that the red-shifted green emission band is due to the increased number of PL centers in the ZnO QDs system and these results are confirmed with the previous reports[15-17]. The ZnO:Fe/Glucose QDs shows a broad blue emission around 465 nm. Therefore, we believed that, this is one of fascinating emission in ZnO QDs which is due to the trap related one. In this study, upto our knowledge, a rare reports was found in ZnO:Fe/Glucose QDs. Therefore, we are proposing that this is a new and interesting emission behavior.

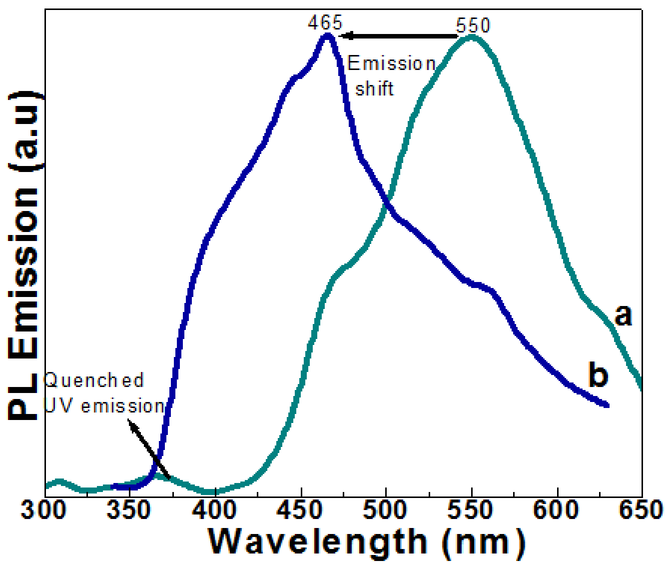


Figure-4
PL emission spectrum of ZnO:Fe(a) and ZnO:Fe/Glucose (b) QD samples

Antibacterial activity analysis: The antibacterial activity study of ZnO:Fe and ZnO:Fe/Glucose QDs were performed in *Escherichia coli* (*E. coli*). Figure-5A shows the antibacterial activity of ZnO:Fe (a) and ZnO:Fe/Glucose (b) QD samples and their killing effects compared in percentage (figure-5B). The ZnO:Fe QDs shows a less zone of inhibition but ZnO:Fe/Glucose QDs shows no zone of inhibition because no bacterial killing effect was occurred. Because in the case of ZnO:Fe/Glucose QDs, the formation of small sized particles are in glucose matrix and in addition more free radicals were formed. Hence, the mechanism for less killing of bacteria in the Fe and Zn/Fe oxide based nanoparticles was clearly discussed in previous report[18-20] whereas Fenton's regent (that's, Fe^{2+}/Fe^{3+}) reacts with hydrogen peroxide and then produces the hydroxyl and peroxide radicals. Therefore we believed that this mechanism is also in good agreement with our results.

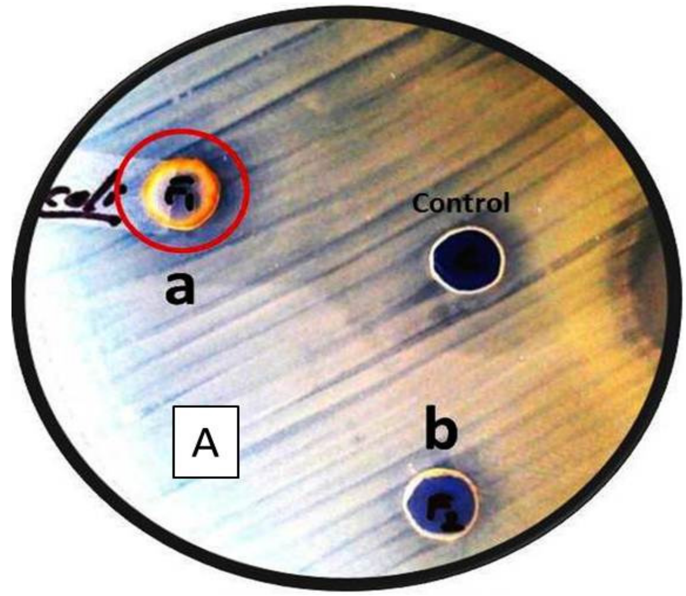


Figure-5A
Antibacterial activity of ZnO:Fe(a) and ZnO:Fe/Glucose (b) QD samples in *E. coli*

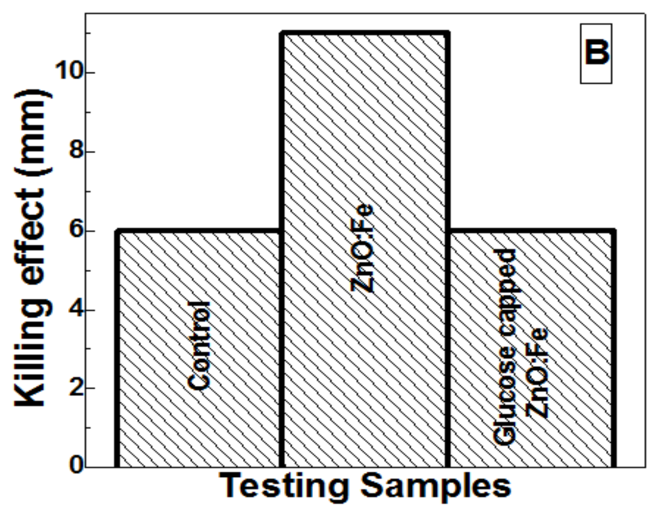


Figure-5 B
Comparisonspectra for killing effect of ZnO:Fe and ZnO:Fe/GlucoseQDs in *E. Coli*

Conclusion

This is a quite simple green friendly method for the synthesis of quantum dots in a very short period and also biocompatible ZnO QDs. The capable ZnO QDs could be developed using this method within a few hours. The material is wild, nontoxic and it is very low cost process. Further, phase purity was confirmed by XRD and its average particles size was observed. In terms of size, various morphology of the particle was clearly pointed out from the TEM results. The wide range of QDs emission of blue and green colours was successfully detected from PL emission results. The cell culture of *Escherichia coli* were exposed to adding the QD samples. The results evidenced were entirely different in ZnO:Fe/Glucose QDs when compared with ZnO:Fe QDs. Therefore, ZnO:Fe/starch QDs are biocompatible to microorganisms and it could be a suitable for various bio-applications.

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