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Original Research

Study structural and up-conversion luminescence properties of polyvinyl alcohol/CaF_2:erbium nanofibers for potential medical applications

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Abstract

Objective(s): This paper describes synthesis Polyvinyl Alcohol/CaF_2:Er nanofibers because of its photoluminescence properties.
Materials and Methods: First, CaF_2:Er nanocomposite synthesized with co-precipitation method. In order to prepare polyvinyl alcohol (PVA)/CaF_2:Er nanofibers, CaF_2:Er nanocomposites were added to the polyvinyl alcohol (PVA) polymer. PVA/CaF_2:Er composite nanofibers were successfully prepared by electrospinning technique.
Results: X-Ray Diffraction (XRD) pattern and Transmission Electron Microscopy (TEM) images indicate that the CaF_2:Er nanocomposite was formed with cubic phase and the average crystalline size was calculated using the Scherrer's equation is about 26-28 nm. Scanning Electron Microscopy (SEM) images show that the diameters of the fine nanofibers are in the range of 60-110 nm. For studying luminescence properties of the nanofibers, the samples excited with different wavelengths and show excellent Up-Conversion luminescence transition.
Conclusion: Photoluminescence spectrums of the PVA/CaF_2:Er nanofibers illustrate up-conversion luminescence process. This unique property can have high potential for laser application and bio-imaging in medical technology.

Keywords: Nanocomposite, Nanofibers, Photoluminescence, Up-conversion

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Introduction

In recent decade, the integration of nanotechnology with molecular biology and medicine has resulted in active developments of a new emerging research area, nanobiotechnology which can significantly advances the current clinical diagnostic and therapeutic method (1). Nanofibers have wide applications in medicine, including artificial organ components, tissue engineering, implant material, drug delivery, wound dressing and medical textile materials.

Recently, researchers have found that nanofiber meshes could be used to fight against the HIV1 virus and be able to be used as contraception. In wound healing nanofibers assemble at the injury site and stay put, drawing the bodies own growth factors to the injury site (2).

Lasers have always played an important role in material processing of devices used in hospitals and doctor's offices from surgical tools and implantable devices to part identification that is permanent, non-corrosive, safe, and non-toxic. Medical technology continues to advance procedures become less invasive and economic pressures demand reduced costs.

Traditionally, lasers have been classified according to the physical construction of the laser (for example gas, liquid, solid state or semiconductor diode) the type of medium which undergoes lasing (e.g., Erbium: Yttrium Aluminium Garnet (Er:YAG)) and degree of hazard to the skin or eyes following inadvertent exposure.

Erbium (Er) lasers are categorized in the mid-infrared range of the electromagnetic spectrum with light emitted as invisible, nonionizing, thermal radiation and have wide application in medical uses especially in dentistry (2-3).

Also, Er laser resurfacing is designed to remove surface-level and moderately deep lines and wrinkles on the face, hands, neck or chest. One of the benefits of Er laser resurfacing is minimal burning of surrounding tissue. This laser causes fewer side effects so the recovery time should be faster than with CO_2 laser resurfacing (4).

CaF_2 nanoparticle is a unique select as host luminescence material because of its high transmittance and low phonon energy and refractive index (5-6).

Up-conversion (UC) luminescence properties of Er have been reported up to now (7-8).

So, We synthesized CaF_2:Er nanocomposites for their photoluminescence properties and used polyvinyl alcohol (PVA) polymer for fabricating PVA/ CaF_2:Er nanofiners by electrospinning method due to its excellent biocompatibility, mechanical properties and its safety.

PVA is commonly used in medical field due to low protein adsorption characteristics, biocompatibility, high water solubility, and chemical resistance. Some of the most common medical uses of PVA are in soft contact lenses, eye drops, embolization particles, tissue adhesion barriers and as artificial cartilage and meniscus (9).

To the best of our knowledge, the work presented here is the first report on Er doped CaF_2 in PVA matrix in the shape of nanofibers.

In this paper, PVA/CaF_2:Er nanofiners synthesized with excellent photoluminescence properties that can be good candidate for laser application and bio-imaging.

Materials and Methods

Synthesis of PVA/CaF_2:Er nanofibers

All the materials for synthesizing CaF_2:Er nanocomposite was purchased from the Scharlau and Merck Company. CaF_2:Er nanocomposite was used in this study prepared with co-precipitation method. For synthesis PVA/CaF_2: Er nanofibers, firstly PVA was dissolved in water bath at 70ºC then CaF_2:Er nanocomposite was added to PVA solution.

The mixture was stirred until a homogeneous solution was obtained. This homogeneous solution was used to

synthesize PVA/CaF_2:Er nanofibers using electrospinning method.
We used electrospinning device model (eSpinner NF CO-N/VI) from Asian Nanostructures Company (ANSTCO) for synthesizing nanofibers.

Characterization of synthetized nanofibrs
PVA/CaF_2:Er nanofibers were character-rized with SEM images and Photolumi-nescence spectrums.

Results and discussion
Structural studies
Figure 1 shows XRD pattern of CaF_2:Er nanocomposite.

All obtained XRD peaks are indexed into the CaF_2 cubic phase of fluorite type structure with space group.
Fm3m. CaF_2 nanoparticles dope with Er^{3+} ions have the same structure as CaF_2 crystal. However, the presence of Er^{3+} ions in CaF_2 lattice leads to a little shift in the CaF_2 picks into small angle in comparison to XRD pattern of pure CaF_2 nanoparticles (10).
The average crystalline size was calculated using the Scherrer's equation is about 26-28 nm (11). Crystalline size was calculated for major peaks whose results are summarized in Table 1.

Table1. The obtained structural parameters of XRD analysis for major peaks.

2θ(deg.)	FWHM (deg.)	hkl	a (Å)	D_{XRD}(nm)
47.014	0.328	220	5.4630 5	26.664
28.267	0.292	111	5.4630 5	28.296

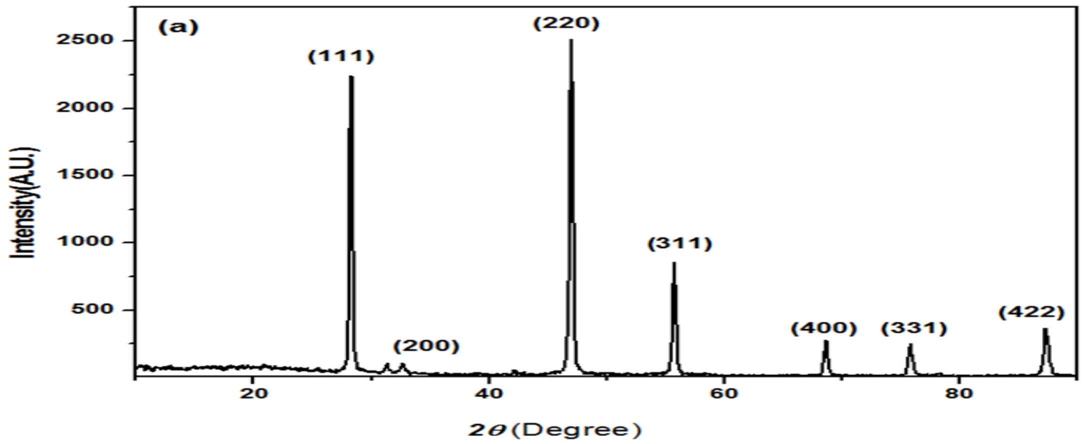

Figure 1. (a) XRD pattern of CaF_2:Er nanocomposite.

TEM (Transmission Electron Microscopy) and SEM (Scanning Electron Microscopy) images were used to observe size and morphology of the samples were taken in central laboratory of Ferdowsi University of Mashhad. TEM images of CaF_2:Er nanocomposite were recorded using a Leo 912AB transmission electron micros copy. The morphologies of PVA/CaF_2:Er nanofibers were recorded using a Leo 1450VP scanning electron microscopy.
TEM images of the CaF_2:Er nano-composite are demonstrated in Figures 2(a) and 2(b). TEM images show that the nanocrystals have approximatelyspherical shape with about 60 nm average sizes, which is consistent with XRD calculated value.

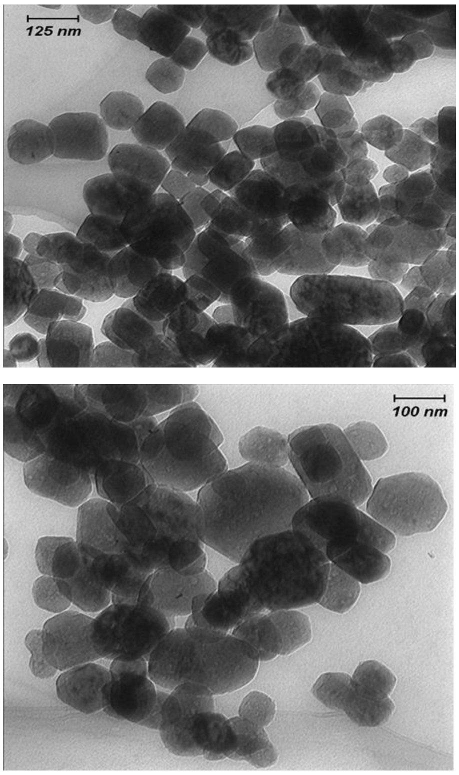

Figure 2. TEM images CaF_2: Er nanocomposite.

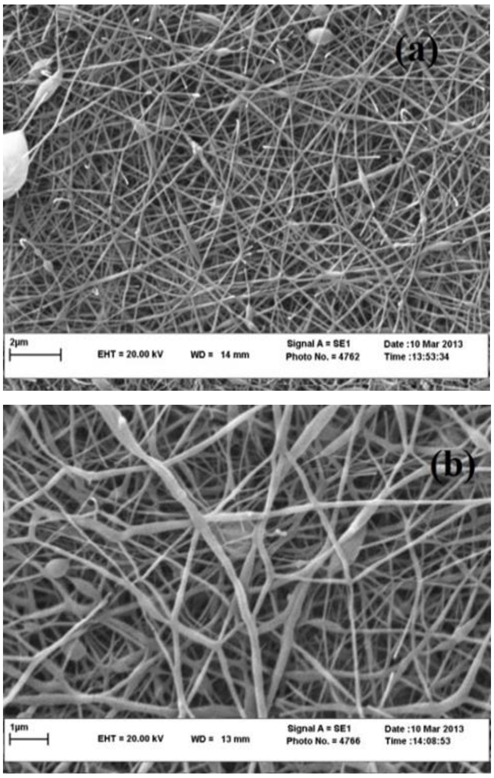

Figure 3. SEM images of PVA/CaF_2:Er nanofibers with 4% (wt%) CaF_2:Er nanocomposite (a) 20000 magnification and (b) 30000 magnification.

Figure 3 exhibit SEM micrographs of the PVA/CaF_2:Er nanofibers with different magnifications. Figures 3(a) and (b) illustrate that nanofibers formed successfully with very fine and uniform diameters. The diameters of PVA/CaF_2:Er composite nanofibers are in the range of 60-110 nm.

Photoluminescence study

Excellent up-conversion (UC) properties of PVA/CaF_2:Er nanofibers shows in Figure 4.

In up-conversion process, samples excite with low energy photons and emits high energy photons in the other words we have electron transition from the higher wavelength to the lower wavelength. Preposition ‘’Up” in UC word refers to higher energy.

This unique feature of luminescence materials makes them excellent select for bio-imaging and laser applications. PVA/CaF_2:Er nanofibers excited at different wavelengths and different electron transitions are showed. All photoluminescence spectrums show UC process. Figure 4(a) shows UC transition at 390 nm. The nanofibers excited with laser at 225 nm and shows broad peak emission at 390 nm attributed to high energy transition $^4G_{11/2}$ -$^4I_{15/2}$.

Figure 4(b) exhibit the nanofibers excited by a monochromatic source at 300 nm. Emission spectrum shows the peak at about 600 nm is attributed to $^2H_{11/2}$ /$^4S_{3/2}$-$^4I_{15/2}$ transition which is in good agreement with Bensalah et al. work (12).

Photoluminescence of PVA/CaF_2:Er nanofibers that excited at 425 nm shows in Figure 4(c).

The Er^{3+} materials that show emission primarily in $^5D_0$-$^7F_2$ (610 nm) transition are especially useful for display applications (13).

Moreover, Figure 5 shows the energy level diagram of the Er^{3+} rare earth ions that have good agreement with above transition.

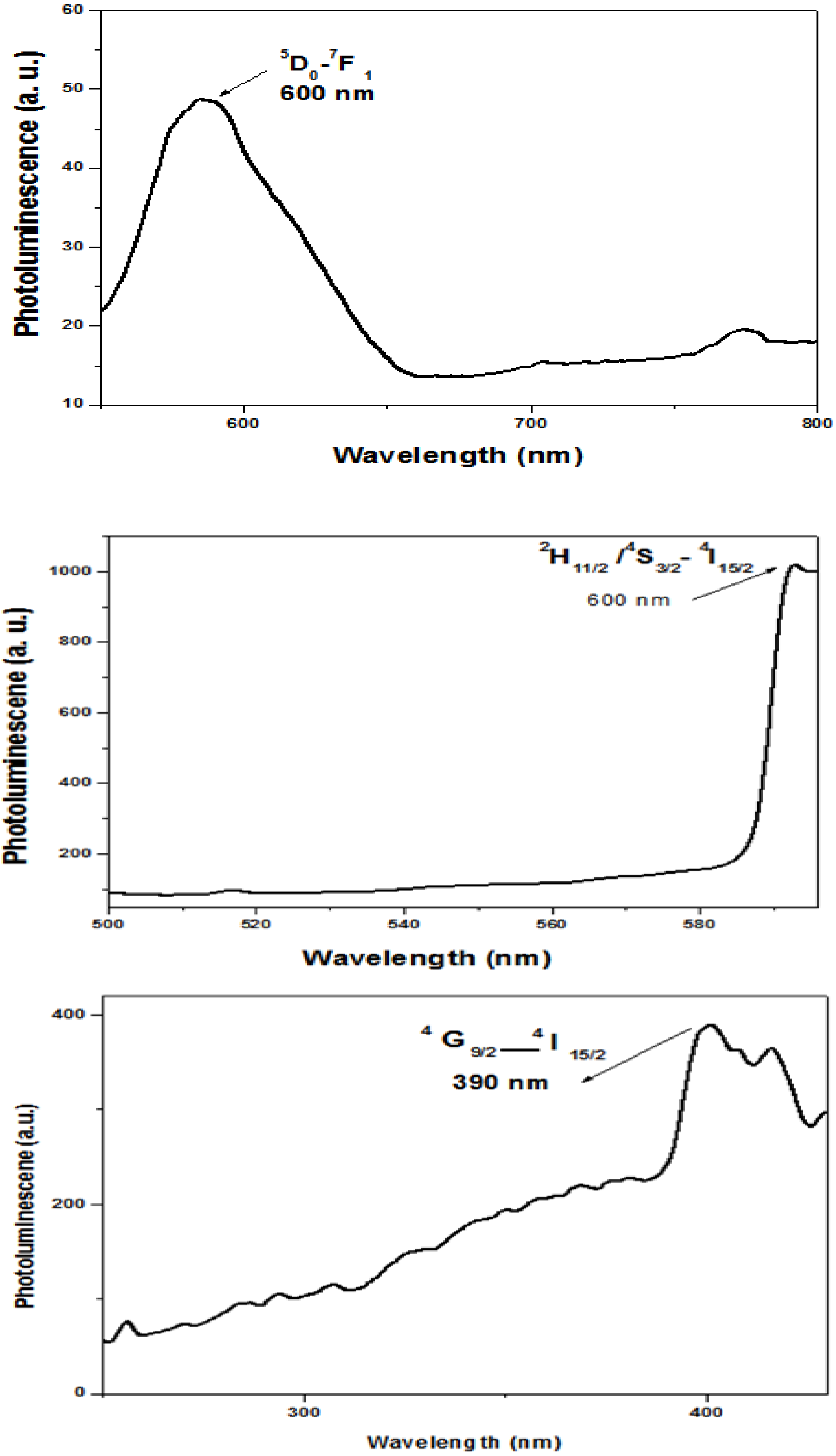

Figure 4. Photoluminescence spectrum of PVA/CaF_2:Er nanofibers excited at (a) 225 nm, (b) 300 nm and (c) 425 nm

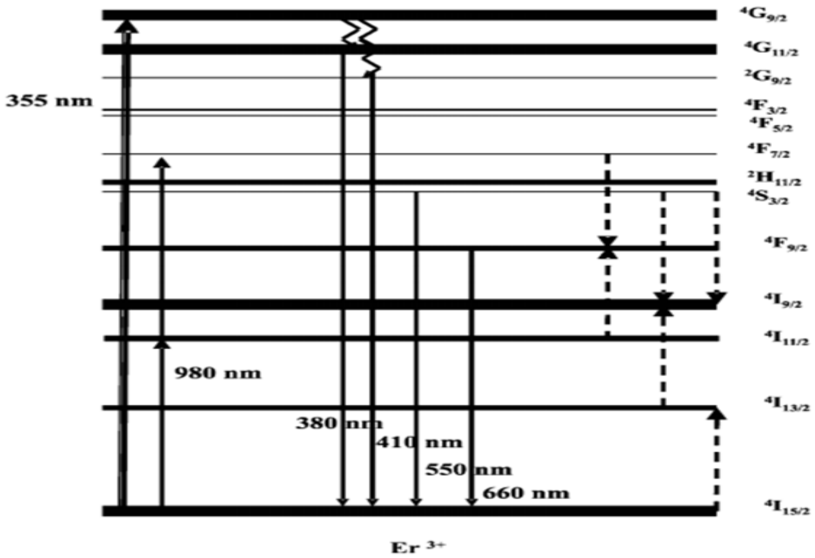

Figure 5. Energy level diagrams of Er3+ and the luminescence process.

Conclusion

In this work, PVA/CaF_2:Er nanofibers successfully synthesized by a co-precipitation and electrospinning approaches. Prepared samples were investigated by XRD, TEM, SEM and photoluminescence techniques. From XRD pattern of CaF_2:Er nanocomposites the average crystalline size was estimated using Scherrer's formula which is found to be about 26-28 nm. SEM images show that very fine and smooth PVA/CaF_2:Er nanofibers are formed with 90 nm average diameter. The presence of Er^{3+} ions in PVA/CaF_2:Er nanofibers significantly increases luminescence properties of the nanofibers. The UC luminescence spectrums show that prepared nanofibers can be good candidate for optical and laser applications in medical technology.

Acknowledgments

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