

Synthesis and characterization of chitosan and poly vinyl pyrrolidone (PVP) capped ZnO nanoparticles and their antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*

S. Satheeskumar^{1*}, K. Ramesh² and N. Srinivasan³

¹Department of Physics, Sri Shanmugha College of Engineering and Technology, Sankari, Salem – 637 304, Tamilnadu, India

²Department of Physics, Sri Vidyaa Vikas College of Engineering and Technology, Tiruchengode, Tamilnadu, India - 637 217

³Department of Physics, Kongu Engineering College, Perundurai, Erode - 638 058. Tamilnadu, India

Abstract: chitosan and poly vinyl pyrrolidone (PVP) capped ZnO nanoparticles were prepared using soft chemical method. Structure and optical properties of prepared samples were investigated using XRD, UV techniques. Further, their antibacterial activities were investigated against *Escherichia coli* and *Staphylococcus aureus* bacteria. A good antibacterial activity was observed from the chitosan capped ZnO nanoparticles.

Keywords: ZnO nanoparticles, chitosan, PVP, Antibacterial activity.

1. Introduction

In recent decades semiconductor nanocrystals have great research attention because of their great potential in opto-electronics and bio-applications [1-3]. Generally the II-VI group semiconductors have been studied due to their unique functions than that of other semiconductors. ZnO is a well known wide bandgap semiconductor because of its unique optical and bio-compatible properties that are huge advantages as a better candidate for bio-applications than metals nanoparticles [4-5]. In day today life, the human beings are infected by microorganisms which results some health hazards, hence, to avoid these problems many researchers have made an attempt to developed different types of ZnO nanostructures and investigated their antibacterial activity [6-8]. The chemical capping method is an extensively used in the synthesis of various nanoparticles since the concentration of capping molecule controls the particles size and reduces the agglomeration [9]. Moreover, the combined formation of inorganic-organic composites can provides interesting properties such as structural, chemical and biological behaviors which was due to the combinatorial effects [10-11]. Therefore, in the present work, we have developed chitosan and PVP capped ZnO nanoparticles using simple chemical method for antibacterial application. Furthermore, the structural and optical properties were investigated. Hence, the observed results were discussed in details.

2. Experimental technique

A standard chemicals of zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), sodium hydroxide (NaOH), chitosan and poly-vinyl pyrrolidone (PVP) were used as precursors with double distilled water (DDW) as a solvent. The detailed sample preparation techniques are described as follows. The previous experimental techniques were adopted with little modification to prepare the uncapped and capped ZnO NPs [12].

2.1. Synthesis of uncapped and capped ZnO NPs

A freshly prepared $\text{Zn}(\text{CH}_3\text{COO})_2$ solution was first allowed to stirring and in this a freshly prepared NaOH was slowly added in drops till the pH reaches 10. Then this mixture solution was stirred vigorously until a white color colloidal solution was formed. Finally particles sedimentation was obtained and then washed several times to remove the unreacted compounds, and then it was centrifuged. After that, the particles were separated from the solution and then dried, to get a ZnO nanoparticles. Further, collected crystal sample was oxidized through annealing treatment and grinded well. Finally, a white colored ZnO powder was obtained and used for further analysis. Similarly, the same procedure was used to prepare the capped ZnO nanoparticles, but the capping solution (chitosan and PVP, respectively) was added in drops into the $\text{Zn}(\text{CH}_3\text{COO})_2$ solution before changing the pH value. Finally, the prepared samples were analyzed under various characterization techniques.

2.2. Antibacterial test

The antibacterial activities of the prepared samples were evaluated using agar well diffusion method. The media and the test bacterial cultures were poured into Petri dishes. The prepared samples of ZnO nanoparticles, chitosan capped ZnO nanoparticles and PVP capped ZnO nanoparticles were mixed with 50 μl DMSO and poured into sterile petri plates. Then allowed to solidify and the individual organism was marked for the inoculated. Hence, the plates were incubated on overnight at 37⁰C and formed zones of inhibition were measured with respect to the control.

3. Results and discussion

3.1. XRD analysis

The crystal structure and particle size was determined using XRD pattern (recorded using PANalytical diffractometer model) and their corresponding patterns are shown in figure 1 of (a) ZnO nanoparticles, (b) chitosan capped ZnO nanoparticles and (c) PVP capped ZnO nanoparticles, respectively. The observed diffraction peaks are matched with the hexagonal structure of ZnO (JCPDS No. 36-1451). The peak broaden indicates the formation of nanometer sized particles in the prepared samples [13]. The Debye Scherrer's formula was used to calculate the average particle size of the Nanoparticles and it is in the range of 15-20 nm. The chitosan and PVP capped ZnO nanoparticles (approximately 16 nm and 17 nm, respectively) shows smaller sizes than that of the uncapped ZnO nanoparticles (approximately 20 nm) because the ZnO particles surface were covered by the capping molecules which reduces the agglomeration and also the diffraction peaks were also slightly different [14].

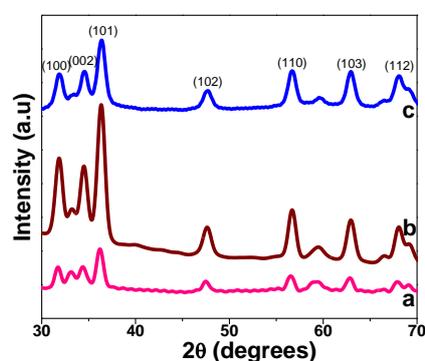


Figure 1. XRD patterns of (a) ZnO NPs, (b) chitosan capped ZnO NPs and (c) PVP capped ZnO NPs.

3.2. UV analysis

The optical behaviors and bandgap energy of the uncapped and capped nanoparticles were observed from the UV spectrum (recorded using Shimadzu UV-Visible spectrophotometer model) and their corresponding results are shown in figure 2 of (a) ZnO NPs, (b) chitosan capped ZnO nanoparticles and (c) PVP capped ZnO nanoparticles, respectively. Then their calculated bandgap energy values are 3.69 eV (336 nm), 3.66 eV (339 nm) and 3.68 eV (337 nm), respectively with direct bandgap nature [15] and a slightly decreased bandgap energy values was observed from the capped nanoparticles due to the presence capping molecules [16].

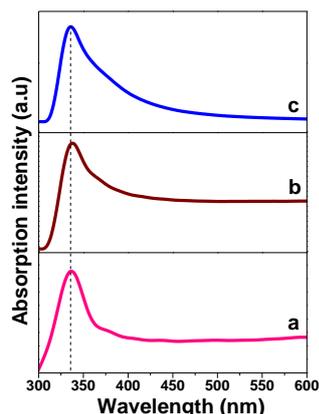


Figure 2. UV optical spectrum of (a) ZnO NPs, (b) chitosan capped ZnO NPs and (c) PVP capped ZnO NPs.

3.3. Antibacterial activity analysis

The antibacterial activity of the ZnO nanoparticles, chitosan capped ZnO nanoparticles and PVP capped ZnO nanoparticles were tested using *Escherichia coli* and *Staphylococcus aureus*. Generally the microbial effects have changed their bacteria's surface morphology when the nanoparticles interacted with a bacterium which was observed in the form of zone of inhibition and colony counting through different methods [17-19]. Figure 3 shows the antibacterial activity of (a) control (b) ZnO nanoparticles, (c) chitosan capped ZnO nanoparticles and (d) PVP capped ZnO nanoparticles, respectively and their corresponding zone of inhibition measurements are given (in figure 5) against *Escherichia coli* with respect to the control. The chitosan capped ZnO NPs has shown an increased zone of inhibition (19 mm, indicated by black circle) than that of others two nanoparticles samples which indicates a higher antibacterial activity. Whereas PVP capped ZnO nanoparticles and uncapped ZnO nanoparticles has shown respective zones of inhibition 17 mm and 15 mm (indicated by black circle) which also indicates a good antibacterial activity. Consequently, smaller particles having the larger surface area available for interaction and it can give more bacterial effects [20-21]. Similarly, the antibacterial activity of these nanoparticles were tested against *Staphylococcus aureus*, it has shown in figure 4. The diameter of zone of inhibition was measured and it is good agreement with reported results [22-25]. The value of dia of zone of inhibition can be increased with increased in the concentration of the nanoparticles. And it maybe depends upon the production of reactive oxygen species. Hence, we believed that our samples may also act the same mechanisms here. Finally, both of the observations (against *Escherichia coli* and *Staphylococcus aureus*) suggests that the chitosan capped ZnO nanoparticles has shown a higher antibacterial effect when compared with other samples, has shown in figure 5. Therefore, we conclude that it can be suitable for antibacterial applications.

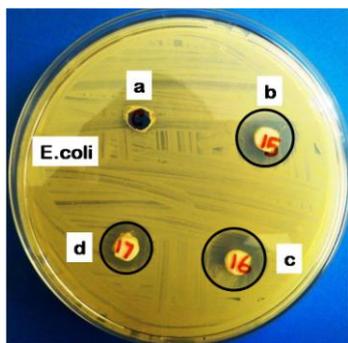


Figure 3. Antibacterial activity of (a) Control, (b) ZnO NPs, (c) chitosan capped ZnO NPs and (d) PVP capped ZnO NPs against *Escherichia coli*

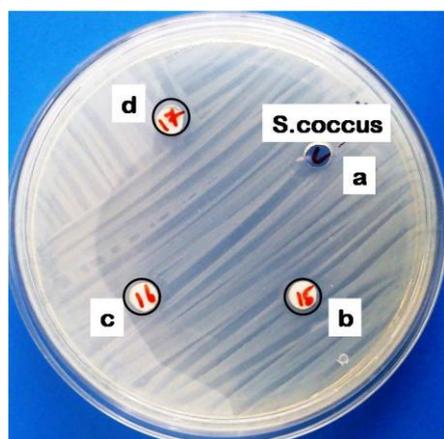


Figure 4. Antibacterial activity of (a) Control, (b) ZnO NPs, (c) chitosan capped ZnO NPs and (d) PVP capped ZnO NPs against *Staphylococcus aureus*

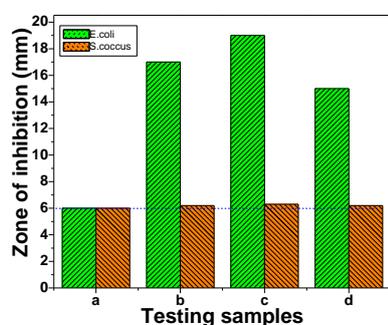


Figure 5. Antibacterial activity of zones of inhibition (a) Control, (b) ZnO NPs, (c) chitosan capped ZnO NPs and (d) PVP capped ZnO NPs against *Escherichia coli* and *Staphylococcus aureus*

4. Conclusion

A successful synthesis of chitosan and poly vinyl pyrrolidone (PVP) capped ZnO nanoparticles were prepared using soft chemical method. Then their structural and optical properties were investigated using XRD, UV techniques. From XRD analysis, a hexagonal crystal structure was observed. An enhanced optical behavior was observed in capped ZnO nanoparticles from UV analysis. Finally, the antibacterial activities were investigated against *Escherichia coli* and *Staphylococcus aureus* and an enhanced antibacterial effect was observed from the chitosan capped ZnO nanoparticles.

References

1. Singh N., Mehra R. M., Kapoor A., and Soga T., ZnO based quantum dot sensitized solar cell using CdS quantum dots. *Journal of Renewable and Sustainable Energy*, 2012, 4(1), 013110.
2. Rosenthal S.J., Chang J.C., Kovtun O., McBride J.R., and Tomlinson I.D., Biocompatible quantum dots for biological applications, *Chem. Biol.*, 2011, 18, 10–24.
3. Jin T., Sun D., Su J.Y., Zhang H., and Sue H. J., Antimicrobial efficacy of zinc oxide quantum dots against *Listeria monocytogenes*, *Salmonella enteritidis* and *Escherichia coli* O157: H7, *Journal of Food Science*, 2009, 74(1), M46-M52.
4. Li M., Lv X., Ma X., Sun F., Tang L., and Wang Z., Direct synthesis of monodispersed ZnO nanoparticles in an aqueous solution, *Materials Letters*, 2007, 61(3), 690-693.
5. Ratkovich A., and Penn R. L., Zinc oxide nanoparticle growth from homogenous solution: influence of Zn: OH, water concentration, and surfactant additives. *Materials Research Bulletin*, 2009, 44(5), 993-998.
6. Wahab R., Kim Y. S., Mishra A., Yun S. I., and Shin H. S., Formation of ZnO micro-flowers prepared via solution process and their antibacterial activity. *Nanoscale research letters*, 2010, 5(10), 1675-1681.

7. Ramani M., Ponnusamy S., Muthamizchelvan C., Cullen J., Krishnamurthy S., and Marsili E., Morphology-directed synthesis of ZnO nanostructures and their antibacterial activity. *Colloids and Surfaces B: Biointerfaces*, 2013, 105, 24-30.
8. Padmavathy N., and Vijayaraghavan R. Enhanced bioactivity of ZnO nanoparticles - an antimicrobial study. *Science and Technology of Advanced Materials*, 2008, 9(3), 035004.
9. Qinglian Wei., Shi-Zhao Kang., and Jin Mu., Green” synthesis of starch capped CdS nanoparticles *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2004, 247, 125–127.
10. Wilkes G.L., Orlor B., and Huang H.H., “Ceramers” hybrid materials incorporating polymeric/oligomeric species into inorganic glasses utilizing a sol–gel approach. *Polym. Prepr.*, 1985, 26: 300–301.
11. Lévy R., Thanh N. T., Doty R. C., Hussain I., Nichols R. J., Schiffrin D. J., Brust M., and Fernig D. G., Rational and combinatorial design of peptide capping ligands for gold nanoparticles. *Journal of the American Chemical Society*, 2004, 126(32), 10076-10084.
12. Vidhya K., Saravanan M., Bhoopathi G., Devarajan V. P., and Subanya S., Structural and optical characterization of pure and starch-capped ZnO quantum dots and their photocatalytic activity. *Applied Nanoscience*, 2014, 1-9.
13. Choi H. H., Ollinger M., and Singh, R. K., Enhanced cathodoluminescent properties of ZnO encapsulated ZnS: Ag phosphors using an electrochemical deposition coating. *Applied physics letters*, 2003, 82(15), 2494-2496.
14. Mumalo-Djokic D., Stern W.B., Taubert A., Zinc oxide/carbohydrate hybrid materials via mineralization of starch and cellulose in the strongly hydrated ionic liquid tetrabutylammonium hydroxide. *Cryst. Growth Design* 2008, 8, 330–335.
15. Irimpan L., Nampoovi V. P. N., Radhakrishnan P., Deepthy A., and Krishnan B., Size dependent fluorescence spectroscopy of nanocolloids of ZnO. *Journal of Applied Physics*, 2007, 102(6), 063524.
16. Alvaro M., Carbonell E., Fornés V., and García, H., Enhanced Photocatalytic Activity of Zeolite-Encapsulated TiO₂ Clusters by Complexation with Organic Additives and N-Doping. *ChemPhysChem*, 2006, 7(1), 200-205.
17. Makhluf S., Dror R., Nitzan Y., Abramovich Y., Jelinek R., and Gedanken A., Microwave-Assisted Synthesis of Nanocrystalline MgO and Its Use as a Bactericide, *Advanced Functional Materials*, 2005, 15 (10), 1708–1715.
18. Lu Z., Li C. M., Bao H., Qiao Y., Toh Y., and Yang X., Mechanism of antimicrobial activity of CdTe quantum dots. *Langmuir*, 2008, 24(10), 5445-5452.
19. Rizwan Wahab., Young-Soon Kim., Amrita Mishra., Soon-Il Yun., Hyung-Shik Shin., Formation of ZnO Micro-Flowers Prepared via Solution Process and their Antibacterial Activity, *Nanoscale Research Letters*, 2010, 5, 1675-1681.
20. Rivero P. J., Urrutia A., Goicoechea J., Zamarreño C. R., Arregui F. J., and Matías I. R., An antibacterial coating based on a polymer/sol-gel hybrid matrix loaded with silver nanoparticles. *Nanoscale research letters*, 2011, 6(1), 1-7.
21. Dong C., Song D., Cairney J., Maddan O. L., He G., and Deng Y., Antibacterial study of Mg (OH)₂ nanoplatelets, *Materials Research Bulletin*, 2011, 46(4), 576-582.
22. Vidhya K., Bhoopathi G., Devarajan V. P., and Saravanan M., Green Synthesis of Glucose Capped ZnO: Fe Quantum Dots: A Study on Structural, Optical Properties and Application. *Research Journal of Recent Sciences*, 2014, 3, 1-8 (2014)
23. Gordon T., Perlstein B., Houbara O., Felner I., Banin E., and Margel S., Synthesis and characterization of zinc/iron oxide composite nanoparticles and their antibacterial properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2011, 374(1), 1-8.
24. George S., Pokhrel S., Xia T., Gilbert B., Ji Z., Schowalter M., Rosenauer A., Damoiseaux R., Bradley K.A., Mädler L., and Nel A.E., Use of a rapid cytotoxicity screening approach to engineer a safer zinc oxide nanoparticle through iron doping, *ACS Nano*, 2010, 4(1), 15-29.
25. Bhadra P., Mitra M. K., Das G. C., Dey R., and Mukherjee S., Interaction of chitosan capped ZnO nanorods with *Escherichia coli*, *Materials Science and Engineering*, 2011, C 31(5), 929-937.
