ZnS:Mn²⁺ Phosphors Capped with Chitosan

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Luminescent II-VI semiconductor like ZnS, CdS, CdSe nanocrystals have attracted a lot of attention in the past two decades due to their unique properties and potential applications in electronics, lighting industry, military and medical fields. Controlling crystallite size and/or doping with luminescent ionic centers can tailor the optical properties of the nanocrystals. Cadmium Selenide (CdSe) quantum particles are today the standard dots for most biolabeling applications involving luminescent tagging. Unfortunately, these quantum dots are not very efficient for electromagnetic or electrical energy conversion into photons of visible light due to the 'unsaturated bonds' on their surfaces providing trapping centers for non-radiative recombination processes to take place. To avoid this drawback for converting the quantum dot into an efficient light emitter, the energy traps on its surface is generally eliminated by growing a thin shell of zinc sulphide (ZnS) around the core quantum dots of CdSe. Not only does this increases the quantum efficiency but also avoids the direct exposure to cadmium or selenium atoms, that are toxic.

In the present work, we introduced a novel biocompatible passivation layer 'Chitosan' on the ZnS nanophosphors, which showed an interesting enhancement in the luminescence efficiency compared to other passivative agents that were generally used in this literature. The nanophosphors were doped with Mn²⁺ ions in order to exhibit orange color when exited with UV light. The synthesis of particles in a solution occurs by chemical reactions resulting in the formation of nuclei and subsequent particle growth. The inorganic wet chemical synthesis used to prepare ZnS:Mn²⁺ nanocrystals is similar to that described in the literature [1] except that synthesis was carried out in water because of its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at room temperature and under ambient conditions. Scanning electron microscopy (SEM) images reveal that the particles have smooth surfaces due to the surface passivation by chitosan roughly around 30 nm in size (figure 1). High Resolution Transmission Electron Microscopy (HRTEM) analysis reveals that the 30nm agglomerates are polycrystalline with distinct grain boundaries (figure 2) with average crystallite sizes of 2.5 nm. This is consistent with the estimation of the crystallite sizes from X-ray diffraction (XRD) analysis that leads to an average crystallite size of 2.2nm. FTIR spectra of chitosan-passivated nanoparticles show strong absorption at 1547 cm⁻¹ and weak one at 642 cm⁻¹. This confirms that amide group is attached to the particles and functionalisation of the particle surfaces with the amide groups will allow surface modifications of the nanoparticles using simple chemical routes. It was found that the chitosan-capped nanoparticles consisted of higher density of crystallites than

other capping agents. This leads to a higher luminescence efficiency of the chitosan-capped $ZnS:Mn^{2+}$ nanoparticles.

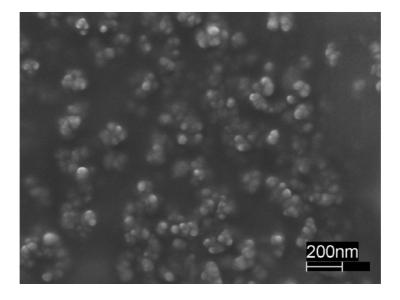


Fig. 1. Scanning electron micrograph of ZnS:Mn²⁺ nanoparticles showing the average agglomerate sizes of around 30 nm.

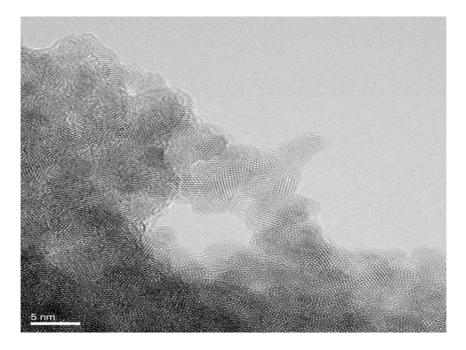


Fig. 2. High Resolution Transmission Electron Micrograph showing individual grain boundaries between 3-5 nm crystallites.

References

[1]. I.Yu, T. Isobe and M.Senna, J.Phys. Chem. Solids, **57** (1996) 373.