



Synthesis and Characterization of Transparent Luminescent ZnS:Mn/PMMA Nanocomposites



¹Marta Dai Prè, ¹Moreno Brugnotta, ¹Alessandro Martucci, ²Joao Antonio S. Bomfim

¹INFM and Dipartimento di Ingegneria Meccanica - Settore Materiali, Università di Padova, Via Marzolo 9, 35131 Padova, Italy

²Centro Ricerche Plast-Optica, Via Jacopo Linussio 1 - 33020 Amaro (UD) - Italy

Abstract: ZnS is a semiconductor ($E_g \sim 3.6$ eV) commercially used as phosphor and as electroluminescent material, especially if doped with Mn^{2+} . Here we describe the integration of manganese-doped ZnS nanoparticles (ZnS:Mn) into transparent PMMA (polymethylmethacrylate) using an in situ polymerization approach. In the first step stable ZnS:Mn nanoparticle (NP) dispersions are prepared and capped with acrylic acid. In the second step the NPs are mixed with MMA and bulk nanocomposites are obtained by radical polymerization.

Synthesis of ZnS nanoparticles

Zinc acetate dihydrate (methanol media) solution was mixed with varying concentrations of manganese acetate tetrahydrate with constant magnetic stirring.

An aqueous solution of sodium sulfide was added with vigorous stirring, immediately resulting in the formation of a precipitate that was separated by centrifugation and washed several times with methanol. The white powder was redispersed in acrylic acid and heated at 90°C in air, turning into a visually transparent and colorless dispersion.

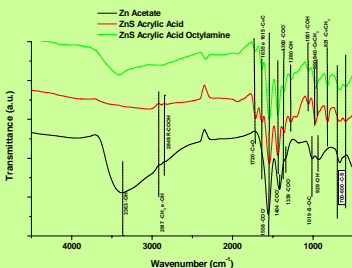
Among the several experiments with varying composition and reactant ratios we performed, best results are obtained for Zn/S=2 and 0.3M Zn when dispersion stability and concentration are considered.

Characterization of NP

1. FTIR characterization

The FTIR spectra of the as-synthesized NPs confirm the presence of residual acetate anions.

After the addition of acrylic acid and multiple washing, the presence of acrylic groups bound to the ZnS NPs is also detected.



2. Optical characterization

Figure 1 shows the UV-VIS absorption spectra obtained by mixing 5 µl of NPs stabilized with acrylic acid in 3 cc of chloroform. In the solutions containing the NPs it can be seen an absorption shoulder onset around 290 nm. This absorption is blue-shifted with respect to the bulk ZnS bulk absorption (330 nm) and it is due to the quantum size effect because the obtained crystals are in the nanometer range. The Mn content has been optimized for getting the highest luminescent intensity. Emission intensity is the highest for 5mol% incorporation, which was chosen as the standard doping level of the ZnS NPs. Figure 2 shows the room temperature photoluminescence spectra of the ZnS:Mn NPs measured with 285 nm excitation wavelength. Photoluminescence for the un-doped ZnS nanoparticles showed two emission bands, one blue emission at ~420 nm and another yellowish green band at 575 nm (fig.3). The Mn doped NPs showed an orange emission around 582 nm (fig.3) that can be attributed to the Mn^{2+} impurity. The intensity of the orange emission (~592 nm) first increased and then decreased with the increase of Mn concentrations (fig.4).

Figure 1: Absorption spectra of ZnS:Mn NPs with different content of Mn dispersed in chloroform

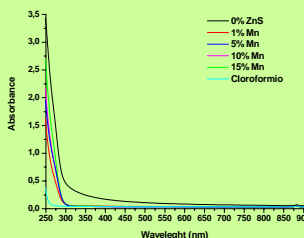
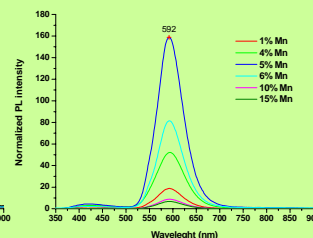
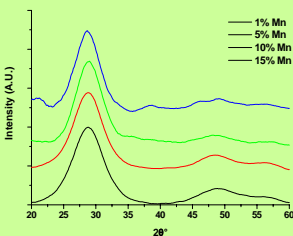


Figure 2: PL spectra of ZnS NPs doped with different content of Mn.

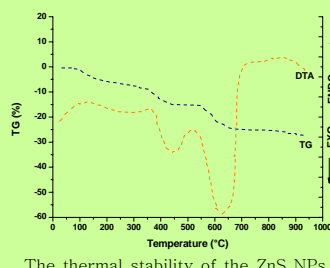


3. XRD characterization of powders



XRD spectra of ZnS NPs doped with different content of Mn. The diffraction peaks correspond to the cubic ZnS phase. The structure remains almost unchanged up to 5% Mn doping. The evaluated mean crystallite size (Scherrer) is 4 ± 1.0 nm.

4. DTA/TG characterization



The thermal stability of the ZnS NPs (doped and undoped) has been studied by DTA-TGA. ZnS NPs oxidize above 500° C forming ZnO.

Figure 3: PL spectra of ZnS NPs un-doped and doped with Mn.

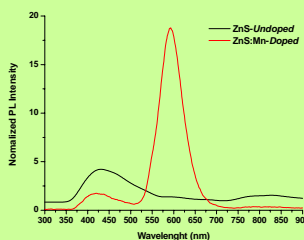
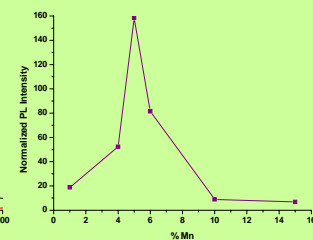
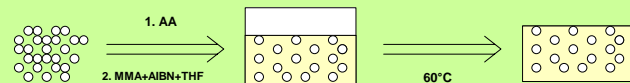


Figure 4: PL intensity vs. at % of Mn.

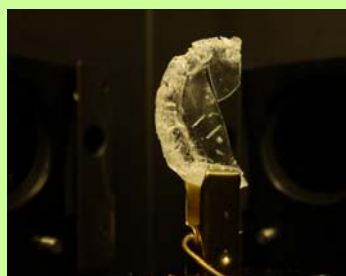


Nanocomposite polymeric material

The surface of ZnS:Mn NPs has been functionalized with acrylic acid and octylamine in order to achieve a stable dispersion of NPs in acrylic copolymers. NPs were then resuspended in a mixture of THF and methyl methacrylate (MMA) and polymerized at 60°C after the addition of a radical initiator. Drying was carried out at room temperature to result in a transparent bulk nanocomposite with varying ZnS:Mn %wt content. Concentration up to 10 wt% has been obtained.



The ZnS:Mn/PMMA nanocomposite is transparent (left), but shows the orange luminescence of the Mn-doped nanoparticles when irradiated with UV light (285 nm).



Conclusions

ZnS NPs doped with Mn^{2+} ions have been synthesized by colloidal chemistry. The developed synthesis permits to obtain high volumes of NPs at room temperature. The surface of the NPs has been functionalized with acrylic acid and octylamine for doping in PMMA. The functionalized NPs have been mixed with MMA and polymerized using a thermally-activated radical initiator. The obtained nanocomposites are transparent and show orange luminescence when irradiated with UV light.



PROJECT COORDINATOR: [Eranno Rasello](mailto:Eranno.Rasello@integrale.it)
INTEGRA Renewable Energies Srl
via dei Missaglia 97, 20142 Milan (Italy)
Tel +39 3921521478 - Fax +39 0289307067
E-mail: r.erasello@integrale.it

TECHNICAL MANAGEMENT: [Sara Padovani](mailto:Sara.Padovani@crp.crf.it)
Centro Ricerche Plast-optica SpA
via J. Linussio 1, 33020 Amaro (Italy)
Tel +39 0433487522 - Fax +39 0433 487555
E-mail: sara.padovani@crp.crf.it

PROJECT OFFICER: [Federica Roffi](mailto:Federica.Roffi@ec.europa.eu)
European Commission
De Meeus Square 8, 1050 Brussels
(Belgium)
Tel +32 2 2954721 - Fax +32 2 2963261
E-mail: federica.roffi@ec.europa.eu