

Magnetic and luminescent multifunctional nanohybrid: $\text{Fe}_3\text{O}_4@ \text{CaF}_2:\text{Tb}^{3+}$: A facile synthesis and characterization

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In the present study, bi-functional hybrid nanomaterial has been synthesized and characterized via facile method and characterized. The synthesized nanomaterial shows both magnetic and luminescent properties which are confirmed by VSM (vibrating sample magnetometer), UV-Vis spectra and the photoluminescence emission spectra. For the magnetic phase, i.e., nanocrystalline magnetite, Fe_3O_4 is used as the core which is then functionalized using polyethylene glycol (PEG) and for the luminescent phase, polyethylenimine (PEI) functionalized CaF_2 doped with Tb^{3+} is used as the emitter. Wherein, both PEG and PEI serve the dual purpose of functionalization as well as stabilization by steric repulsion. The structure and morphology of the synthesized bifunctional hybrid nanomaterial are studied with the help of scanning electron microscopy (SEM) and X-ray powder diffraction.

Keywords: Magnetic nanoparticles, Luminescent nanoparticle, Nanohybrid, Fe_3O_4 , CaF_2 , Tb^{3+} doping, Biocompatible, Co-precipitation

1 Introduction

Nanoparticles (NPs) are submicron moieties (1 to 100 nm) made up of inorganic or organic materials, which depict several novel properties when compared with the bulk materials. Magnetic nanoparticles are the nanostructured materials of current interest, due to their use in advance technology, bio-compatibility and medical applications. The magnetic NPs show unique properties such as superparamagnetic property, high coercivity, low Curie temperature, high magnetic susceptibility, etc. Among the various magnetic nanomaterials, magnetite (Fe_3O_4) nanoparticles have been extensively studied¹ due to their broad range of applications like magnetic fluids, data storage, catalysis and bio-applications². The super paramagnetic magnetite (Fe_3O_4) nanoparticles have different striking features, including ease of synthesis, chemical stability, narrow size distribution, and high dispersibility in various solvents²⁻⁴. In addition, Fe_3O_4 NPs also exhibit high biocompatibility^{5,6}. The magnetic NPs can be functionalized with luminescent nanoparticle phase giving a hybrid nanomaterial which has both the properties of a magnetic NPs and luminescent NPs. Furthermore, with an eye on possibly altering the structure and properties of the parent nanoparticles and creating multifunctional materials,

doping of magnetite nanoparticles with other metal ions has been explored⁷⁻⁹. The inorganic luminescent materials based on rare earth ions have been generally utilized for preparation such nano-hybrids due to their higher optical properties, such as high quantum yield, long lived emission, narrow bandwidth, and large stokes shift. These characteristics of dual nano-hybrids make them fit for biological applications such as magnetic bio-separation, detection of biological entities (cell, protein, nucleic acids, enzyme, bacteria, virus, etc.), magnetic resonance imaging (MRI), magnetic fluid hyperthermia (MFH) and targeted drug delivery¹⁰⁻¹². The luminescent phase NPs (organic compounds, polymers, quantum dots and rare earth-based) binds with microorganisms, antibodies, antigens, polypeptides or tumor tissue^{13,14}, resulting in a bio-complex which can be easily detected on irradiation with UV or NIR radiations. These nano-materials have been reported to enhance drug delivery¹⁵. For non-radiative relaxation in the luminescence, Ln^{3+} ions have been utilized due to their appropriate lattice¹⁶. The fluorides, has low phonon energy, high transparency and thus, serve as perfect host materials among the inorganic matrices. Moreover, CaF_2 has been reported as an ideal host matrix as it shows optically isotropic structure, high stability, non-hygroscopic behavior, non-toxicity and biocompatibility of among all the other fluorides make it¹⁷. Nanohybrid structures with

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suitable dual or multifunctional properties have potential to display various applications in biology, biochemistry, pharmacy, industry, medicine and optoelectronics and lightening¹⁸.

Both the magnetic core and the luminescent phase must be biocompatible to yield a nanohybrid is also bio-compatible product. The magnetic phase Fe_3O_4 has been reported as biocompatible¹⁹ and as well as the luminescent phase Tb^{3+} doped CaF_2 has been said to have non-hygroscopic, non-toxicity and biocompatibility properties¹⁷. These modern biochemical and physicochemical approaches based on nanotechnology could be utilized to enhance the vital properties of these nanomaterials. However, it is important to select the materials for the fabrication of nanostructure and devices with controllable physical and chemical properties.

As mentioned above the biocompatibility aspect must be considered in choosing the luminescent phase as well magnetic phase. Hence, a properly functionalized magnetic core is made to form a core shell with the luminescent phase, which can be designed by functionalizing Fe_3O_4 with PEG and adding this magnetic core during the synthesis of Tb^{3+} doped CaF_2 via co-precipitation method. The method opted here gives biocompatible multifunctional nanohybrid that shows both magnetic property and luminescent property owing to its magnetic core and the luminescent phase, respectively. Here we discuss the synthesis of a multi-functional nanohybrid wherein the magnetic phase is synthesized, i.e., nano-crystalline magnetite, Fe_3O_4 and is used as the core which was then functionalized using polyethyleneglycol (PEG). The luminescent phase is polyethylenimine (PEI) functionalized CaF_2 doped with Tb^{3+} as the emitter. Wherein, both PEG and PEI serve the dual purpose of functionalization as well as stabilization by steric repulsion. The Tb^{3+} doped hybrid of polyethylene glycol (PEG) functionalized Fe_3O_4 and polyethylenimine (PEI) functionalized CaF_2 [$\text{Fe}_3\text{O}_4@ \text{CaF}_2:\text{Tb}^{3+}$] NPs have been synthesized, characterized and studied in this work.

2 Experimental Details

2.1 Chemicals and solvents used

Ferrous sulphate exsiccated (dried) extra pure, ($\text{FeSO}_4 \cdot \text{ca.}1.5\text{H}_2\text{O}$), iron (III) chloride (anhydrous purified) and ammonia solution (25 %) are purchased from Merck. The chemicals, calcium chloride (anhydrous, granular), poly (ethylene glycol), ammonium fluoride (ASC reagent), polyethylenimine

(branched), terbium (III) nitrate penta hydrate are purchased from Sigma-Aldrich, whereas, ethanol (AR 99.9 %) is purchased from Changshu Hongsheng Fine Chemicals Co Ltd. All chemicals are used without any further purification(s).

2.2 Method of preparation

The facile synthesis of the Fe_3O_4 NPs and CaF_2 NPs are adopted and the biocompatibility of the final hybrid product opens up to a wide range of applications.

2.2.1 Synthesis of PEG functionalized Fe_3O_4

Fe_3O_4 is prepared via a simple co-precipitation method⁷ at a moderate temperature of 50 °C. 0.3259 g of FeCl_3 is dissolved in 10 mL distilled water and 0.1528 g of FeSO_4 dissolved in 10 mL distilled water which is added to the previous solution (so that the amount of Fe^{3+} and Fe^{2+} are in the ratio of 2:1) in a round bottom flask and stirred for homogenization under N_2 atmosphere, followed by addition of 0.7 g PEG (in 5 mL distilled water) and stirred for 1 h at a temperature of 50 °C. Then, 40 mL distilled water is added to the RB and immediately 20 mL of 25 % NH_3 solution (black colored ppt of Fe_3O_4 is formed immediately after the addition of NH_3 solution) is added and stirred for another 1 h at 50 °C. The precipitate obtained is centrifugated and washed several times with water and ethanol to remove excess surfactants and ammonia. The black colored precipitate is collected and dried at room temperature and powdered after drying for characterization.

2.2.2 Synthesis of CaF_2 and Tb^{3+} doped CaF_2

0.4217 g of CaCl_2 is dissolved in 10 mL distilled water in a round bottom flask and added 0.0870 g of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (dissolved in 5 mL distilled water) and is stirred for 1 h under N_2 atmosphere for preparing 5 % doped material for preparation of CaF_2 . doping is not added The NH_4F solution (0.2963 g dissolved in 10 mL distilled water) dropwise added to the above reaction mixture and stirred for 2 h to obtain an opaque white suspension. The reaction mixture is then centrifuged to obtain the white precipitate of $\text{CaF}_2:\text{Tb}^{3+}$ which is then centrifuged, washed several times via with distilled water and ethanol, and finally dried at room temperature.

2.2.3 Synthesis of $\text{Fe}_3\text{O}_4@ \text{PEG}/\text{CaF}_2:\text{Tb}^{3+}$ hybrid

The magnetic and luminescent nanohybrid $\text{Fe}_3\text{O}_4@ \text{PEG}/\text{CaF}_2:\text{Tb}^{3+}$ is synthesized by a modified facile co-precipitation method. Wherein, the calcium

Table 1 – The amounts of various components for the synthesis of the nanohybrid

Sample name	Amount of Fe ₃ O ₄	Amount of CaCl ₂	Amount of NH ₄ F	Amount of Tb(NO ₃) ₃ .5H ₂ O	Doping percentage
Fe ₃ O ₄ @PEG/CaF ₂ :Tb ³⁺	0.11161 g	0.4217 g	0.2963 g	0.0870 g	5 %

precursor (CaCl₂ dissolved in distilled water) is mixed with a specific amount of the dopant, Tb(NO₃)₃.5H₂O and stirred for 1 h under nitrogen atmosphere followed by reduction by adding a certain amount of NH₄F dropwise and stirred for 2 h under nitrogen atmosphere, which gives the precipitate of CaF₂ followed by dropwise addition of water dispersed Fe₃O₄ and is stirred for another 1 h under nitrogen atmosphere at room temperature.

Here the ratio of the amount (in grams, Table 1) of Fe₃O₄ and all other components in hybrid material is 1:5 and the luminescent phase CaF₂ is functionalized with PEI (by adding 0.49 g of PEI after addition of Tb(NO₃)₃.5H₂O).

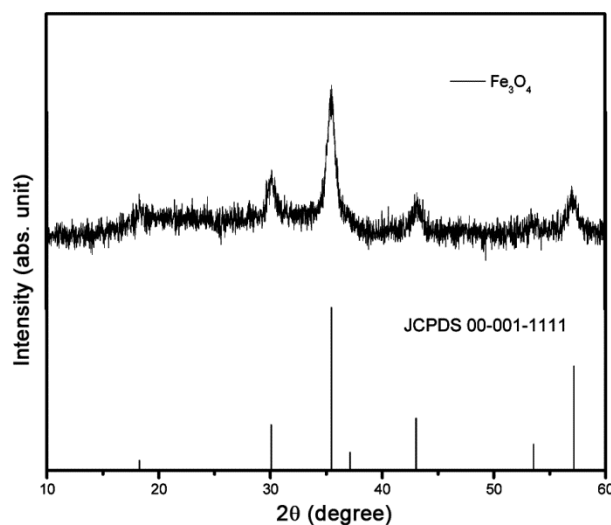
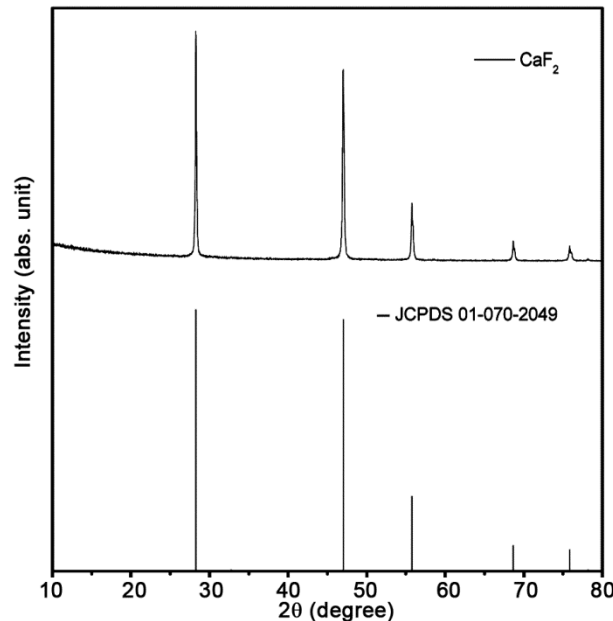
3 Results and Discussion

3.1 Powder-XRD analysis

The XRD patterns of Fe₃O₄ (functionalized with PEG), is shown in Fig. 1 and the diffraction peaks are in agreement with the standard values for cubic Fe₃O₄ (JCPDS Reference Code 00-001-1111) and Space group: Fd-3m (227). The XRD results indicate that the products obtained are Fe₃O₄ nanoparticles and Scherrer equation is used for calculating average size of the Fe₃O₄ NPs and is found to be ~14 nm. The XRD patterns of CaF₂ nanoparticles are shown in Fig. 2, and the diffraction peaks are in agreement with the standard values for cubic CaF₂ (JCPDS Reference Code 01-070-2049) Space group: Fm-3m (225). The XRD results indicate that the products obtained are CaF₂ nanoparticles and Scherrer equation is used for calculating average size of the CaF₂ NPs and is found to be ~29 nm. Figure 3 shows the XRD patterns of Fe₃O₄@ CaF₂:Tb³⁺ nanohybrid. The peaks shown in Fig. 3 clearly indicate that the hybrid have peaks corresponding to both the Fe₃O₄ and CaF₂.

3.2 Scanning electron microscope (SEM)

The morphology of synthesized multifunctional nanohybrid (Fe₃O₄@PEG/CaF₂:Tb³⁺) is studied by scanning electron microscope. From Fig. 4 it is evident that synthesized hybrid nanoparticles are nearly spherical in shape and size of particles are in the range from 10 to 50 nm with average particle size 30 nm, which supports the XRD results.

Fig 1 – X-ray diffraction pattern of Fe₃O₄ (functionalized with PEG) nanoparticles.Fig. 2 – X-ray diffraction pattern of CaF₂ nanoparticles.

3.3 UV-visible absorption spectra

UV visible absorption spectra for CaF₂ and CaF₂:Tb³⁺ dispersed in ethanol are recorded in alcohol dispersion. The peak (Fig. 5) at around 214 nm corresponds to (5 % Tb³⁺ doped) CaF₂:Tb³⁺ which is not observed in the case of pure CaF₂ indicating that this peak appears due to the dopant Tb³⁺ and thereby,

indicating the successful doping with the facile synthesis method mentioned above.

3.4 Photoluminescence spectra

The ideal excitation for Tb^{3+} was 220 nm which results in several emissive transitions. The obtained spectrum correlates well to the emissions for $^5D_4 \rightarrow ^7F_6$ (488 nm), $^5D_4 \rightarrow ^7F_5$ (541 nm), $^5D_4 \rightarrow ^7F_4$ (581 nm) and $^5D_4 \rightarrow ^7F_3$ (620 nm). The bands at 490 nm, 586 nm and

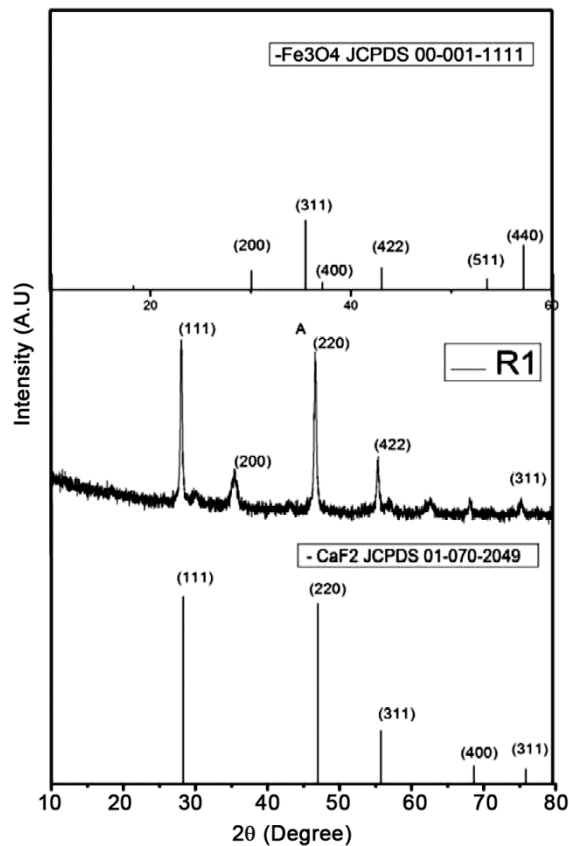


Fig. 3 – X-ray diffraction pattern of the multifunctional nanohybrid ($Fe_3O_4@PEG/CaF_2:Tb^{3+}$), sample R1 plotted with the standard X-ray diffraction pattern of Fe_3O_4 (JCPDS 00-001-1111) and CaF_2 (JCPDS 01-070-2049).

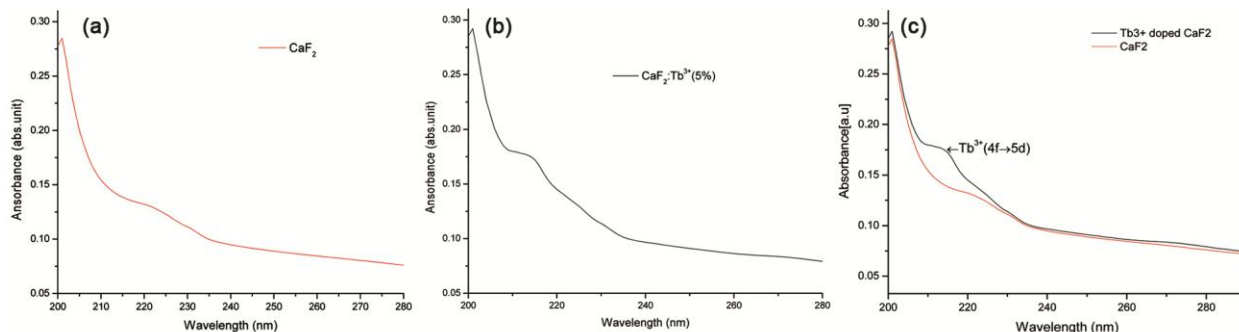


Fig. 5 – The UV-visible absorption spectra of (a) CaF_2 , (b) $CaF_2:Tb^{3+}$ (5 %) and (c) magnified UV-visible absorption spectra of CaF_2 and $CaF_2:Tb^{3+}$ (5 % doping), which shows a peak at 214 nm due to Tb^{3+} .

621 nm exhibit comparable intensity (the latter two peaks are not clearly distinguishable due to the broad emission band of the host CaF_2 around 575 nm to 625 nm) which are exceeded by the prominent transition at 544 nm (Fig. 6). The measured spectrum of the Tb^{3+} doped particles are in accordance to literature data²⁰. It is also seen that the intensity of the broad peak at 575 nm to 625 nm of the host CaF_2 decreases with the introduction of iron oxide NPs. Moreover, the introduction of iron oxide NPs in $CaF_2:Tb^{3+}$ lowers the intensity of the prominent peaks of Tb^{3+} , with the most intense peak at 544 nm.

3.5 Magnetic behaviour of Fe_3O_4 , $Fe_3O_4@CaF_2$ and $Fe_3O_4@CaF_2:Tb^{3+}$

The magnetic properties of the synthesized iron oxide containing NPs are studied via vibrating sample magnetometer (VSM) (Fig. 7). However, the magnitude of magnetization of the synthesized nano-

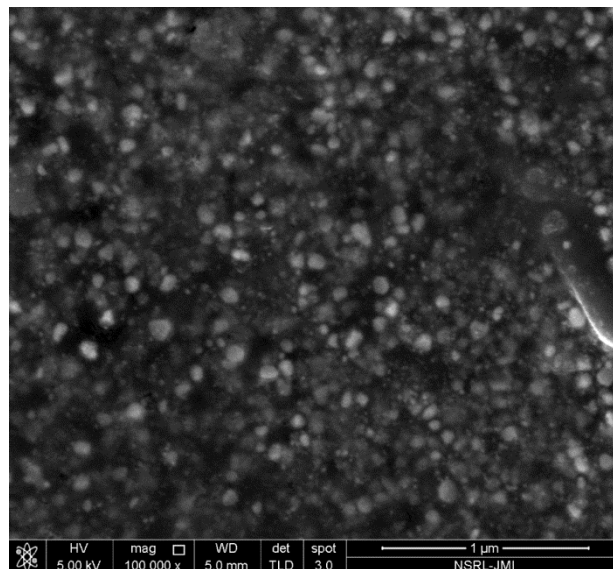


Fig. 4 – SEM Image of $Fe_3O_4@CaF_2:Tb^{3+}$ nanohybrid.

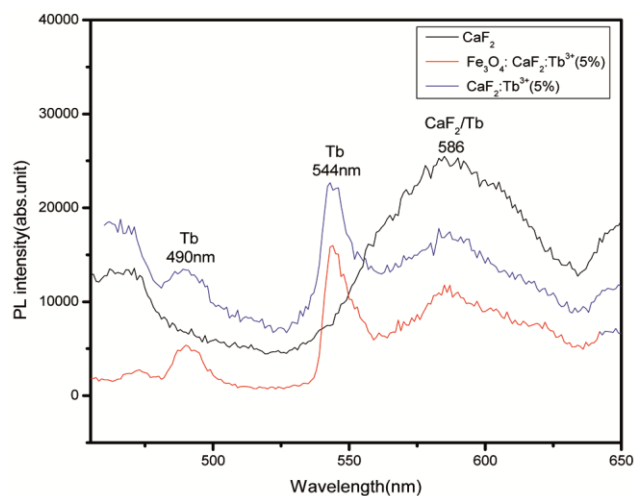


Fig. 6 – Photoluminescence emission spectra of CaF_2 , $\text{CaF}_2:\text{Tb}^{3+}$ (5 %) and $\text{Fe}_3\text{O}_4:\text{CaF}_2:\text{Tb}^{3+}$ (5 %) at $\lambda_{\text{ex}}=220$ nm.

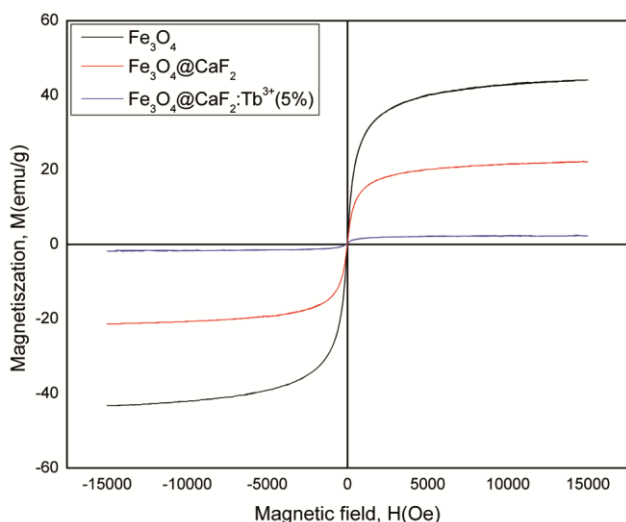


Fig. 7 – The magnetic behavior of the synthesized nanohybrid in comparison to the pure iron oxide NPs.

hybrid $\text{Fe}_3\text{O}_4:\text{CaF}_2:\text{Tb}^{3+}$ is low in comparison to that of the pure Fe_3O_4 . This can be explained as there is the possibility of magnetic & luminescent quenching and this is due to the large amount of Fe_3O_4 in case of the pure iron oxide NPs as compared to $\text{Fe}_3\text{O}_4:\text{CaF}_2:\text{Tb}^{3+}$.

4 Conclusions

A bifunctional, magnetic-luminescent, nanomaterial is synthesized using a simple, co-precipitation method. The synthesized nanomaterial is characterized via XRD and SEM. However, VSM (vibrating sample magnetometer) is used to analyze the magnetic properties of synthesized material. UV-vis and

photoluminescence spectroscopy are used to analyze luminescent properties of the nanomaterial. The described hybrid nanomaterial is sensitive to external magnetic fields. The obtained product is attracted to magnets both in the solid state (as a dry powder) and in water dispersed state as a colloid. The nanohybrid shows intense emission peak at 544 nm and is expected to show an intense green luminescence under a UV lamp. Such a luminescence is also expected in an aqueous system. This nanohybrid product shows simultaneously magnetic and luminescent properties and can be used for various medical & industrial applications. However, the mechanism of this phenomena and the influence of the environment should be examined and discussed in further research.

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