



Photoluminescence and Induction Heating Studies of $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ Magnetic-Luminescent Nanocomposite for Hyperthermia Application

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A 5 at.% Dy^{3+} ions doped CaWO_4 nanoparticles ($\text{CaWO}_4:5\text{Dy}$) were synthesized by hydrothermal method using polyethylene glycol (PEG) as solvent medium and capping agent. The phase purity and crystalline properties of the prepared nanoparticles were obtained from the XRD analysis. TEM images revealed that the $\text{CaWO}_4:\text{Dy}^{3+}$ have particles of size approximately in the range 30-50 nm. The prepared magnetic luminescence nanocomposite exhibits a high saturation magnetization. The prepared nanocomposite can achieve hyperthermia temperature (42 °C) in a short period by applying the alternating magnetic field, externally. The nanocomposite also shows photoluminescence properties. Nanomaterials described in this work can be used for optical imaging as well as hyperthermia applications.

Keywords: Iron oxide nanoparticles, Magnetic-luminescent nanocomposites, Hyperthermia.

INTRODUCTION

During the recent years, lanthanide doped luminescence nanomaterials are widely studied by many researchers due to their various applications in different fields. Such luminescence materials are highly stable, colour tunable, high intensity so such materials are used in the field of display devices, LED, fluorescence lamp, X-ray imaging *etc.* [1].

For the luminescence study proper choice of host materials is important one; host with high photon energy, low ionicity are not suitable for luminescence purpose [2]. The host materials, which consist of vanadate, niobate and/or tungstate ions, which can improve the luminescence intensity since these ions can exhibit the emission in broad ultraviolet-visible range and the UV-visible emission energy can easily be transferred to the lanthanide ions resulting in the improvement of the luminescence intensity of lanthanide ions [3]. For white light emitter applications among lanthanide ions, trivalent Dy^{3+} ions doped in ABO_4 are the promising materials as compared with other lanthanide because of its luminescence emission range from blue to yellow [4-6].

When such luminescence materials are made composite with magnetic materials (specially Fe_3O_4), these prepared nanocomposites exhibit interesting luminescence characteristics as

well as magnetic properties. Such prepared materials are commonly known as magnetic-luminescent nanocomposites (MLN). In most of the cases, Fe_3O_4 are selected as magnetic materials rather than Co and Ni since Fe_3O_4 materials are non-toxic, cost effective materials and biocompatibility in human cells. Now a days, the MLN are widely used for biomedical applications such as bioimaging, cell tracking, drug delivery, bio-sensing, contrasting agents and nanomedicines [7,8].

Hyperthermia is a potential therapeutic method used for the treatment of cancer using magnetic materials. Hyperthermia involves heating certain part of body organ/tissue, in a low temperature range of 41-46 °C [9,10]. In hyperthermia applications, the MLN materials play significant role, where the magnetic part (Fe_3O_4) of nanocomposite gives the required heat for hyperthermia effect when an AC magnetic field is applied externally whereas the lanthanide doped luminescence part is useful for imaging during *in vivo* and *in vitro* study.

In present study, 5 at.% Dy^{3+} ions doped CaWO_4 nanoparticles using polyethylene glycol (PEG) as reaction medium as well as capping agent were synthesized. Due to the non-toxic in nature and high boiling point, PEG is suitable for the reaction to be carried out at high temperature. Moreover, such lanthanide doped luminescence materials are made composite with magnetic nanoparticles *i.e.* Fe_3O_4 , so that the resulting

composite becomes magnetic luminescence nanocomposite, which posses multifunctional properties.

EXPERIMENTAL

The chemicals *viz.* calcium nitrate tetrahydrate [(Ca(NO₃)₂·4H₂O)], dysprosium acetate [(Dy(CH₃COO)₃], sodium tungstate dehydrate (Na₂WO₄·2H₂O), polyethylene glycol 4000 (PEG-4000), ferrous chloride (FeCl₂·4H₂O), ferric chloride (FeCl₃) and deionized water were procured from the reputed commercial sources and used as such throughout the synthesis of the nanomaterials.

Synthesis of Fe₃O₄ nanoparticles: For the preparation of Fe₃O₄ nanoparticles, 7.50 g of PEG-4000 was poured into 150 mL of deionized water then solution was heated at 50 °C with stirring for 0.5 h. Again 1.4910 g of FeCl₂·4H₂O was added in the above solution and stirred for 15 min followed by the addition of 2.433 g of FeCl₃ while stirring continuously for 30 min. Thereafter, about 30 mL of NH₄OH was added, continuously stir for about 1 h and the resulting solution was kept overnight. After this process, the black precipitates were separated using magnetic separation method then the resulting dried black precipitation was used for further analysis.

Synthesis of Dy³⁺ ions doped CaWO₄ nanoparticles: Calcium nitrate tetrahydrate (2.692 g) and dysprosium acetate (0.204 g) were dissolved together in 50 mL of solvent. In another beaker, sodium tungstate dehydrate (3.838 g) was dissolved in PEG medium. Then, two liquid solutions were allowed to mix uniformly using a stirring for about 30 min, which resulted in the formation of white precipitate. Then the whole mixture were allowed to react using hydrothermal method. The reaction product was collected after centrifugation and washed several times using acetone.

Synthesis of Fe₃O₄@CaWO₄:5Dy³⁺ (1:1): The Fe₃O₄@CaWO₄:5Dy³⁺ nanocomposite was synthesized in same ratio. 2, 5, 10, 15 and 20 mg of Fe₃O₄ were reacted with 2, 5, 10, 15 and 20 mg of CaWO₄:Dy³⁺, respectively. All the mixture were mixed with 1 mL of PEG solvent. Then, the mixer were ultrasonicated for 2 h.

Characterization: The PAN alytical powder X-ray diffractometer (X-PertPRO) equipped with a CuKα (1.5406 Å) radiation source and Ni filter was used for X-ray analysis of the prepared nanoparticles. The functional groups present in the prepared sample was identified by using FT-IR spectroscopy, the Perkin-Elmer Spectrum Two (FT-IR) recorded in the range of 4000-400 cm⁻¹. The shape and size of the synthesized nanocomposite was studied by Transmission electron microscope (JEOL JEM-2100, Japan) operated at 200 kV.

The photoluminescence (PL) spectra and lifetimes of the nanocomposite were recorded using a Hitachi F-7000 FL spectro-photometer equipped with a 150 W Xenon lamp as a source. All of the measurements were carried out at room temperature. The magnetic measurements were carried out by using vibrating sample magnetometer (VSM) at room temperature using a Lakeshore VSM 7410 instrument in an applied magnetic field of ± 1.5 T. The measurements of the induction heating ability of the magnetic nanoparticles and nanocomposites were performed using Easy Heat 8310, Ambrell,

UK. The sample concentrations of 2, 5, 10, 15 and 20 mg of the magnetic-luminescent nanocomposites dispersed in one mL of distilled water were measured for their heat generation efficiency.

RESULTS AND DISCUSSION

XRD studies: The X-ray diffraction (XRD) patterns of CaWO₄:5Dy nanoparticle is shown in Fig. 1. The pattern of the peaks are indexed to the tetragonal phase in accordance to the reference no. 00-01-0806 having lattice parameter a = 5.24 Å, b = 5.24 Å, c = 11.38 Å and unit cell volume V = 312.47 Å³. The sharpness of the peaks indicate that the prepared nanoparticles were crystalline in nature. The calculated crystallite size using Scherrer's equation at the (112) plane is 12 nm. There is no extra phase arising from any the impurity and precursor indicating that the prepared samples is pure tetragonal phase of CaWO₄ nanoparticles.

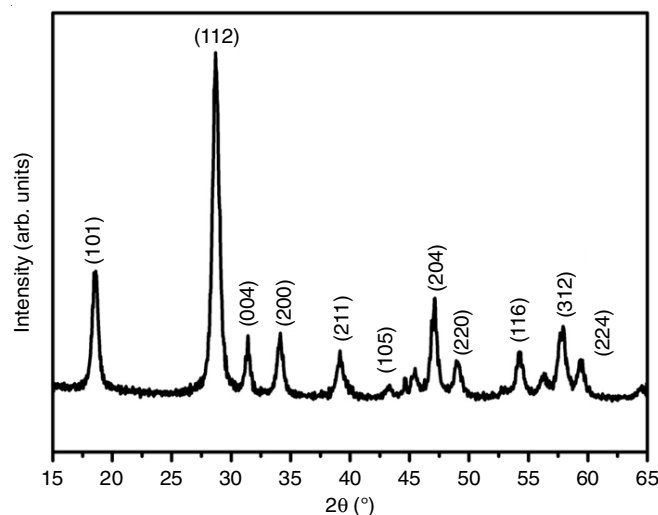


Fig. 1. XRD pattern of CaWO₄:5Dy nanoparticles

FTIR studies: For further confirmation of formation of the CaWO₄ nanocrystal structure, the FTIR spectra of CaWO₄:5Dy nanoparticles in the range of 4000-400 cm⁻¹ are shown in Fig. 2. The peaks at 1372 cm⁻¹, 1562 cm⁻¹, 1638 cm⁻¹ and 3382 cm⁻¹ are related with O–H stretching and H–O–H bending vibrations [11], respectively. These peaks are related to vibrations of water and polyethylene glycol (PEG) which is used in preparation of nanoparticles. The small peaks at 885 cm⁻¹ is related to O–W–O stretching vibration. The peaks at around 1031 and 885 cm⁻¹ are related V₁ and V₃ vibration modes of the WO₄ groups, respectively [12]. The peak at 2878 cm⁻¹ is related to CH₂ vibration of the polyethylene glycol molecule.

TEM studies: The TEM images of CaWO₄:5Dy nanoparticles are shown in Fig. 3a-b. It was observed that the prepared sample does not found to present a particular types of shape but most of the shapes of particles were cubical in nature. The particles size of the nanoparticles were in the range of 30-80 nm. The crytality of the prepared samples can be seen in SAED pattern, which is shown in Fig. 3b. The white spots in the patterns indicates the prepared nanoparticles were crystalline in nature which is also expected from the XRD data.

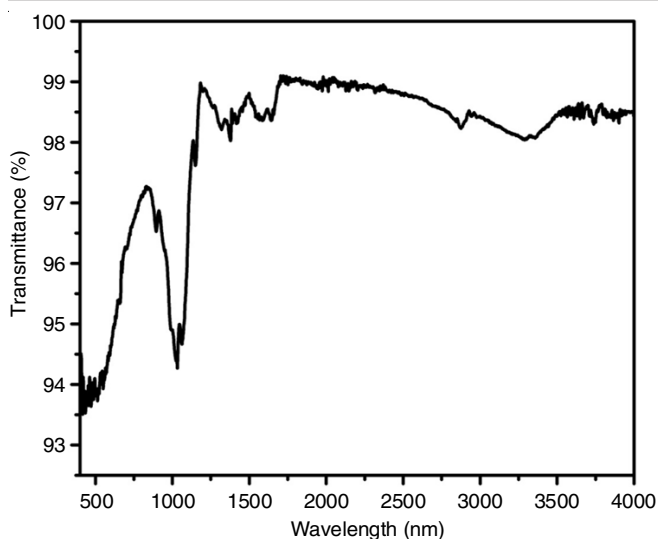


Fig. 2. FTIR spectra of $\text{CaWO}_4:5\text{Dy}$ nanoparticles at room temperature

VSM study: Fig. 4 shows the magnetization (M) versus applied magnetic field (H) for pure Fe_3O_4 nanoparticles and $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ nanocomposite. It was observed that pure Fe_3O_4 nanoparticles shows the saturation of magnetization (M_s), magnetic remanence (M_r) and coercivity (H_c) values of 43.94 emu/g, 5.80 emu/g and 113.78 Gauss, respectively. And for $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ nanocomposite shows the M_s , M_r and H_c values of 10.88 emu/g, 1.59 emu/g and 113.55 Gauss respectively. The M_s value for the Fe_3O_4 is high compared to and $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ nanocomposite and related to the good response of pure Fe_3O_4 nanoparticles towards the applied external magnetic field. However, due to the presence of non-magnetic part CaWO_4 , in $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ nanocomposite, the M_s value of $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ is low. Due to lower concentration and non-magnetic portions, the $\text{Fe}_3\text{O}_4@$

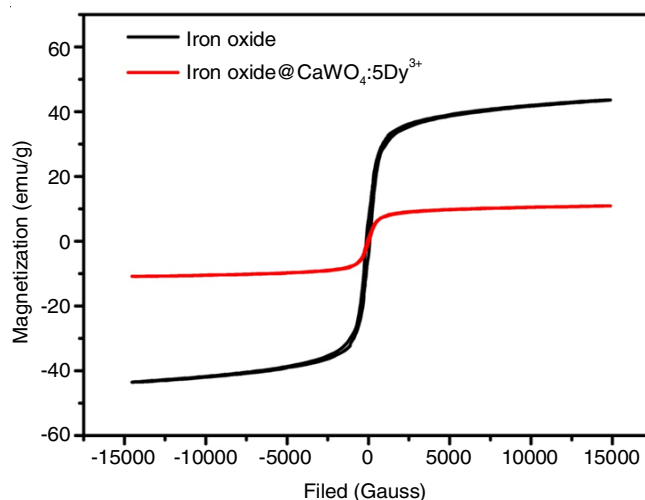


Fig. 4. Plot of magnetization versus applied magnetic field for the Fe_3O_4 nanoparticles and $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ nanocomposite

$\text{CaWO}_4:5\text{Dy}^{3+}$ nanocomposite show the low value of M_s and the M_r but still nanocomposite show the good response to the applied external magnetic field.

For ideal superparamagnetic nanoparticles, the value of H_c should be zero, however, the observed H_c values were not zero, which can be attributed due to the agglomeration of nanoparticles. Therefore, the synthesized magnetic luminescence nanoparticles can be used as good candidates for hyperthermia application.

Photoluminescence studies: Fig. 5a shows the excitation and emission spectra of $\text{Fe}_3\text{O}_4@ \text{CaWO}_4:5\text{Dy}^{3+}$ nanocomposite. Fig. 5a shows the excitation spectra of the nanocomposite monitored at 575 nm of emission wavelength. The maximum broad peak at 240 nm (Fig. 5a) was related to the charge-transfer transition from the oxygen atom to the central tungsten

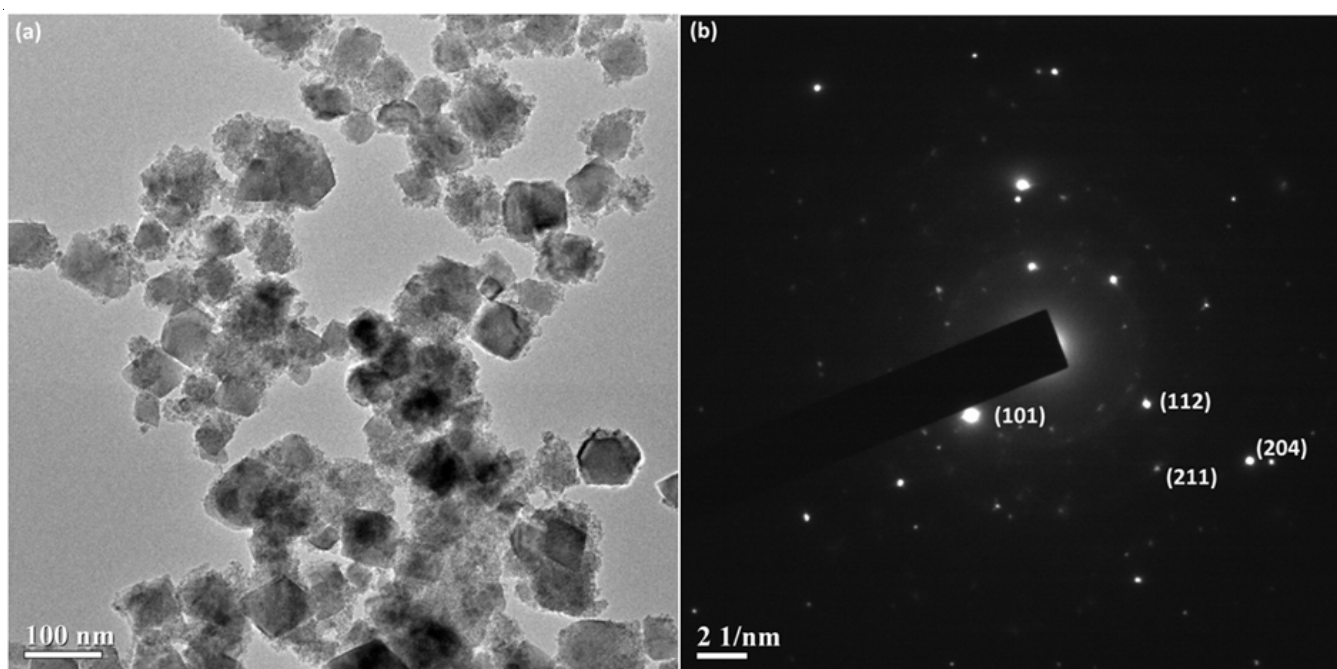


Fig. 3. Transmission electron microscope image of (a) and SAED patterns (b) of $\text{CaWO}_4:5\text{Dy}$ nanoparticles

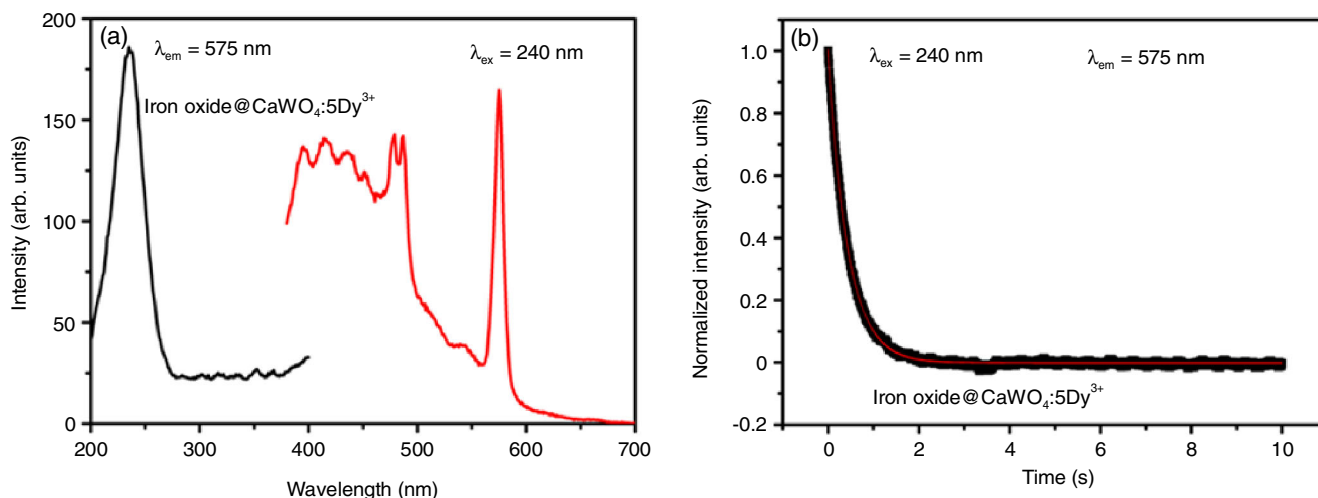


Fig. 5. Photoluminescence spectra of CaWO₄:5Dy nanoparticles (a) excitation and emission spectra and (b) Decay curve monitored at $\lambda_{\text{ex}} = 240$ nm and $\lambda_{\text{em}} = 575$ nm

ions within the WO₄⁻ [13]. The small peaks centre at 351 and 369 nm were related to transition from ⁶H_{15/2} ground state to the excited states of Dy³⁺ ions, *i.e.* ⁶P_{7/2} and ⁶P_{5/2}, respectively [14]. From the emission spectra, the host emission and maximum peaks at (478, 485) and 575 nm were observed, which is related to the Dy³⁺ ion transitions from ⁴F_{9/2}, ⁶H_{15/2} and ⁴F_{9/2} to ⁶H_{13/2}, respectively [15].

The decay curves of the prepared nanocomposite in Fig. 5b monitored at 575 nm excitation wavelength and 240 nm emission wavelength were studied. The decay curves were found fitted with bi-exponential. For bi-exponential fitted the following equation were used [16,17]:

$$I_t = I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

where I_1 and I_2 are the intensities at different time intervals and their corresponding lifetimes are τ_1 and τ_2 . The average lifetime (τ_{av}) of biexponential decay can be calculated using eqn. 2:

$$\tau_{\text{av}} = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2} \quad (2)$$

The calculated average lifetime values is 0.46 s. It was observed that the prepared nanocomposite show good photoluminescence properties indicating that the prepared nanocomposite can be used bioimaging purposed.

Hyperthermia study: The induction heating experiment was carried out by Fe₃O₄ nanoparticles at of 300 A for 600 s. The suspensions magnetic nanoparticles were prepared by dissolving 2, 5, 10, 15 and 20 mg of magnetic samples in 1 mL of distilled water. The heat generation from Fe₃O₄@CaWO₄:5Dy³⁺ nanocomposite at 300 A is shown in Fig. 6. It was found that the slopes of each temperature *versus* time plots increases with increasing Fe₃O₄ concentration. The nanocomposite having 2 and 5 mg can't achieve hyperthermia temperature (42 °C). While 10, 15 and 20 mg samples were able to achieve hyperthermia temperature and the time taken to achieved hyperthermia temperature were 265, 197 and 81 s, respectively. From these observations, one can inferred that the prepared

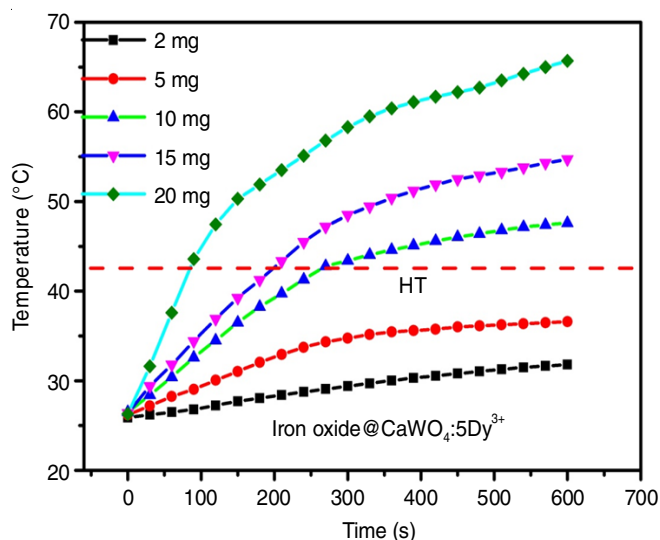


Fig. 6. Induction heating profiles for different concentrations (2-20 mg/mL) of Fe₃O₄@CaWO₄:Dy³⁺ samples at 300 A

nanocomposite can be used for hyperthermia method in cancer treatment.

Conclusion

Highly crystalline Dy³⁺ ions doped CaWO₄ nanoparticles were prepared using hydrothermal method. From the XRD study, the prepared nanoparticles were found to be pure crystalline with tetragonal phase. Moreover, the prepared samples were well capped by capping agent PEG as indicated from the FTIR analysis. The prepared nanocomposite Fe₃O₄@CaWO₄:5Dy³⁺ show a high saturation magnetization and luminescence properties. Moreover, the synthesized nanocomposite can also achieve the hyperthermia temperature at a short time. Thus, the prepared nanocomposite can be used in the field of hyperthermia and bioimaging purposes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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