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Functional Modification of Photoluminescent Behaviour of 6-O-Triphenylmethylchitosan Embedded Zinc Sulphide based Nanocomposites: Synthesis and Characterization

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The 6-O-triphenylmethylchitosan (TPMC)-modified zinc sulfide (ZnS) nanoparticles were successfully prepared by sol-gel method. The optical and structural properties of the composites were ascribed to the formation of ZnS nanoparticles. The TPMC-modified ZnS nanoparticles have been fabrication during the polymerization process. The produced nanoparticles were examined by FTIR, UV-Vis and photoluminescence (PL) spectra, TEM, XRD and AFM techniques. The XRD diffraction patterns of crystallite size of TPMC-modified ZnS was 30 nm and formed with a sphalerite cubic structure. Similarly, TEM images of the prepared TPMC-modified ZnS nanoparticles were revealed the spherical and porous surfaces of the composites. AFM results has showed that the particles nearly spherical and uniformly distributed. The PL emission was found to be 450 nm when excited at 350 nm. Based on the experimental results, the fabricated TPMC-modified ZnS nanoparticles are ideal candidates in the field of bio-imaging applications.

Keywords: Nanoparticles, Sol-gel method, Zinc sulphide, Bio-imaging, Composites, Photoluminescence.

INTRODUCTION

Majority of zinc sulfide (ZnS) nanostructures are promising functional materials with unique properties suitable for biomedical and electronic applications [1]. It is chemically and optically stable with low toxicity which as a fluorescent label for bio-imaging applications. ZnS nanoparticles have unique optical properties when the size is reduced from bulk to nanoparticles. Due to their multifunctionalization, ZnS-based nanoparticles have been used as contrast agents [2,3]. Several studies have recently been reported on ZnS nanoparticles that find potential applications in the biomedical field [4-8]. In recent years, there has been increasing interest in incorporating metal nanoparticles into natural polymer matrices [9,10]. Natural polymers serve as capping agents used to prevent nanoparticle aggregation and improve optical properties for bio-imaging applications.

Chitosan is a natural polymer (β-(1,4)-linked D-glucosamine units) polysaccharide. It is a cationic polymer containing amino (-NH_2) and hydroxyl (-OH) groups. Introducing hydrophilicity into chitosan improves it's self-assembly and functional properties [4-6]. Biopolymeric chitosan is a non-toxic, hydrophilic, adhesive, biodegradable, biocompatible, high mechanical strength and antibacterial activity properties [11-13]. It has widely used for environment, food production, pharmacy, plant growth, dye/metal ion removal applications [7,8,14]. Chitosan is also not a carcinogen when broken down [15-17]. The basic idea was to use organic soluble 6-O-triphenylmethylchitosan as the starting material for the acylation reaction. Several acylation reactions have been reported for this material. 6-O-triphenylmethylchitosan (TPMC) is more convenient to achieve regioselective chemical modification of chitosan in a homogeneous reaction system [16,18]. The solubility in acetic acid and the rigidity of chitosan limit its use in biomedical applications. However, chitosan derivatives may replace the use of chitosan. ZnS based nanoparticles modified chitosan derivatives used for the optical and absorbent properties.

Chitosan derivatives would be an ideal choice for surface modification of nanomaterials instead to use of pure chitosan. In the last two decades, Biodegradable chitosan and its derivatives have been proven to be an excellent candidate for tissue engineering, biological and drug delivery applications, *etc.* [19-21]. Though, the several studies have been completed structural and luminescence properties of polymer nanocomposites such as enzymatic glucose biosensor of chitosan coated ZnO/Pt nanoparticles [22], ZnS:Mn^{2+} synthesized *via* co-precipitation method with photoconductivity and photoluminescent behaviour [23], ZnS modified polyvinyl pyrrolidone nanoparticles and ZnS nanocrystals doped multicolour electroluminescent through capping agent of pyridine [24], gold incorporated polyaniline-itaconic acid magnetic nanocomposite [25], mechanochemical prepared CS/ZnS nanocrystals [26], superparamagnetic polyaniline/itaconic acid/Fe_3O_4, PANI /itaconic acid/CuO nanocomposites for antimicrobial and heavy metal ions removal [27,28], oxalic acid/ZnS NPs [29] and inorganic-organic transparent coating (ZnS/PUR) were synthesized by *in situ* polymerization method [30]. Also, ZnS nanostructures showed greater photocatalytic activity behaviour, which promote enhances its efficiency in several eco-friendly applications [31-35].

In present work, the fabrication of ZnS nanoparticles modified with 6-O-triphenylmethyl chitosan (TPMC) was successfully prepared by sol-gel method. Materials were characterized by FTIR, UV-visible, photoluminescence (PL), TEM, XRD and AFM. Surface morphology and crystallite size AFM results of TPMC/ZnS nanoparticles were obtained from 30 nm and which showed that the particles were nearly spherical and uniformly distributed. PL emission spectrum was found to be 450 nm when excited at 350 nm. These kinds of modified ZnS nanoparticles has been used in various field of area such as heavy metal ion removal nanotechnology, food manufacturing, biomedicine, pharmacy, industry wastewater treatment and pigment removal.

EXPERIMENTAL

Chitosan flakes with a degree of deacetylation of 98% and a weight average molecular weight (Mw) were procured from Panvo Organics Pvt. Ltd., Chennai, India. Triphenylmethyl chloride obtained with test confirmation from a commercial source was used. Laboratory grade solvents such as methanol, pyridine and methylene chloride (Sigma-Aldrich Company, India) were used in the synthetic work. Zinc acetate, hexahydrate and sodium sulfide, liquid NH_4 from Merck Chemicals, India was used and all solutions were made up of double distilled water.

Synthesis of 6-O-triphenylmethyl chitosan (TPMC): Exactly, 46.9 mol of *n*-phthaloyl-6-O-triphenylmethyl chitosan and hydrazine monohydrate (1. 56 mol) were placed in distilled water (100 mL) and the temperature (100 ºC) was maintained for 10 h. The above reaction mixture was well stirred to obtain a homogeneous mixture. The reaction mass was then cooled to room temperature and stirred with an overhead stirrer for 30 min. Finally, after washing the sample with water, the sample was separated with a vacuum pump and filtered to remove residual hydrazine. After drying the obtained sample in a vacuum dryer, it was added to methanol at 40 ºC for 8 h. The yield of TPMC product produced was found to be 87.3%.

Fabrication of ZnS nanoparticles: After adding 0.02% (w/v) in TPMC and 0.1 M $Zn(OAc)_2$ to a beaker containing 2.5 g of aqueous Na_2S solution (0.1 M), the reaction mixture was continuously stirred at 1000 rpm for 5 h. Additionally, the pH was adjusted to 10 by adding 1 M NH_3 solution. The resulting precipitate was separated, vacuum dried and washed with distilled water. Finally, the dried particles were stored in vials for further characterization.

Characterization: The maximum absorption of TPMC-modified ZnS nanoparticles was observed by UV-Vis spectra on a Shimadzu 1800 spectrometer using a 1 cm quartz cell. Chemical structure of the TPMC-modified ZnS nanoparticles was characterized using an Alpha Bruker FT-IR spectrophotometer (KBr pellets) in the range of 4000–400 cm^{-1} at room temperature. The crystallinity and phase content were studied using an XRD machine (GNR APD-2000 PRO) and Cu-*K*α radiation. The XRD data obtained from 2θ ranges from 2 to 60º with a sample step size of 0.02º and a sample count time of λ of 2s. TEM images measured the nanosize and morphology were examined using a LEO 906 (Zeiss, Germany) operating at 80 kV. The size of ZnS nanoparticles incorporating TPMC polymer was investigated. The photoluminescence (PL) spectrometry was used to recorded the PL emission spectra (model: Horiba Jobin Yyon) FL spectrometer with dual grating excitation (450 W CW xenon lamp) and emission (1200 grooves/mm) monochromator. AFM study was performed using a SNOM/AFM device collected at ISM-CNR12. An air-based AFM and a conical quartz fiber probe are used.

RESULTS AND DISCUSSION

UV-Vis studies: Fig. 1 shows the UV-Vis absorption spectra of ZnS and TPMC-modified ZnS nanoparticles [36]. It is observed that the peaks appeared at 350 nm (3.8 eV) for the TPMC-coated ZnS nanocrystals and at 360 nm (3.6 eV) for the ZnS NPs, respectively. The absorption peak is strongly blue-shifted relative to the uncoated ZnS NPs, indi-

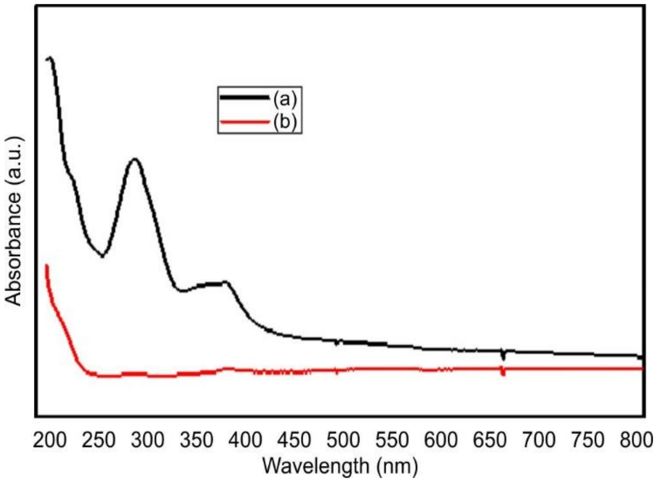

Fig. 1. UV spectra of (a) pure ZnS NPs (b) TPMC modified ZnS NPs

cating that the chitosan derivative. TPMC is attached to the ZnS surface. Modified ZnS NPs reduce the particle size edge absorption of blue-shifted nanocrystals and produce quantum confinement effects with zinc sulfide [7,8]. Absorption peaks of both surfaces modified and unmodified ZnS NPs seems to be at higher wavelength than bulk ZnS. Generally, a blue shift should be observed, which is due to the interaction of chitosan and 6-O-triphenylmethylchitosan.

FTIR studies: The development of ZnS NPs has revealed the modification of certain peaks in the lower region of FTIR spectra and it has confirmed the formation of nanoparticles. A characteristic peak appears at 570 cm^{-1}, indicating Zn-S stretching (Fig. 2a). The biopolymeric chitosan derivative peaks has been observed at 3410 cm^{-1}, 2820 cm^{-1}, 1640 cm^{-1}, 1350 cm^{-1}, 1125 cm^{-1} and 1060 cm^{-1} which is corresponds to amino (-NH$_2$), hydroxyl (-OH) overlapping groups, C=O-acetylated groups, modified CH$_3$ groups, elongated or bent (C-OH) groups. A new peak has been appeared at 565 cm^{-1} associated with the presence of zinc sulfide and a Zn-S stretch (Fig. 2b). The important shift of TPMC-modified ZnS NPs in the ZnS peak has been observed, which is due to the interaction of chitosan and ZnS NPs [1,25].

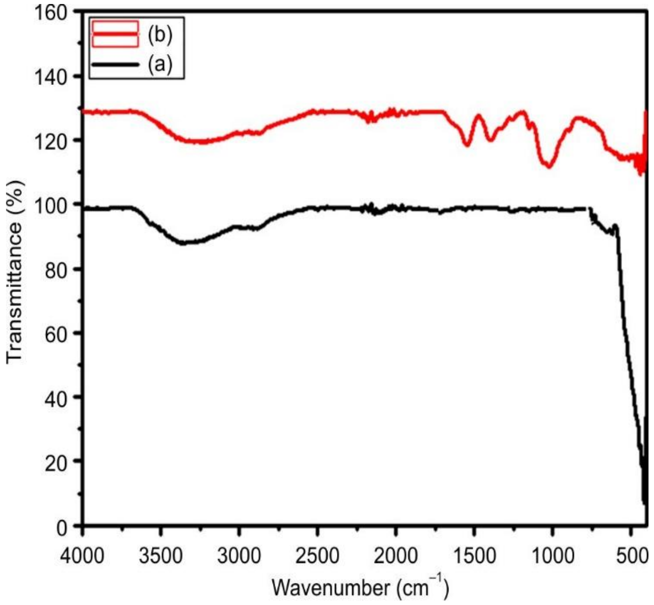

Fig. 2. FTIR spectra of (a) pure ZnS NPs (b) TPMC modified ZnS NPs

XRD studies: Fig. 3 shows the X-ray diffractogram of ZnS and TPMC-modified ZnS NPs. The diffraction peaks at 28.5º, 48º and 56.2º are associated with the [111], [220] and [311] lattice planes of zinc sulfide (ZnS) and assigned to the sphalerite structure of the ZnS NPs [32]. All diffraction peaks were agreed well with the standard (JCPDS No. 05-0566). A similar type of diffraction pattern has also been observed in ZnS-TPMC. However, the peak intensity of ZnS-TPMC has been decreased compared to ZnS alone. This is because of the crystallite size of surface-modified ZnS, which is reduced compared to ZnS NPs. The broadened peaks of both unmodified and TPMC-modified ZnS NPs were indicated the nano crystallinity [22,24]. Debye-Scherrer equation was used to determine the crystallite size, which was found to be 70 nm and 30 nm for ZnS and ZnS-TPMC, respectively.

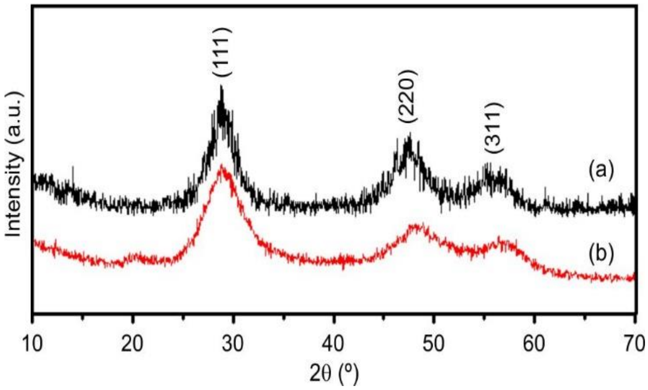

Fig. 3. XRD patterns of (a) ZnS NPs and (b) TPMC modified ZnS NPs

TEM studies: The TEM images of TPMC-modified ZnS NPs have been depicted in Fig. 4, which demonstrated the dispersion of ZnS NPs through a chitosan-derivative NPs matrix with low aggregation and uniform distribution of ZnS-TPMC nanostructures [33]. The TEM images of nanoparticles have shown the nano crystallinity with an average crystallite size of 3 nm which indicating the spherical shape of the crystalline particles (ZnS). SAED image patterns of transparent rings has been associated with the [111], [220] and [311] crystal planes of zinc sulfide, which observe the nanoscale XRD patterns [26,30].

AFM studies: The AFM images was used to observe the surface morphology unmodified ZnS and ZnS-TPMC NPs and it has helped to confirm the spherical particle sizes between 80 and 120 nm (Fig. 5a-b). TPMC has been reported to play a significant role in controlling the shape and size of ZnS NPs, by acting as a stabilizing and capping agent during the synthesis process. This influence helps achieve uniform particle morphology and narrow size distribution, which are critical parameters for optimizing the optical and functional properties of ZnS NPs [29,37-39].

Photoluminescence (PL) studies: Fig. 6 show that the surface of the produced ZnS incorporated in the TPMC composite has been investigated by PL technique. ZnS NPs modified with functionalized chitosan exhibited PL emission at 450 nm under 350 nm excitation, attributed to surface states or deep-level defects influenced by the surface modification of modified chitosan [3,35,40]. TPMC-modified ZnS has been observed near the conduction band and valence band formation of investigated sulfur [23,40].

Conclusion

The prepared biopolymeric ZnS nanocomposite using 6-O-triphenylmethylchitosan (TMPC) exhibited excellent photoluminescent behaviour. X-ray diffraction analysis revealed a crystallite size of approximately 30 nm, confirming the formation of a sphalerite cubic structure. UV-Vis absorption studies showed a significant blue shift for the TPMC-coated ZnS nanocrystals compared to unmodified ZnS, indicating successful coating with TPMC. AFM analysis demonstrated that the spherical nanoparticles ranged from 80 to 120 nm in size and were uniformly distributed. Photoluminescence emission was observed at 450 nm upon excitation at 350 nm. These chitosan-modified ZnS nanoparticles hold promising potential for applications across various fields.

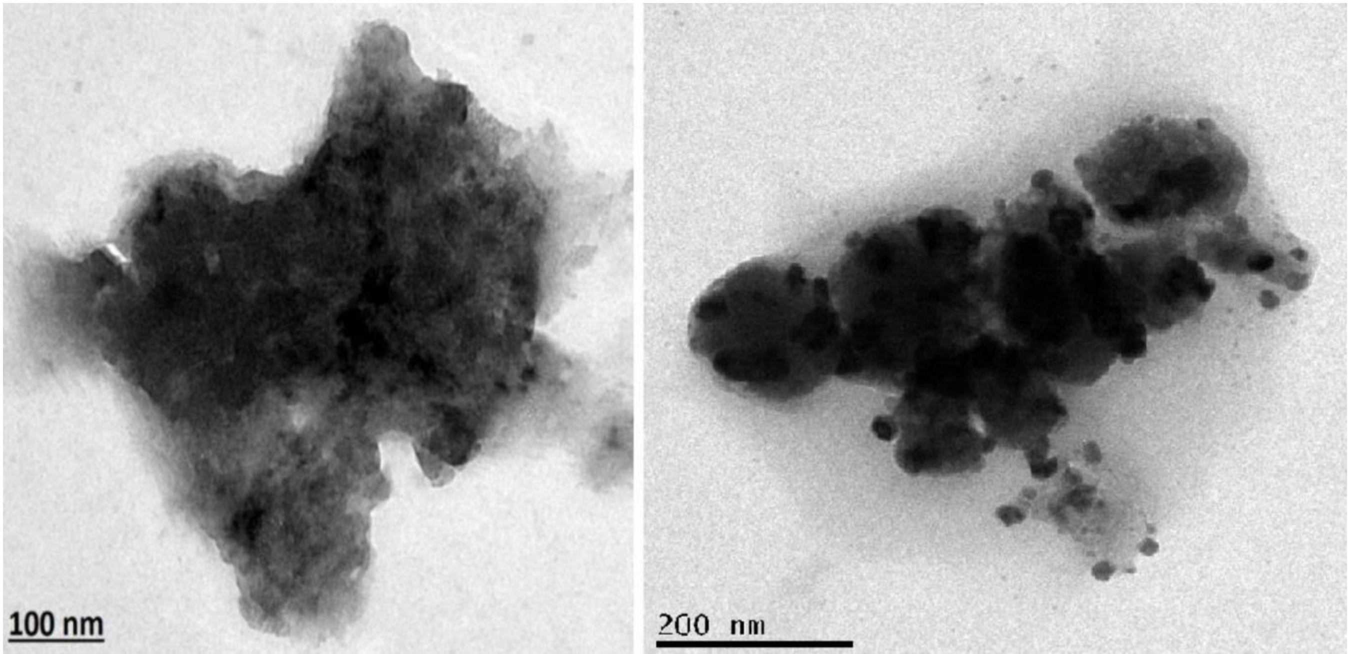

Fig. 4. TEM images of TPMC modified ZnS nanoparticles

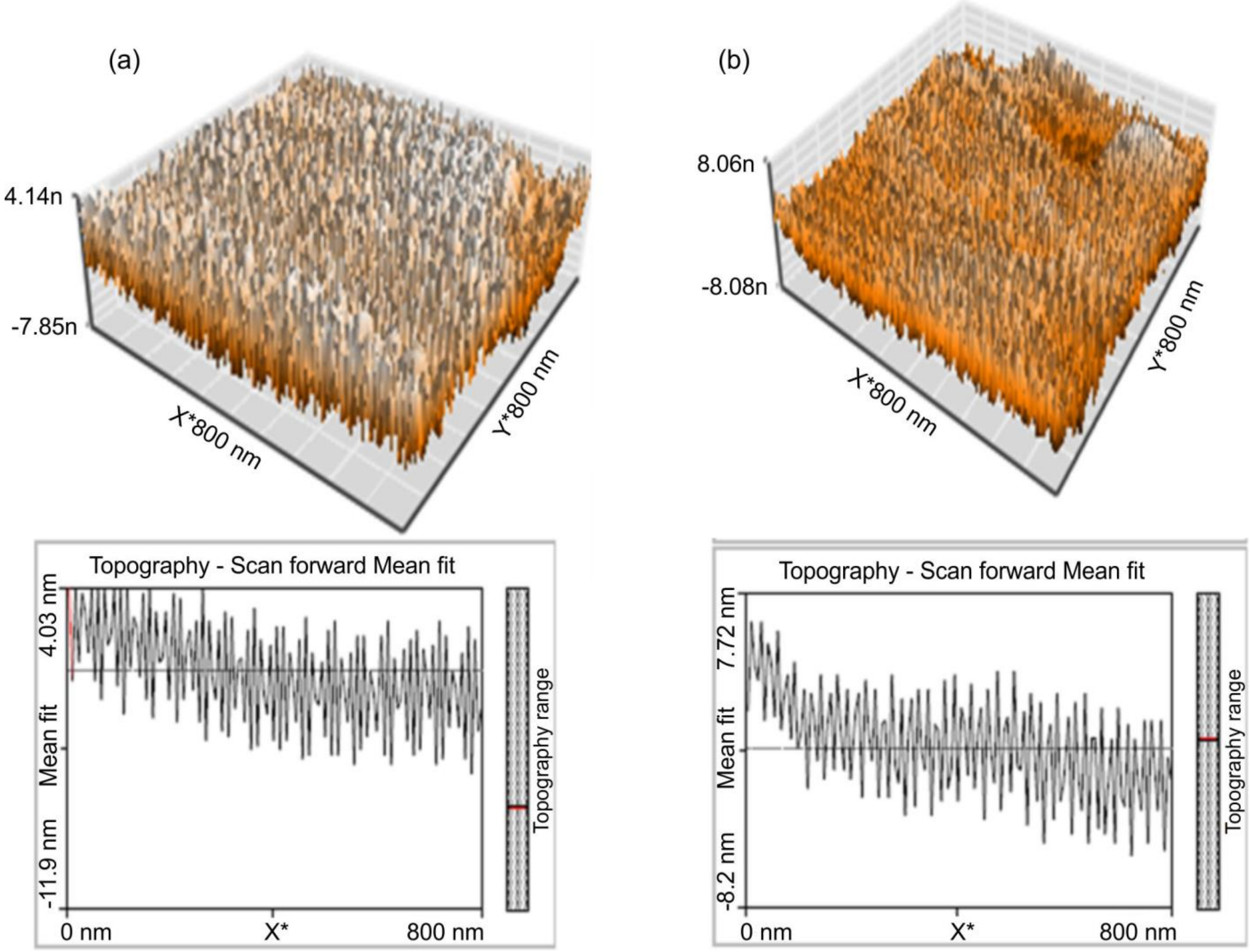

Fig. 5. AFM patterns of (a) ZnS nanoparticles and (b) TPMC modified ZnS nanoparticles

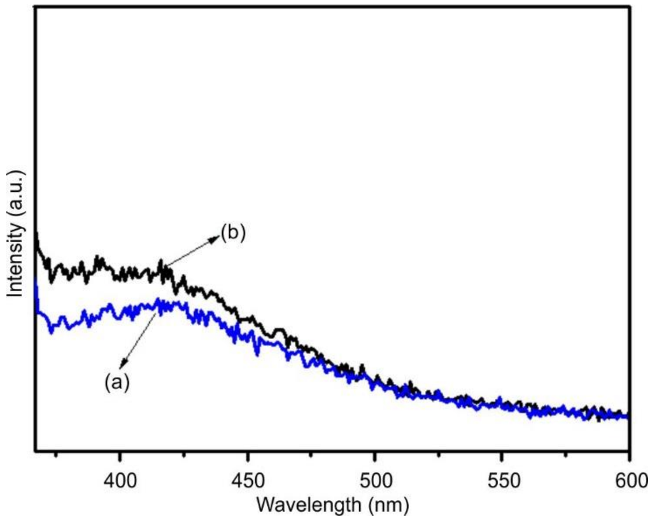

Fig. 6. PL spectra for (a) ZnS NPs and (b) TPMC modified ZnS NPs

CONFLICT OF INTEREST

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

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