Multifunctional ZnS:Mn/$NaGdF_4$:Yb:Er nanostructure for multimodal bio-imaging

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1. Introduction

Inorganic luminescent nanostructures have gained much attention of biomedical researcher.[1] Binary semiconductor quantum dots were widely considered as an efficient down conversion luminescent probes for bio-imaging due to their better luminescence properties. Fluoride based up-conversion nanoparticles were widely investigated for bio-imaging application due to their better physical and chemical properties. Previous researchers attempted to synthesize composite nanostructures using separately synthesized ZnS:Mn and $NaGdF_4$:Yb:Er (NGF:Yb:Er) particles assembled in different matrix. [2] In present work, we have attempted to synthesize ZnS:Mn/$NaGdF_4$:Yb:Er (ZnS:Mn/NGF:Yb:Er) nanocomposite by single step hot injection method.

2. Synthesis of ZnS:Mn/NGF:Yb:Er nanocomposite

Starting materials like acetates of Zn and Mn along with elemental sulfur were dissolved in 15 mL oleylamine solvent in a three-neck flask. The mixture was degassed at 160 °C under vacuum for 30 min. After degassing, the flask was filled with N_2 gas and further heated to 280 °C for 60 min. Meanwhile, Trifluoroacetates of sodium, gadolinium, ytterbium and erbium were mixed together in 5 mL of oleylamine in a separate three-neck flask. The mixture was degassed at 160 °C under vacuum. Degassed solution was loaded to a glass syringe and injected into the ZnS:Mn particle containing flask at 280 °C and was maintained for 2 h. The resultant mixture was cooled to 80 °C and washed with ethanol.

3. Result and discussion

Powder XRD

Acquired XRD reflections of ZnS:Mn/ NGF:Yb:Er were indexed to the hexagonal $NaGdF_4$ (JCPDS No. 27-0699) and ZnS (JCPDS No. 01-0792). Obtained peaks of ZnS:Mn in the composite shows sharp reflections. No diffraction peaks related to any other phases or impurities were observed.

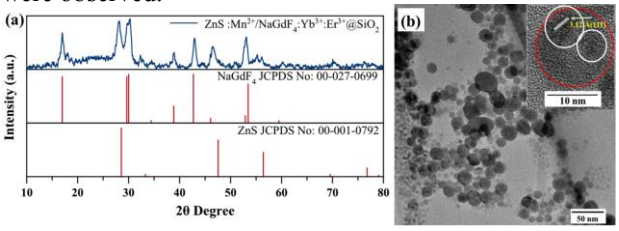

Figure 1. (a) XRD pattern (b) TEM and HRTEM of ZnS:Mn/NGF:Yb:Er nanocomposite

TEM analysis

Synthesized nanoparticles appeared as bulged sphere-like shape with different sizes (Figure 1(b)). Hybrid nature of ZnS:Mn/NGF:Yb:Er particles was realized in the HR-TEM (Figure 1 (b) onset) images. Crystalline planes of ZnS (111) were clearly observed (3.12 Å)

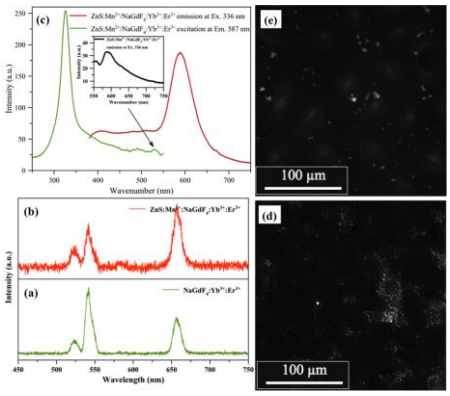

Figure 2. Upconversion luminescence of NGF:Yb:Er (a), ZnS:Mn/NGF:Yb:Er (b), downconversion luminescence of ZnS:Mn/NGF:Yb:Er (c) corresponding upconversion (d) and down conversion optical bioimage (e)

Luminescence and bio-imaging

The emission spectra of ZnS:Mn/NGF:Yb:Er was compared with NGF:Yb:Er to identify the emission difference in presence of ZnS:Mn particles under 980 nm (Figure 2 (a,b)). In vitro up-conversion luminescence (970 nm excitation) imaging of cultured HeLa cells incubated with ZnS:Mn/NGF:Yb:Er nano composite were examined using lab made optical setup. Clear emission signals from HeLa cells incubated with ZnS:Mn/NGF:Yb:Er was observed upon 970 nm excitation in the HeLa cells region. Down-conversion imaging process was observed under 365 nm excitation.

3. Conclusions

Acquired bio-imaging results show that the multi-modal luminescence ability of ZnS:Mn/NGF:Yb:Er synthesized nanocomposite is fit with the up-conversion as well as down-conversion imaging.

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References

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