



Surface Modified Chitosan with Cadmium Sulfide Quantum Dots as Luminescent Probe for Detection of Silver Ions

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In present work, the surface modified cadmium sulfide quantum dots (CdS QDs) was synthesized with chitosan for the detection of silver ions. Chitosan was employed as matrix medium to fabricate CdS QDs, resulting in the formation of novel QDs/chitosan composite. The CdS quantum dots surface coated with chitosan were analyzed using UV-vis spectrophotometer, X-ray diffraction and transmission electron microscope. The chitosan + CdS QDs exhibited high aqueous solubility with better steadiness. By using chitosan + CdS, the silver ions were not only detected but also reduced to nanosize due to the reducing property of chitosan. The mechanism of fluorescence quenching of chitosan + CdS by Ag⁺ was investigated using photoluminescence spectroscopy.

Keywords: CdS quantum dots, Chitosan, Metal ion detection, Quenching mechanism.

INTRODUCTION

Most of the metallic nanoparticles like calcium, copper, iron, silver, titanium, zinc and oxalate are employed in various medical, electrical and even in household applications which synthesized from both green and chemical methods [1-10]. The fascination in these materials have been mainly inspired by their vital quantum properties, nevertheless technological features of these materials are being given full contemplation [11]. Owing to quantum confinement, quantum dots have an exclusive electronic and optical properties. The quantum dots exhibit remarkable advantages, like large fluorescence quantum yields, very high photo bleaching threshold and outstanding photo stability [12-15].

Revised core-shell quantum dots (QDs) have been used as fluorescence labels to stain biological models and for cancer cells identification [13,16]. The change of surface charges of quantum dots caused by either chemical or physical interaction between metal ions that affects the effectiveness of electron-hole recombination in core [17]. Cadmium sulfide embedded with matrixes like polystyrene, polyvinyl alcohol, polyethylene glycol (PEG) *etc.*, have been employed for various applications [18-24].

Chen & Rosenzweig [25] demonstrated the copper and zinc ions analysis by utilizing a CdS luminescent quantum dot capped by various ligands. Gattas-Asfura & Leblanc [26] synthesized a peptide coated on CdS for optical detection of Cu²⁺ and Ag⁺ ions. It is confirmed that cadmium sulfide quantum dots (CdS QDs) show a broader emission peak, which represented that the particles contain more surface defects [27,28]. The analysis of heavy ions, especially Cu²⁺, in the environmental and biological samples are extremely important [29].

Chitosan is a biopolymeric materials found in crab shells. Moreover, chitosan has good chelating ability with transition metal ions, which makes it possible for its metal ion complexes to be used as precursors to synthesize quantum dots [30,31]. Due to its unique structures, chitosan exhibit multidimensional properties and applied in the widely in the biomedical and other industrial areas [32-35]. Some of the recent works focused on the materials and also wide range of applications using chitosan based composites [36-41]. In this present investigation, an attempt is made to synthesize CdS QDs-chitosan composite under mild conditions, which can chelated the metal ions in less reaction time. Chitosan also acts as the stabilizing agent and allow the growth of quantum dots. By varying the concen-

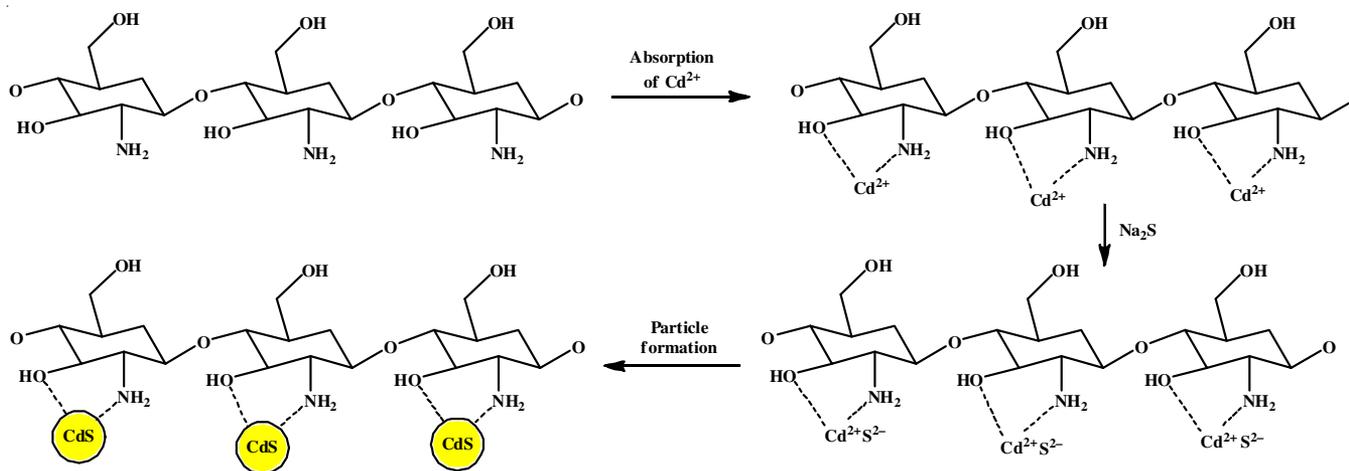


Fig. 1. Reaction mechanism of CdS/chitosan composite with absorption and growth of quantum dots in chitosan matrix

tration of the reducing agent, different size of CdS/chitosan and variation in luminescence were observed.

EXPERIMENTAL

Cadmium acetate, sodium sulfide and silver nitrate were purchased from Merck, India, chitosan with 85% of deacetylation, with high molecular weight and viscosity of 200 cps was purchased from Sigma-Aldrich. Throughout the experimental work, deionized water was used.

Formation of chitosan matrix: Initially, 1 mL glacial acetic acid was added to 49 mL of deionized water and stirred for 10 min followed by the addition of 1 g of chitosan under constant stirring. The clear solution was sonicated for 20 min at room temperature using ultrasonication bath and filtered using Whatman filter paper. Cadmium acetate of 10 mM in 20 mL of deionized water was mixed separately and added chitosan solution dropwise and stirred for 10 h. Long period of stirring reaction is to make well chelation of Cd^{2+} ions in the chitosan matrix.

Now, the freshly prepared 10 mM sodium sulfide in 20 mL of deionized water was added to the cadmium chelated chitosan matrix. The sulfide ions combined with cadmium ions in the matrix and initiated the growth of quantum dots. The formation of CdS QDs was observed by colour change which occurs from colourless to light yellow. The overall reaction mechanism is shown in Fig. 1.

Detection of silver ions: Few drops of 10 mM silver nitrate dissolved in 50 mL of deionized water was added to CdS/chitosan solution, immediate colour change was observed, which indicate that fluorescent quenches have taken place. An easy method of detection of silver ions by quantum dots is done by colour quenching effect, where the light yellow colour was completely quenches to golden brown colour when 100 μL silver nitrate solution was added.

Characterization: the UV-Visible spectral analysis was performed by using Jasco V-650 series spectrophotometer with a wavelength of 200 to 800 nm possessing with a scanning speed of 400 nm/min. X-ray diffraction was carried out by X-Pert Pro diffractometer using step scan technique and with $\text{CuK}\alpha$ radiation (1.500 Å, 40 KV, 30 mA) in θ - 2θ configuration.

Photoluminescence measurement was performed using Perkin-Elmer lambda 55 with UV light. TEM analysis of the metal nanoparticles was performed on a JEOL model PHILIPS instrument operated at an accelerating voltage of 120 KV. The SEM images were obtained using JSM-6390 instrument with accelerating voltage of 20 V and magnification of 23 K.

RESULTS AND DISCUSSION

Synthesis of CdS/chitosan composite solution: Synthesis of CdS/chitosan composite solution was prepared in two ways: The first step is to chelate between cadmium ions to chitosan, followed with the rapid addition of Na_2S . Fig. 2a-b shows the change in the absorption spectra of Cd^{2+} /chitosan complex and CdS/chitosan composite, respectively. After addition of Na_2S , the shoulder present at 277 nm in the Cd^{2+} /chitosan complex disappears. This peak is associated with the electronic transition of nitrogen on the secondary amide and primary amine groups present in chitosan and its disappearance implies an interaction is occurred between the newly formed CdS and chitosan at 430 nm.

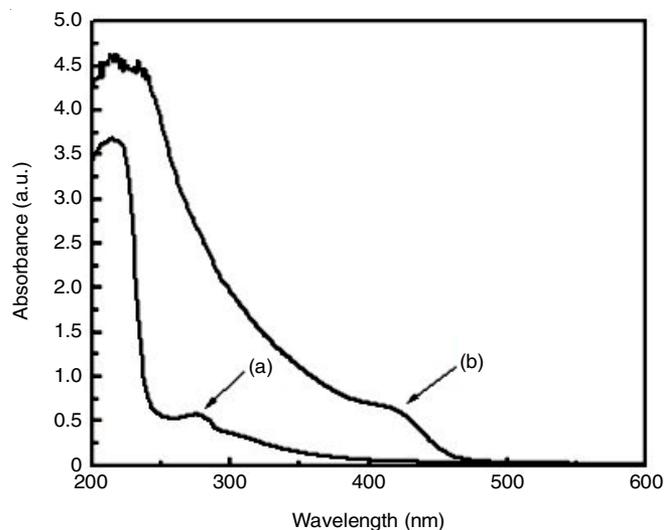


Fig. 2. UV spectra of (a) Cd^{2+} /chitosan and (b) CdS/chitosan composite with $\text{Cd}(\text{Ac})_2$ and Na_2S

Effect of precursor concentration with CdS QDs size:

The effects of concentration of both cadmium acetate and sodium sulfide were performed to know the possible greatest effect on QD size. By varying the concentration of $\text{Cd}(\text{OAc})_2$ from 1, 5 and 10 mM, with constant Na_2S concentration at 5 mM, a little change in the size of CdS QDs was observed (Fig. 3) [35]. However, when the concentration of Na_2S varied from 1, 5 and 10 mM, with constant concentration of $\text{Cd}(\text{OAc})_2$ at 10 mM, a significant change in CdS QD size was observed (Fig. 4). The obtained results suggested that the sizes of QDs in the chitosan matrix are controlled primarily by Na_2S . Huang *et al.* [36] have recorded similar results using CdS QDs synthesized by chelating cadmium to sulfonated bisvinyl-A (BSS) followed by injection of hydrogen sulfide (H_2S).

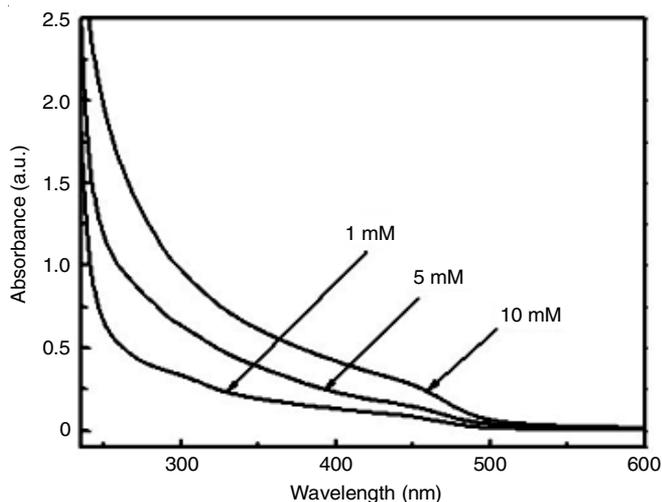


Fig. 3. UV-visible spectra of CdS/chitosan composite with different concentration of $\text{Cd}(\text{OAc})_2$ while Na_2S constant

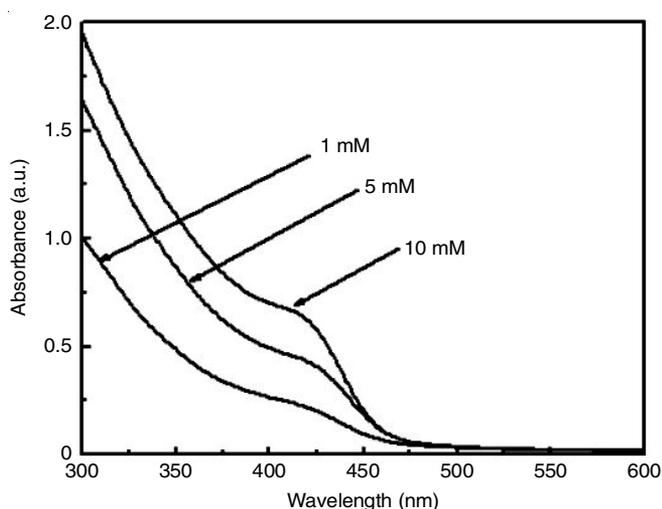


Fig. 4. UV-visible spectra of CdS/chitosan composite with different concentration of Na_2S while $\text{Cd}(\text{OAc})_2$ constant

It is believed that this effect occurs since the nucleation of QDs is limited at lower concentrations of Na_2S resulting in rapid depletion of precursors. Decreased concentrations result in a smaller equilibrium concentration and so smaller QD nanocrystals. Furthermore, the presence of the chitosan polymer

hinders further growth and aggregation of the nanocrystals. Herein, only variation was in concentration but the amount of addition of Na_2S was same, since increase in the volume of Na_2S increases the particle size which leads to aggregation.

Detection of silver ions by quantum dots: Fluorescence was best achieved at a Na_2S precursor of 5 mM and silver was well absorbed when compared to that of other concentrations. Different concentration of silver nitrate was added to the reaction and the colour changes were observed in the reaction mixture indicating the presence of silver ions on the chitosan matrix. The UV visible spectra clearly shows λ_{max} at 419 nm indicating the presence of silver nanoparticles on CdS QDs-chitosan composite (Fig. 5).

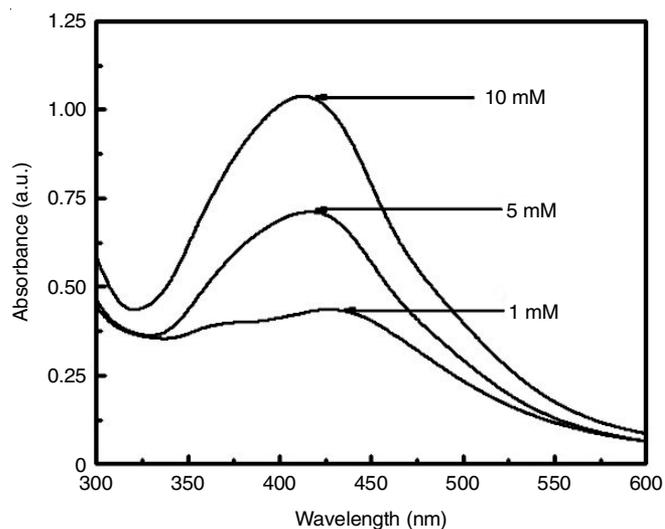


Fig. 5. UV-vis spectra of CdS/chitosan composite after addition of different concentration of AgNO_3

Quenching mechanism: Luminescence of CdS QDs-chitosan composite was observed at the range of high intensity of reducing agent Na_2S . The excitation was given at 360 nm so that the first emission at 440 nm and thus intensity reduces with increases in silver nitrate concentration (Fig. 6). The photoluminescence spectra of CdS was recorded at room temperature with excitation wavelength of 360 nm. The spectra was observed to be broad and the emission occurred at a lower energy value than that of the corresponding excitonic emission band. Change in the colour after adding silver nitrate into CdS QDs-chitosan composite shows the quenching in fluorescence of quantum dots.

X-ray diffraction analysis: The observed broad peaks in XRD pattern are attributed to the hexagonal arrangement of CdS nanocrystals as shown in Fig. 7. The CdS nanoparticles can possess hexagonal phase with (002) plane as reported earlier by Hu *et al.* [37]. Bragg's reflection observed in XRD pattern at $2\theta = 28.56^\circ$ and 32.456° corresponds to (0 0 2) and (1 1 0) facets of crystalline of cadmium sulfide quantum dots (JCPDS No: 41-1049). The sample contains same phase hexagonal structure.

The X-ray diffraction pattern of silver ions after being absorbed by CdS QDs-chitosan composite is shown in Fig. 8, which confirms the existence of both silver and quantum dots.

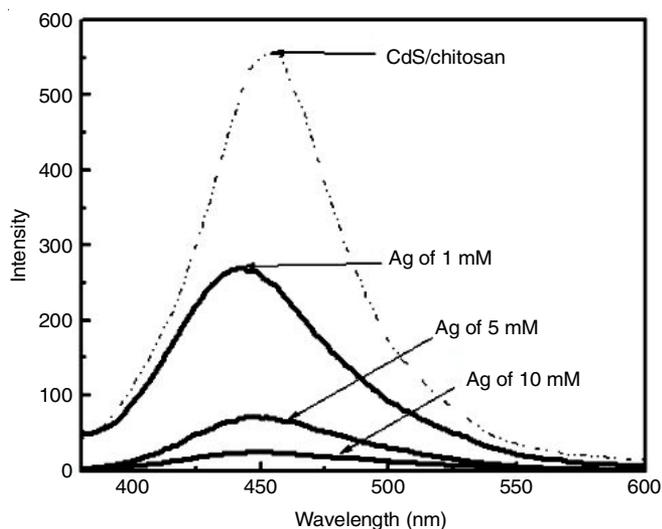


Fig. 6. Quenching effect of CdS/chitosan composite before and after addition of silver ions

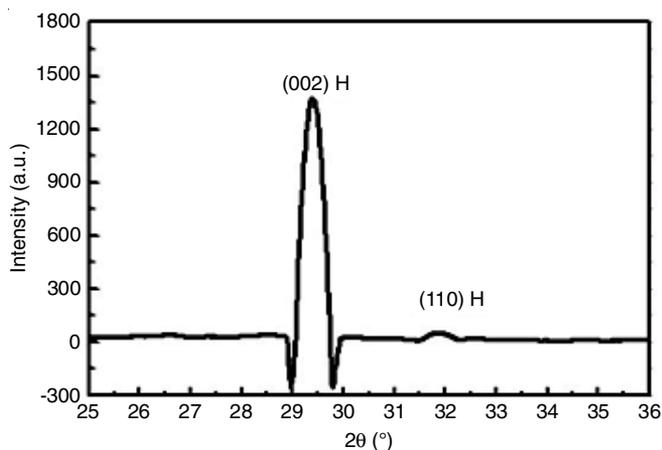


Fig. 7. XRD pattern of CdS/chitosan composites

Braggs reflection observed in XRD pattern at $2\theta = 38.245^\circ$ related to the (1 1 1) of crystalline silver (JCPDS No: 87-0720).

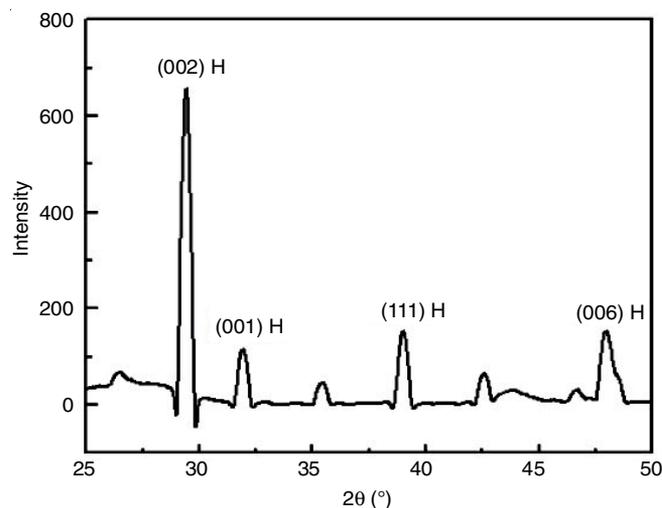


Fig. 8. XRD pattern of silver capped CdS/Chitosan composite

The Ag + CdS QDs-chitosan composite consist of mixed phase of both hexagonal and cubic structures of silver nanoparticles.

Morphology studies: SEM micrographs of CdS QDs-chitosan composite is depicted in Fig. 9a, which resembles a dot like structure of average size of 55.39 nm. The average size of Ag capped CdS QDs-chitosan composite was 83.22 nm with rod shape was also observed (Fig. 9b). The EDAX spectra were used to find the elemental composition of Ag capped CdS QDs-chitosan composite. From the spectra shown in Fig. 10a, it was found that elements Cd and S are present in the composite of CdS QDs-chitosan composite. Similarly, silver capped CdS QDs-chitosan composite (Fig. 10b) showed the presence of silver, which confirms that silver ions were trapped in the CdS QDs-chitosan composite successfully.

TEM: TEM micrographs of CdS QDs-chitosan composite before and after the addition of silver ion are shown in Fig. 11. The average size of CdS quantum dots in the CdS QDs-chitosan composite matrix with narrow size of about 7.51 nm, which clearly indicated that the quantum dots closely packed. It is

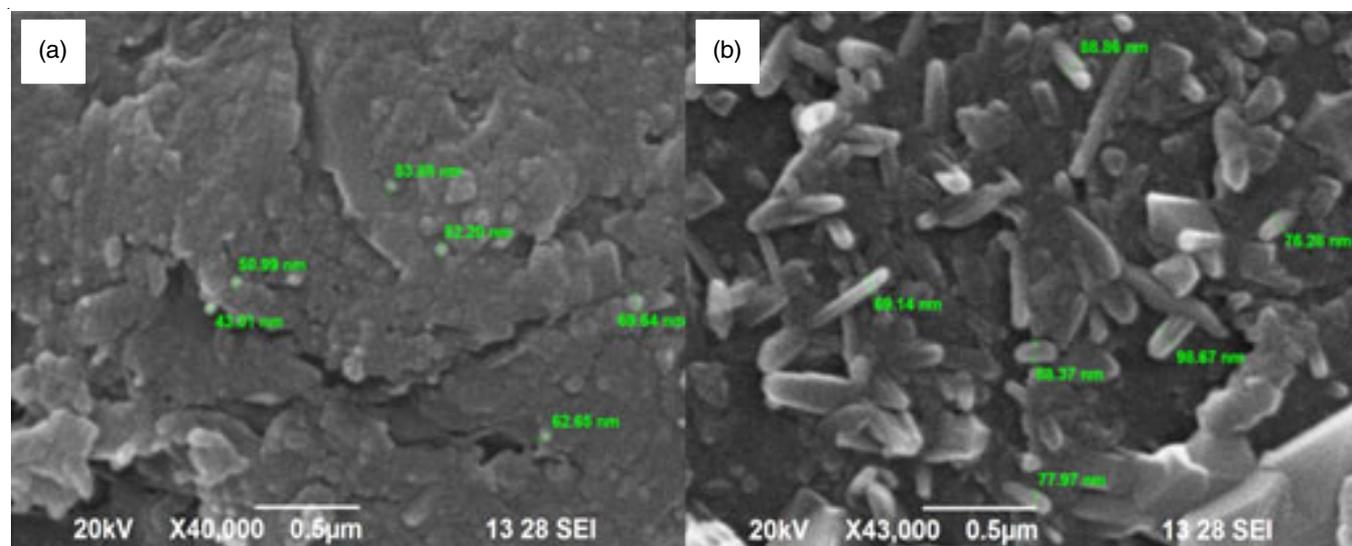


Fig. 9. SEM micrograph of chitosan/CdS (a) and silver + chitosan/CdS composite (b)

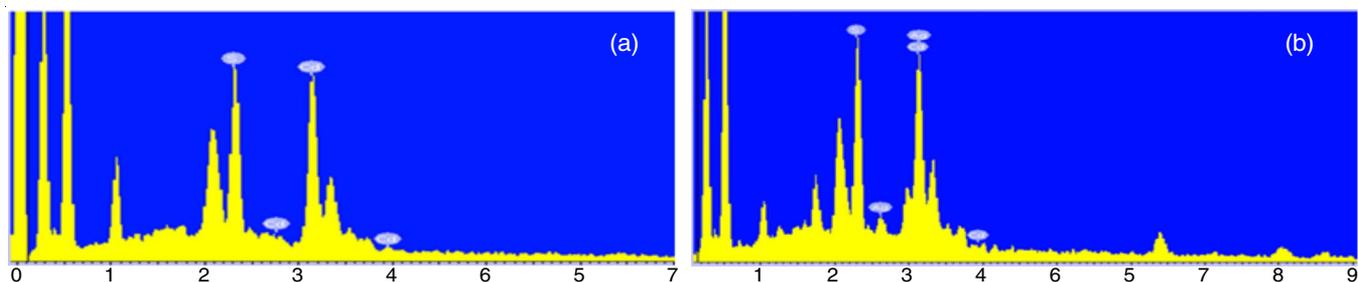


Fig. 10. (a) EDAX spectra of CdS/chitosan before addition of silver nitrate and (b) after addition of silver nitrate

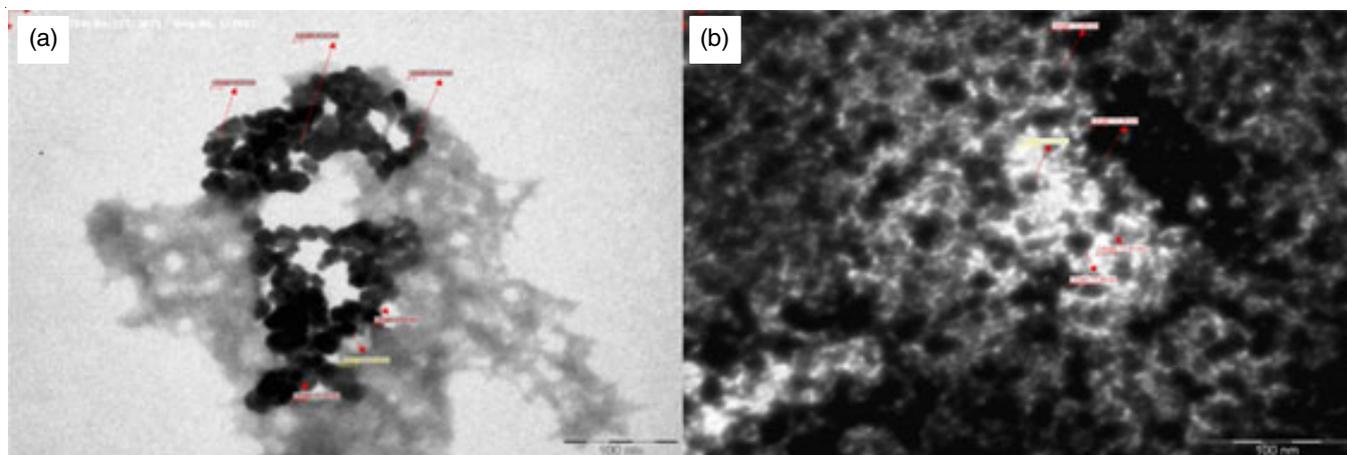


Fig. 11. (a) TEM micrograph of CdS/chitosan and (b) silver capped to CdS/chitosan composite

also found that the size of nanoparticles marginally increase after the addition of silver, which might be attributed due to the formation of silver ion attached on the surface of CdS QDs. Nanospheres appearance was due to the formation of nanovesicles as the chitosan has dried on the TEM grid. The Ag capped CdS/chitosan QDs (Fig. 11b) appears as dark spots of agglomerated and overlaid QDs. However, every chitosan nanovesicles do not appear to have QDs associated with them which again may be a result of the diffusion limited process of QD formation. From Fig. 11b, it is clearly observed that chitosan matrix was light before the addition of silver and it turns dense after the addition of silver ions, which indirectly responsible for the quenching of fluorescence.

Conclusion

Formation of CdS quantum dots in chitosan matrix was been characterized using UV-visible, photoluminescence, XRD, SEM with EDAX and TEM techniques. Detection of silver ions by CdS QDs-chitosan composite by fluorescence quenching as analyzed by photoluminescence. The silver ions also reduced to nanosize, which was observed from TEM analysis. The particle size was 7.51 nm and shape was found to be spherical for CdS QDs-chitosan composite and rod structure for Ag capped CdS QDs-chitosan composite. Crystalline structure of CdS quantum dots was hexagonal in shape as deduced from XRD analysis.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. D. Zhang, X.-L. Ma, Y. Gu, H. Huang and G.-W. Zhang, *Front. Chem.*, **8**, 799 (2020); <https://doi.org/10.3389/fchem.2020.00799>
2. S. Patil and R. Chandrasekaran, *J. Genet. Eng. Biotechnol.*, **18**, 67 (2020); <https://doi.org/10.1186/s43141-020-00081-3>
3. G. Vinci and M. Rapa, *Bioengineering*, **6**, 10 (2019); <https://doi.org/10.3390/bioengineering6010010>
4. A.A. Yaqoob, H. Ahmad, T. Parveen, A. Ahmad, M. Oves, I.M.I. Ismail, H.A. Qari, K. Umar and M.N.M. Ibrahim, *Front. Chem.*, **8**, 341 (2020); <https://doi.org/10.3389/fchem.2020.00341>
5. N. Kulkarni and U. Muddapur, *J. Nanotechnol.*, **2014**, 510246 (2014); <https://doi.org/10.1155/2014/510246>
6. A.B. Sengul and E. Asmatulu, *Environ. Chem. Lett.*, **18**, 1659 (2020); <https://doi.org/10.1007/s10311-020-01033-6>
7. Y.-X. Zhang and Y.-H. Wang, *RSC Adv.*, **7**, 45129 (2017); <https://doi.org/10.1039/C7RA07551K>
8. V.A. Niraimathee, V. Subha, R.S.E. Ravindran and S. Renganathan, *Int. J. Environ. Sustain. Dev.*, **15**, 227 (2016); <https://doi.org/10.1504/IJESD.2016.077370>
9. K. Rurack, M. Kollmannsberger, U. Resch-Genger and J. Daub, *J. Am. Chem. Soc.*, **122**, 968 (2000); <https://doi.org/10.1021/ja992630a>
10. Z. Beyene and R. Ghosh, *Mater. Today Commun.*, **21**, 100612 (2019); <https://doi.org/10.1016/j.mtcomm.2019.100612>
11. D. Šajinovic, Z.V. Šaponjic, N. Cvjeticanin, M. Marinovic-Cincovic and J.M. Nedeljkovic, *Chem. Phys. Lett.*, **329**, 168 (2000); [https://doi.org/10.1016/S0009-2614\(00\)00990-8](https://doi.org/10.1016/S0009-2614(00)00990-8)
12. S. Emin, N. Sogoshi, S. Nakabayashi, M. Villeneuve and C. Dushkin, *J. Photochem. Photobiol. Chem.*, **207**, 173 (2009); <https://doi.org/10.1016/j.jphotochem.2009.07.002>
13. W.C.W. Chan, D.J. Maxwell, X.H. Gao, R.E. Bailey, M.Y. Han and S.M. Nie, *Biotechnology (Faisalabad)*, **13**, 40 (2002).

14. S.K. Vemuri, R.R. Banala, S. Mukherjee, P. Uppula, G.P.V. Subbaiah, G.A.V. Reddy and T. Malarvilli, *Mater. Sci. Eng. C-Mater. Biol. Appl.*, **99**, 417 (2019); <https://doi.org/10.1016/j.msec.2019.01.123>
15. H. Mattoussi, J.M. Mauro, E.R. Goldman, G.P. Anderson, V.C. Sundar, F.V. Mikulec and M.G. Bawendi, *J. Am. Chem. Soc.*, **122**, 12142 (2000); <https://doi.org/10.1021/ja002535y>
16. W.C.W. Chan and S.C. Nie, *Science*, **281**, 2016 (1998); <https://doi.org/10.1126/science.281.5385.2016>
17. D.E. Moore and K. Patel, *Langmuir*, **17**, 2541 (2001); <https://doi.org/10.1021/la001416t>
18. H. Zhao, E.P. Douglas, B.S. Harrison and K.S. Schanze, *Langmuir*, **17**, 8428 (2001); <https://doi.org/10.1021/la011348q>
19. K. Senthil, D. Mangalaraj and S.K. Narayandass, *Appl. Surf. Sci.*, **169-170**, 476 (2001); [https://doi.org/10.1016/S0169-4332\(00\)00732-7](https://doi.org/10.1016/S0169-4332(00)00732-7)
20. T. Kippeny, L.A. Swafford and S.J. Rosenthal, *J. Chem. Educ.*, **79**, 1094 (2002); <https://doi.org/10.1021/ed079p1094>
21. F.M. Antolini, T. Pentimalli, R. Di Luccio, M. Terzi, M. Schioppa, L. Re, L. Mirengi and L. Tapfer, *Mater. Lett.*, **59**, 3181 (2005); <https://doi.org/10.1016/j.matlet.2005.05.047>
22. H. Wang, P. Fang, Z. Chen and S. Wang, *Appl. Surf. Sci.*, **253**, 8495 (2007); <https://doi.org/10.1016/j.apsusc.2007.04.020>
23. J.X. Yao, G.L. Zhao, D. Wang and G.R. Han, *Mater. Lett.*, **59**, 3652 (2005); <https://doi.org/10.1016/j.matlet.2005.07.005>
24. D. Wu, X. Ge, Z. Zhang, M.Z. Wang and S.L. Zhang, *Langmuir*, **20**, 5192 (2004); <https://doi.org/10.1021/la049405d>
25. Y. Chen and Z. Rosenzweig, *Anal. Chem.*, **74**, 5132 (2002); <https://doi.org/10.1021/ac0258251>
26. K.M. Gattas-Asfura and R.M. Leblanc, *Chem. Commun.*, **21**, 2684 (2003); <https://doi.org/10.1039/B308991F>
27. J.L. Chen and C.Q. Zhu, *Anal. Chim. Acta*, **546**, 147 (2005); <https://doi.org/10.1016/j.aca.2005.05.006>
28. S.J. Lai, X.J. Chang, Mao, Y. Zhai, N. Lian and H. Zheng, *Ann. Chim.*, **97**, 109 (2007); <https://doi.org/10.1002/adic.200690080>
29. B. Krajewska, *React. Funct. Polym.*, **47**, 37 (2001); [https://doi.org/10.1016/S1381-5148\(00\)00068-7](https://doi.org/10.1016/S1381-5148(00)00068-7)
30. M. Rinaudo, *Prog. Polym. Sci.*, **31**, 603 (2006); <https://doi.org/10.1016/j.progpolymsci.2006.06.001>
31. T. Chandy and C.P. Sharma, *Biomater. Artif. Cells Artif. Organs*, **18**, 1 (1990); <https://doi.org/10.3109/107311990009117286>
32. W. Paul and C.P. Sharma, *S.T.P. Pharma Sci.*, **10**, 5 (2000).
33. R.A.A. Muzzarelli and C. Muzzarelli, *Adv. Polym. Sci.*, **186**, 151 (2005); <https://doi.org/10.1007/b136820>
34. M.N.V. Ravi Kumar, *React. Funct. Polym.*, **46**, 1 (2000); [https://doi.org/10.1016/S1381-5148\(00\)00038-9](https://doi.org/10.1016/S1381-5148(00)00038-9)
35. J. Dilag, H. Kobus and A.V. Ellis, *Forensic Sci. Int.*, **187**, 97 (2009); <https://doi.org/10.1016/j.forsciint.2009.03.006>
36. J. Huang, Y. Yang, B. Yang, S. Liu and J. Shen, *Polym. Bull.*, **36**, 337 (1996); <https://doi.org/10.1007/BF00319234>
37. H. Hu, S.-C. Kung, L.-M. Yang, M.E. Nicho and R.M. Penner, *Sol. Energy Mater. Sol. Cells*, **93**, 51 (2009); <https://doi.org/10.1016/j.solmat.2008.03.011>
38. R. Othayoth, P. Mathi, K. Bheemanapally, L. Kakarla and M. Botlagunta, *J. Microencapsulation*, **32**, 578 (2015); <https://doi.org/10.3109/02652048.2015.1065921>
39. B.N. Singh, V. Veeresh, S.P. Mallick, Y. Jain, S. Sinha, A. Rastogi and P. Srivastava, *Int. J. Biol. Macromol.*, **133**, 817 (2019); <https://doi.org/10.1016/j.ijbiomac.2019.04.107>
40. B.N. Singh, V. Veeresh, S.P. Mallick, S. Sinha, A. Rastogi and P. Srivastava, *Int. J. Biol. Macromol.*, **153**, 1 (2020); <https://doi.org/10.1016/j.ijbiomac.2020.02.173>
41. L. Suresh, P.K. Brahman, K.R. Reddy, and J.S. Bondili, *Enzyme Microbial Technol.*, **112**, 43 (2018); <https://doi.org/10.1016/j.enzmictec.2017.10.009>