NANOMATERIALS FOR LUMINESCENCE AND HYPERTHERMIA APPLICATIONS

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Abstract

SnO$_2$, ZnO, YPO$_4$, YVO$_4$ and CaMoO$_4$ nanoparticles show the luminescence in violet-blue to green region. When rare-earth ions (RE$^{3+}$) are doped into the above hosts, an improvement of luminescence is observed due to energy transfer from host/sensitizer to RE$^{3+}$. In hexagonal phase of YPO$_4$:(Eu$^{3+}$, Ce$^{3+}$/Bi$^{3+}$), water molecules remain within the pores extending along the c-axis and such water molecules are stable up to 800 °C and do not freeze at -50°C. Switching on and off of luminescence are performed through redox reaction in La/GdPO$_4$: (Tb$^{3+}$, Ce$^{3+}$). Again, functionalized Fe$_3$O$_4$ superparamagnetic ferrofluids prepared by chemical route show the heating behaviour up to the hyperthermia temperature (42 °C) under AC magnetic field. 1 mg of oleic acid (OA) coated Fe$_3$O$_4$ nanoparticles shows high cytotoxicity (70%) in cancer cells (1 million) under AC magnetic field.

Introduction

Nanomaterials are those materials in which at least one side of the constituent particles lies in between 1-100 nm (1 nm = 10$^{-9}$ m = 0.1 Å). Since size is so small, surface to volume atomic ratio in a particle is high and thus, it possesses excess energy as compared to bulk and naked eye cannot see extremely small particles. Here, bulk means material, which has large particle size (D > 500 nm). This can be confirmed by Mössbauer, electron microscopy, atomic force microscopy (AFM), scanning transmission electron microscopy (STEM) and calorimetric studies. With decrease in particle size, the followings are observed: quantum size effect on optical properties of semiconductors, ferromagnetic to superparamagnetic transition in magnetic material, increase of electrical resistivity or metallic to disorder/semiconducting, change in the optical and acoustic phonons, extreme hardness or change in mechanical strength, change in thermal conductivity, increase in active sites in catalysis, etc. [1]. This suggests the change in intrinsic properties of materials with decrease of particle size or reduced dimensions as compared to bulk. Materials will be of metals, alloys, oxides, sulfides, nitrides, carbides and borides, etc. However, the materials useful in society will be great important. In such situation, we have to choose materials so that it has high impact to society. Usefulness of nanomaterials in basic sciences (biology, chemistry, physics, materials science and engineering) and their applications brought nanoscience and nanotechnology. Manipulation and engineering of such small particles will help in generation of fuel, display devices, tissue engineering, bio-separation, health care sector, cancer therapy, diagnosis and advanced nuclear reactors, etc. in economic ways. In my opinion, nanotechnology has merits and demerits in our society depending on ways of uses though this brought the revolution in sciences. However, we have to think security, safety and future consequences of this revolution. In fact, nanomaterials should be used under a frame work governed by ethics and law in order to maintain sustainable environment.
In this article, I present a few examples of nanomaterials, which are useful in luminescence devices and hyperthermia based cancer therapy and nanomaterials are prepared in the laboratory of Chemistry Division, BARC.

**Luminescence Devices**

Over the last decade, the semiconducting nanomaterials such as SnO$_2$, TiO$_2$, SnO$_2$-TiO$_2$, ZnO, A$_2$O$_3$ (A = Y, Gd, La), AVO$_4$, APO$_4$, CaMoO$_4$, and their compounds with rare earth ions (RE$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$, Tb$^{3+}$, Sm$^{3+}$) were prepared by chemical routes [2, 3]. These particles can produce emission in UV, visible and NIR regions (Fig. 1). Improvement in luminescence was found by the following: (a) energy transfer from host to RE$^{3+}$, (b) core-shell model, (b) dispersion in another dielectric medium, (c) removal of quencher, (d) heating, (f) co-doping with Li$^+$, Bi$^{3+}$ or sensitizer, which either enhance absorption cross-section or overlapping of the emission band of the sensitizer or host with absorption band of activators. Quantum size effect in optical study of ZnO and PbSe was

![Fig. 1: Photographs of GdVO$_4$:RE after UV excitation: (a) dispersed particles and (b) films [2].](image)

**Confined Water**

![Fig. 2: Types of hydrogen bonding when (1) salt is added to water, (2) water is contacted with hydrophilic (A) and hydrophobic (B) surfaces, (3) water is in different confined regions.](image)
observed. It suggests the red shift in absorption/emission peak with increase of particle size. Switching on and off of luminescence was performed in Ce\textsuperscript{3+} co-doped LaPO\textsubscript{4}:Tb\textsuperscript{3+} and GdPO\textsubscript{4}:Tb\textsuperscript{3+} through redox reactions [3].

For the first time, the free water on the surface of particles and confined water in the pores or interstitial water in the hexagonal structure of orthophosphate (REPO\textsubscript{4}) were confirmed using NMR technique [4]. There are different types of hydrogen bonding present in water depending on container/interface/region (Fig. 2). This finding will be useful in production of water molecules from 10 to 10\textsuperscript{10} in a particle under controlled NIR/microwave excitation. Also, this concept will be useful in biological system, therapy, micro-chips, etc. in which limited water molecules are needed. Luminescence quenching in such hexagonal REPO\textsubscript{4} phase was observed and this is due to content of confined water, which is near to metal ion (Y\textsuperscript{3+}/Bi\textsuperscript{3+}/Eu\textsuperscript{3+}) and far from PO\textsubscript{4} group. This confined water is not frozen even at -50 °C due to less number of H-bonding. In such system, the water molecules are stable up to 800 °C [5, 6]. The REPO\textsubscript{4} compounds are available in rocks. This finding will give an alternative evidence for possibility of water present in rocks available in many planets, where temperature level goes up to 800 °C.

Hyperthermia based Cancer Therapy

Magnetic nanoparticles (MN) of Fe\textsubscript{3}O\textsubscript{4}, CoFe\textsubscript{2}O\textsubscript{4}, NiFe\textsubscript{2}O\textsubscript{4}, Co-Fe-B, FePd, Co and Ni were prepared by chemical routes. These were tested for heating behaviour under AC magnetic field (265 kHz frequency, 80-400 Oe field). Fe\textsubscript{3}O\textsubscript{4} coated with polyethylene glycol (PEG) were incorporated into thermally sensitive liposome. 6-carboxy fluorescein (CF) was used as indicator. The enhanced release of CF in presence of magnetic nanoparticles at 42 °C was found. Fe\textsubscript{3}O\textsubscript{4} MN coated with PEG and oleic acid were tested in a human breast cancer cell line (MCF7) [1,7]. Killing of cancer cells was found up to 70% within 10 minutes for oleic acid (OA) coated MN (Fig. 3). Bi-functional properties of MN-Luminescence (Fe\textsubscript{3}O\textsubscript{4}-YPO\textsubscript{4}:Eu) having very high specific absorption rate (SAR = 100%) and red emitter at 615 and 695 nm nm, which is in range of biological window were tested in mouse fibrosarcoma (Wehi 164) tumor cells by Prussian blue staining. The intra-cellular uptake of MN was observed. In order to perform site selective of cancer cells (including metastability), some new approaches are under process. Now, in vivo study in mice...
study shows significant decrease of tumour size within 8 days in the presence AC magnetic field when MN were incorporated in mice (Fig. 4). This study will be useful in clinical trials.

Note

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