Optical Characterization of Infrared Emitting Nd³⁺ doped Hydroxyapatite nanoparticles prepared by hydrothermal method

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Abstract: Trivalent Nd doped hydroxyapatite (HAp) nanoparticles were prepared by a hydrothermal method using calcium nitrate and diammonium phosphate as precursors. Well crystallized nanoparticles of size less than 200 nm with hexagonal plate and rod morphologies were obtained at a reaction temperature of 180 °C. Under 808 nm excitation the nanoparticles exhibit strong near infrared emission at 1064 nm. All the emission spectral properties such as emission intensity and fluorescence decay time are found to decrease with Nd³⁺ concentration. In Hap 0.5% Nd shows the highest decay time of 159 μs and highest emission at 1064 nm emission.

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1. Introduction

Hydroxyapatite (HAp) has drawn a great interest from researchers because of its potential use as biomedical materials such as bone fillers [1-3] bone tissue engineering scaffolds [4] bioactive coatings [1], soft tissue repairs [5-8], drug/ protein/gene loading and delivery systems [9-13] and column chromatography for rapid fractionation of biomolecules [14,15] because of their excellent biocompatibility, osteoconductive properties, and similarity to the component of human bones [16]. HAp nano materials are also potential candidates for use in cell targeting, fluorescence labelling, imaging and diagnosis [17, 18] etc. In addition, HAp is also exploited as a model compound to mimic the biomineralization process [19, 20].

The physical, chemical, and biological properties of HAp are controlled by its crystal structure and composition. Substitution of Ca^{2+} with other metal ions into the HAp structure is one of the effective ways to improve the properties of HAp. Metal ions such as Ag^+ , Cu^{2+} , and Zn^{2+} in the HAp lattice can affect its crystallinity, morphology, and lattice parameters. The advantages of doping HAp with foreign elements pertinent to orthopaedic applications were reported by others. For example, Y-doped hydroxyapatite [21] has been studied for humidity sensor applications due to its high affinity for water molecules [22]. The doping of HAp with Zn^{2+} significantly increased osteoblast adhesion [23]. Webster et al. [24] reported that the Bi^{3+} would be the best choice of dopant to enhance properties of HAP pertinent for bone implant applications.

Recently, there has been so much interest in trivalent rare earth (RE) doped nanomaterials for several biophotonics applications such as optical imaging, therapy, and drug delivery [25-27]. Though this technology has already been proposed for several biophotonics applications, it is

still immature mainly due to the lack of proper materials that satisfies several requirements viz. high efficiency, non-toxicity, small size, low cost of production, biocompatibility, etc. Due to the similarity with bone material fluorescent HAp nanoparticles can be considered as a suitable contrast agent in medical imaging applications. There are several reports on the synthesis and application of Eu^{3+} -doped HAp as optical contrast agent [28, 29] where the red fluorescence from Eu^{3+} can be used to image cells under UV excitation.

However, the inherent limitations of the short wavelength excitation and emission in cellular imaging viz. tissue autofluorescence under UV excitation and low penetration depth due to scattering makes this technique almost unable to acquire intracellular details at greater depth. To circumvent these limitations recently near infrared (NIR) emitting nanomaterials are considered and the application of such materials shows very promising results. In this paper, we report for the first time, Nd^{3+} -doped HAp with strong NIR emission properties. Considering the better biocompatible nature of HAp we propose that under optimized conditions, the synthesized nano phosphors could be a potential optical contrast agent in medical imaging applications. The novelty in this work is the development of a biocompatible near infrared nano phosphors for biomedical imaging applications.

2. Experimental

2.1. Synthesis of Nd^{3+} doped HAp

Nd^{3+} -doped HAp powders were prepared following a hydrothermal method as follows: calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (GFS chemicals, 99.9%) and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) (Sigma Aldrich, 99%) were used as calcium (Ca) and phosphate (P) sources, respectively. HAp was synthesized by dissolving the above compounds separately in double distilled water with the molar ratio of 1:0.6 in order to maintain the stoichiometric ratio of

HAp (Ca/P ratio is 1.67). The pH of the phosphate solution was adjusted to 9 by adding ammonium hydroxide (30%). For preparing Nd-doped HAp, Neodymium nitrate hexahydrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.9%) was added at 0.5, 1, 2 and 4 mol % relative to HAp in calcium nitrate solution. After that the phosphate solution was added dropwise to the calcium solution which was vigorously stirred. Then, the mixed solution was transferred to a Teflon lined stainless steel autoclave and placed in an oven (30400, Barnstead Thermolyne, U.S) at 180°C for 24 h for further reaction. Afterward, the autoclave was cooled down to room temperature naturally. The precipitate obtained was washed and separated by centrifugation (Z323, Labnet, U.S.) for 10 min at 10000 rpm using double distilled water for four times and then dried at 100°C overnight. Finally, the dried powders obtained were crushed with mortar and pestle and calcined at 1300°C for 1 h in a muffle furnace (KSL 1500, MTI, U.S.) before further characterization. The schematic presentation of the procedure is given in Fig.1.

2.2. Characterization Methods

The phase of the prepared samples was identified by powder X-ray diffraction method using a Cu-K α ($\lambda=1.5\text{\AA}$) radiation (RIGAKU Ultima IV X-ray diffractometer). The morphology and particle size distribution of the samples were observed using a Hitachi S5500 field emission scanning transmission electron microscope (FE-STEM) operated at 30 kV in secondary electron mode. Elemental compositions were estimated by the energy dispersive x-ray analysis (EDAX) equipped with the FE-STEM. To examine the particle size and other structural information, high resolution transmission electron microscopy (HRTEM) measurements were performed using a high resolution TEM (JEOL -2010 I). Dynamic Light Scattering (DLS) measurements were done using the Zetasizer Nano ZS (Malvern Instruments) with a 4mW He-Ne laser (632 nm).

Infrared spectrum was collected using an FTIR spectrometer (JASCO FT/IR 6300) using KBr pellet method. Raman studies were performed in a back scattering geometry, under laser excitation wavelengths 1064 nm, using a locally assembled Micro-Raman with HR 320 Horiba Jobin-Yvon spectrograph. The UV-VIS-NIR optical absorption spectrum was collected using a spectrophotometer (Perkin Elmer Lambda 950, U.S.). Fluorescence emission characterization was done using a near infrared (NIR) 808 nm power tunable fiber coupled Fabry Perot laser diode (Thorlab, Model LM14S2) and the emission of the sample was taken using a quanta Master 51 fluorescence spectrometer from Photon Technology International Inc. The fluorescence decay kinetics of the samples were recorded on spectrofluorimeter (model Quanta Master40, Photon Technology International (PTI) Inc.) using the Single Shot Transient Digitizer technique with a nitrogen dye laser (PTI part GL-3300 + GL-302) excitation source. The nitrogen laser has an 800 ps pulse width that pumps a high resolution dye chamber to give 514 ± 0.04 nm light. The collected decay curve was analysed using built in software provided by PTI.

3. Results and discussion

3.1. Phase and Morphology

Fig. 2 shows the unit cell structure of Nd^{3+} doped HAp. HAp crystal structure belongs to the hexagonal system with $P6_3/m$ with unit cell dimensions of $a=b=9.432\text{\AA}$ and $c=6.881\text{\AA}$, $\alpha = 90.0^\circ$ $\beta = 90.0^\circ$ $\gamma = 120.0^\circ$ [30]. The ionic radius similarity between Ca^{2+} ($1.12\text{\AA}$) and Nd^{3+} ($1.09\text{\AA}$) [31] in the apatite lattice makes them a good host for Nd^{3+} doping.

The XRD patterns of the various concentration of Nd^{3+} doped HAp nanoparticles is shown in Fig.3. It is obvious that both the as prepared and heat treated X-ray diffractions of the samples can be well indexed as a pure hexagonal phase ($P6_3/m$ Space group), agreeing well with the values of the standard data (Pdf file # 74-566). In the case of the sample with Nd^{3+} , the

characteristic diffractions of Hexagonal HAp are still obvious and no other phases related with doped component can be detected.

The as-prepared Nd^{3+} doped HAp shows low crystallinity. In order to increase the crystallinity, the nanoparticles were heat treated at 1300°C for 1 h. The X-ray diffraction analysis shows that the particles retain their as-precipitated phase with better crystallinity, while the SEM image shows only change in the morphology, where the particle morphology becomes isolated now. Solid state sintering appears to be responsible for this substantial increase in crystallinity, and change in morphology.

The SEM study indicates nanocrystalline nature of the materials with narrow particle size distributions. A representative SEM photographs (shown in Fig.4(b)) for Nd-HAp (1%), heated at 1300°C sample indicates the particle size distribution from 60 to 95 nm as shown in the histogram Fig.4 (c). A close up view of the particle through TEM shows the morphology of the particles. As shown in Fig. 5 the TEM images of Nd-HAp shows purely hexagonal morphology with a combination of rods and plates.

The compositional distribution was obtained by Energy Dispersive X-ray (EDX) line-scanning analysis, and the spectrum recorded through the center of an individual HAp nanoparticle is shown in Fig. 6. EDX clearly indicates the presence of Ca, Nd, P and O as indicated by their representative positions in the EDX spectrum.

Dynamic light scattering (DLS) measurements were performed to explore the aggregations and stability of the nanoparticles within the solution. The DLS measurements of Nd-HAp (1%) nanoparticles in deionized water were performed at a concentration of 0.1 mg/mL^{-1} and the result is shown Fig. 7. According to this measurement the hydrodynamic size of the nanoparticle is estimated to be 280 nm with a FWHM of 82 nm. The increase of size compared

to the SEM and TEM images can be attributed to the HAp coating with the water molecules and solvent ions that produce a hydrodynamic shell around the nanoparticles when they are in solution. The majority of the nanoparticles fall within the stated ranges with less aggregation and high stability.

3.2. FTIR and Raman Spectroscopy

The FTIR spectra of Nd^{3+} doped HAp sample is shown in Fig. 8. The typical bands of hydroxyapatite can be seen obviously. The band observed at 3570 and 636 cm^{-1} were due to the OH ions [32]. The bands observed at 602 and 565 cm^{-1} were assigned to the $(\text{PO}_4)^{3-}$ bending mode (ν_4), while the anti-symmetric (ν_3) and symmetric (ν_1) stretching modes of $(\text{PO}_4)^{3-}$ appeared at 1090, 1037, 962 cm^{-1} accordingly. The $(\text{CO}_3)^{2-}$ stretching were observed at 1457 cm^{-1} . Complementary information can be obtained from the Raman Spectrum shown in Fig. 9. It is observed that the ν_1 (PO_4) band at 1282 cm^{-1} was very intense and characteristic in Raman spectra of HAp. This mode was associated to the totally symmetric (ν_1) P-O-P stretching mode of the free tetrahedral phosphate ion. The vibrational bands at 1150 and 1475 cm^{-1} is attributes to asymmetric ν_4 and ν_3 (P – O) stretching. The Nd^{3+} substituted HAp synthesized in this study exhibits a strong variation shift due to sinterization of the particle at 1300°C and the ion substitution in the 1000 cm^{-1} to 2000 cm^{-1} region, when compared to the pure HAp's [33].

3.3. Optical Characterizations

Absorption spectrum (Fig. 10) shows almost all well-defined Nd^{3+} transitions with the strongest peak at 806 nm. All absorption bands are identified using the standard spectroscopy notation as indicated in the spectrum. The overall appearance of the spectrum is very similar to other Nd^{3+} doped materials. The absorption bands of Nd^{3+} ion corresponds to transitions from the $^4\text{I}_{9/2}$ ground state to the various excited levels. By fitting the absorption spectral data with Judd-

Ofelt model [34,35], we can predict the radiative quantum yield using the equation $\mu_{\text{rad}} = (\tau_{\text{rad}}/\tau_{\text{lum}})$ [36].

Here τ_{lum} is the fluorescence decay time and τ_{rad} is the radiative decay time calculated using the expression

$$\frac{1}{\tau_{\text{rad}}} = A_{\text{rad}}(J' \rightarrow J) = \frac{64\pi^4 e^2}{3h(2J'+1)\lambda^3} \left(\frac{n(n^2+2)^2}{9} S_{\text{ed}} + n^3 S_{\text{md}} \right) \quad (1)$$

where A_{rad} represents the radiative transition probability for transition from excited state with singular momentum quantum number J' to ground state J . For Nd^{3+} the excitation of the $^4\text{F}_{3/2}$ level results in four emission bands which corresponds to the transitions from the excited $^4\text{F}_{3/2}$ level to $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{13/2}$ and $^4\text{I}_{15/2}$ levels, h is plank's constant, n is the refractive index ($n=1.65$ for HAp), λ is the peak absorption band wavelength, and e is the charge of the electron. S_{ed} and S_{md} are the electric dipole and magnetic dipole line strengths calculated using the expressions [36]

$$S_{\text{ed}}(J' \rightarrow J) = \sum_{t=2,4,6} \Omega_t \left| \left\langle (S', L') J' \right| U^{(t)} \left| (S, L) J \right\rangle \right|^2 \quad (2)$$

$$S_{\text{md}} = \frac{h^2}{16\pi^2 m^2 c^2} \left| \left\langle (S', L') J' \right| L + 2S \left| (S, L) J \right\rangle \right|^2 \quad (3)$$

Where Ω_2 , Ω_4 , Ω_6 are the Judd-Ofelt phenomenological parameters and the $\|U^{(t)}\|$ factor represent the doubly reduced transition matrix elements of rank t ($t=2,4,6$). The best set of Ω parameters are determined by a standard least square fitting of the experimental oscillator strength(f_{exp}) to the theoretical oscillator strength(f_{cal}) formula [37] and the values obtained are $\Omega_2 = 16.6 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 5.2 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 9.6 \times 10^{-20} \text{ cm}^2$. Following this procedure a radiative decay time of 205 μs was obtained. A summary of the Judd-Ofelt calculation results are tabulated in Table 1 and 2.

The NIR emission spectra obtained for HAp doped with Nd^{3+} concentration of 0.5, 1, 2, and 4 Mol % were obtained by exciting it with an 808 nm diode laser under identical

experimental conditions with a power density of 1.4 Wcm^{-2} . The emission spectra for various concentration of Nd^{3+} along with the as-prepared Hap with Nd^{3+} (1%) are shown in Fig. 11. All emission spectra show the three characteristic emission bands originating from the $^4\text{F}_{3/2}$ excited state and centered at 924 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$), 1060 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$), and 1348 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$) with the 1060 nm band having the greatest intensity. The significant reduction in the emission intensity of the as-prepared material is due to the low crystallinity nature of the as-prepared material. Comparison of the emission intensity shows that the 0.5% doping of Nd^{3+} yielded the highest emission intensity which further decreased with higher Nd^{3+} concentrations. This reduction in the fluorescence intensity at higher Nd^{3+} concentration can be attributed to Nd^{3+} self-quenching (concentration quenching). The concentration quenching might be explained on the basis of following two factors: (i) the excitation migration due to resonance between the activators was enhanced when the doping concentration was increased, and thus the excitation energy reaches quenching centers, and (ii) the activators were paired or coagulated and were changed to quenching centers [38]. For Nd^{3+} ions, the cross relaxation process involve the depopulation of emitting $^4\text{F}_{3/2}$ level via the transition $^4\text{F}_{3/2}: ^4\text{I}_{9/2} \rightarrow ^4\text{I}_{15/2}: ^4\text{I}_{15/2}$ and $^4\text{F}_{3/2}: ^4\text{I}_{9/2} \rightarrow ^4\text{I}_{13/2}: ^4\text{I}_{15/2}$; while the energy migration involves the exodus of excitation between the excited and nearest neighbor ground state Nd^{3+} ions through $^4\text{F}_{3/2}: ^4\text{I}_{9/2} \rightarrow ^4\text{I}_{9/2}: ^4\text{F}_{3/2}$ transitions. The fluorescence decay curve obtained for the 1060 nm emission bands in Nd^{3+} HAp (0.5, 1, 2 and 4 Mol %) are shown in Fig. 12. The decay curve was fitted by the double exponential function (38),

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (4)$$

where A_1 and A_2 are the fitting parameters and τ_1 and τ_2 are the fluorescence decay times and the average decay time (τ_{av}) was obtained using the expression [39],

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (5)$$

The decay times obtained from the curve fitting were found to be 159 μ s for HAp Nd³⁺ (0.5 Mol %), 139 μ s for (1 Mol %), 70 μ s for (2 Mol %) and 54 μ s for (4 Mol %). By taking the ratio of fluorescence decay time to radiative decay time a maximum radiative quantum yield of 77% was obtained. Considering the better biocompatibility of the hydroxyapatite based materials the 77% radiative quantum yield obtained offers many potential applications of the present materials in biomedical applications as near infrared contrast agents. We are currently investigating the *in vitro* and *in vivo* medical imaging application of this material.

4. Conclusions

In conclusion, hydrothermal method is considered as successful method for the synthesis of hexagonal shaped nanocrystalline hydroxyapatite Ca₁₀(PO₄)₆(OH)₂ substituted with Neodymium (III). The successful incorporation of Nd³⁺ in the crystalline phase make the nanoparticles as potential near infrared emitting phosphor with emission at 1064 nm. Considering the better biocompatibility of HAp, the present Nd³⁺ doped HAp could offer several exciting applications in biomedical area such as infrared imaging, targeted drug delivery and other image guided therapeutic application.

Acknowledgements

Authors GAK and DKS would like to acknowledge the financial support from the National Science Foundation Partnerships for Research and Education in Materials (NSF-PREM) grant N0-DMR-0934218. We are thankful to Dr. Kelly Nash and Dr. Chris Mimun for technical help with microscopy imaging and dynamic light scattering measurements. Solange gratefully acknowledge the financial support to ConaCyt through the `beca mixta (N0: 297497) and

the Strengthening Program of academic research projects and Mexican students in the University System of Texas. CS acknowledges the financial support from DST-FIST (India Grant no.SR/FST/PSI-174/2012).

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Table.1.Experimental and calculated oscillator strengths of the observed absorption bands with

Transition from $^4I_{9/2}$	Wavenumber(cm^{-1})	Mol.Ext.Coeff. (cm.mol/l^{-1})	$f_{\text{exp}} (10^{-6})$	$f_{\text{cal}} (10^{-6})$	their spectral band assignments and molar extinction coefficient s.
$^4F_{3/2}$	11612	290	1.27	3.21	
$^4F_{5/2}$	12389	1959	8.58042	10.08	
$^4S_{3/2} + ^4F_{7/2}$	13395	1881	8.23878	7.57	
$^4F_{9/2}$	14630	219	0.95922	1.09	
$^4G_{5/2}$	17185	3900	17.082	48.05	
$^4G_{9/2}$	19621	3987	17.4631	24.6	
$^4G_{11/2}$	21557	1460	6.3948	5.36	
$^2P_{1/2}$	23221	393	1.72134	0.71	

Table. 2 .Calculated radiative spectral properties of the emission transitions from the $^4F_{3/2}$ excited state.

Transition from $^4F_{3/2}$ to	Frequency	Electric dipole line strength(S_{ed})(10^{-20}cm^2)	Transition probability(A_{ed})(s^{-1})	Radiative decay time (τ_{rad})(μs)
$^4I_{15/2}$	5450	1.7382	179	205
$^4I_{13/2}$	7496	2.0352	544	
$^4I_{11/2}$	9520	4.64844	2544	

$^4\text{I}_{9/2}$	11363	1.7382	1618	
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Fig. 1 Schematic diagram of the synthesis of Nd³⁺ HAp nanoparticles

Fig. 2 The unit cell structure of Nd^{3+} doped HAP indicating the positions of various metal atoms in a unit cell.

Fig.3 XRD pattern of Nd^{3+} HAP particles in comparison with standard reference

(a)

(b)

(c)

Fig. 4 SEM micrograph of (a) as-prepared Nd^{3+}HAp nanoparticles, (b) heat treated 1% Nd^{3+}HAp , (c) Particle size distribution of Nd^{3+}HAp nanoparticles.

Fig. 5 TEM micrograph of Nd³⁺ HAp powder.

Fig. 6 EDX spectrum of Nd³⁺ HAp indicating the presence of Ca, O, P and Nd in the particle.

Fig. 7 Dynamic light scattering (DLS) measurements of Nd HAp (1%) particles in deionized water.

Fig. 8 Infrared vibrational spectrum of Nd³⁺ HAp particles showing the presence of various functional groups.

Fig. 9 Raman Spectrum of Nd³⁺HAp particles.

Fig. 10 Optical absorption spectrum of Nd³⁺HAp particles at 4% Nd³⁺ concentration indicating the spectral notations of various observed bands.

Fig. 11 Comparison of the emission spectra of the as-prepared (AP) and heat treated Nd^{3+} HAP nanoparticles at 808 nm excitation.

Fig. 12 Fluorescence decay curve of 1064 nm emission with different Nd^{3+} concentrations.