Journal of Fluorine Chemistry 182 (2016) 104–108

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

α-$NaYF_4$:Yb:Er@AlPc$(C_2O_3)_4$-Based efficient up-conversion luminophores capable to generate singlet oxygen under IR excitation

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ARTICLE INFO

Article history:
Received 8 October 2015
Received in revised form 25 December 2015
Accepted 28 December 2015
Available online 31 December 2015

Keywords:
Fluorides
Rare-earth
Luminophores
Up-conversion
Singlet oxygen

ABSTRACT

Cubic $NaY_{1-x-y}Yb_xEr_yF_4$ solid solutions which are capable of more than 4% up-conversion luminescence energy yields (excitation by 974 nm laser radiation; 1 W/cm^2 excitation power density) have been prepared for a broad range of Yb and Er concentrations. Estimates for the up-conversion luminescence energy yields for the appropriate $NaY_{1-x-y}Yb_xEr_yF_4$ solid solutions are also presented. Successful conjugation of AlPc$(C_2O_3)_4$ aluminum phthalocyanine with $NaY_{0.885}Yb_{0.1}Er_{0.015}F_4$ specimen and photodynamic activity of this conjugate under laser excitation at 974 nm have also been reported.

1. Introduction

The modern development of materials science, which has proceeded with the integration of physics, chemistry and biology, has resulted in the creation of a wide range of broadly-applicable novel compounds. One such family of materials includes inorganic fluorides. Compounds of this class that have been doped with rare earth ions are of particular interest because of their unique properties. Fluoride powders are used as precursors for the synthesis of optical ceramics [1–4], catalysts [5], white light sources [6,7], TV/computer display components, alkaline battery cathodes [8], high-efficiency solar panel components [9], up-conversion luminescence labels in medicine [10], etc.

The first studies of the latter phenomenon (i.e., up-conversion) for Yb-Er, Yb-Tm and Yb-Ho rare earth element couples were carried out by Ovsyankin [11] and Auzel [12] in the 1960s. Up-conversion transforms lower energy near-infrared radiation, which can easily penetrate biological tissues, to higher energy visible light. Alkaline, alkaline earth and rare earth fluorides exhibit highly efficient up-conversion luminescence due to their short-wave phonon matrix spectra and their ability to form solid solutions over broad composition ranges that incorporate the activating rare earth ions. Both cubic and hexagonal modifications of sodium yttrium tetrafluoride [13,14] NaYF4 are efficient luminophores which have been used for more than forty years [15–17]. However, despite significant progress in the development of up-conversion luminophores (including nanotechnology achievements of the last decade), the theoretically possible limit of up-conversion efficiency for NaYF4 has yet to be achieved. In addition, efficiency of up-conversion is not linearly dependent upon the power of the excitation source The quantum yield of up-conversion luminescence increases with the pump power density [18,19]. This dependence has the form of a quadratic function. For use in medicine need small pump density, not more than 1 W/cm2. At such densities pump power quantum yield of nanopowders less than 1%. Therefore, in order to use such luminescent nanoparticles in biophotonics at lower excitation power density levels, one should cover them with special coatings [20–23], or use plasmonic nanoparticles [24,25], or doped fluoride matrices with additional dopants (Li, Mn, Na), which distort crystalline lattices [26,27], etc. Coatings prevent quenching of up-conversion luminescence by nanoparticle surface. In reviews [28–30] describes a number of techniques, consisting in the creation of a core-shell architectures, the core - the up-conversion phosphor, and the shell-organic (e.g., polyethyleneimine, citric acid) or inorganic substances. Inorganic substances are the undoped and doped other rare earth elements matrix material or silicon.

Up-conversion fluoride nanoparticles are chemically inert; they are also stable when they are exposed to irradiation and, therefore, they can be used for the complex fluorescent immunology

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http://dx.doi.org/10.1016/j.jfluchem.2015.12.012
0022-1139/

coloring, flow-type cytometry and in vivo, in situ, ex situ biomedical visualization [31–33]. Up-conversion luminophores implemented in biomedical research should satisfy the following criteria:

- they should be capable of forming stable colloid solutions,
- their nanoparticles should be ~30–100 nm in size,
- surfaces of their nanoparticles could be functionalized,
- their up-conversion luminescence should have a relatively high energy yield,
- they should have minimal toxicity (if any), they should be stable from chemical and photochemical points of view, and they should be easily removable from the organism.

Another advantage of rare earth doped fluoride nanoparticles as luminophores, e.g., in comparison with quantum dots and/or organic dyes, is their relatively narrow luminescence lines (this is in addition to already mentioned photostability [34] and biological inertness [35–37]).

Despite the large number of publications about the synthesis and luminescence properties of $NaYF_4$, there are very few articles describing preparation of $NaYF_4$ by one of the simplest techniques, namely, by precipitation of $NaYF_4$ from aqueous solutions. The use of the latter method can lead to the sufficient cuts in the costs of $NaYF_4$ manufacturing. However, the aforementioned precipitation technique should be accompanied by strict control over the properties of the prepared specimens. These properties are important for determining the optimal synthetic conditions and sample compositions which allow maximum up-conversion luminescence energies and affect the sensitivity and outcome of biomedical studies.

Therefore, we have focused our present study, which is a continuation of our previous research [38–41], upon the determination of optimal Yb–Er concentration ratios for $NaYF_4$:Yb:Er@AlPc$(C_2O_3)_4$ (where Pc = Phthalocyanine) nanoparticles in order to provide the highest possible energy yield under 974 nm laser irradiation. Also, the present paper covers our results for the generation of singlet oxygen ($^1O_2$) under said irradiation of $NaYF_4$:Yb:Er@AlPc$(C_2O_3)_4$ nanoparticles and $^1O_2$ photodynamic activity determined by the rate of irreversible chemical quenching of $^1O_2$.

2. Experimental

X-Ray phase analysis was carried out with the use of a DRON–4 M diffractometer (CuKα_1 radiation, pyrolytic graphite monochromator, Powder 2.0 software), and scanning electron microscopy (SEM) was done with the use Carl Zeiss NVision 40 device (1 kV accelerating voltage).

We used 99.9 wt% pure NaF, 99.99 wt% pure $Y(NO_3)_3{\cdot}6H_2O$, Yb$(NO_3)_3{\cdot}6H_2O$ and $Er(NO_3)_3{\cdot}5H_2O$ (LANHIT) as well as 99.9% pure 25 kDa polyethyleneimine (Aldrich), anhydrous AlPc$(C_2O_3)_4$ (octa-4,5-carboxyphthalocyanine anhydride, NIOPIK, Moscow, Russia) and doubly-distilled water as our starting materials. All specimens were prepared by precipitation from aqueous solutions by mixing the corresponding 0.35 M aqueous rare earth nitrates with 0.35 M aqueous sodium fluoride under vigorous stirring. The filtered precipitates were then washed twice with bi-distilled water. Precipitated nanoparticles were annealed at 600 °C for 1 h. The annealing temperature was selected at this level in order to avoid phase transition of ambient temperature-unstable cubic $NaYF_4$ to the room temperature-stable hexagonal $NaYF_4$ modification [42].

3. Preparation of α-$NaYF_4$:Yb:Er@AlPc$(C_2O_3)_4$ conjugates

Annealed sub-micron α-$NaY_{0.885}Yb_{0.1}Er_{0.015}F_4$ nanoparticles were dispersed in aqueous polyethyleneimine at 60 °C under ultrasonication for 1 h, treated with 0.4 M solution AlPc$(C_2O_3)_4$ in *N*-Methyl-2-pyrrolidone at 95 °C for 3 h, centrifuged at 8000 rpm for 10 min, separated from matrix solution, and dried at 70–80 °C. In order to determine the singlet oxygen quantum yield and photodynamic activity of α-$NaYF_4$:Yb:Er@AlPc$(C_2O_3)_4$ conjugates (α-$NaYF_4$:Yb:Er nanoparticles with conjugated AlPc$(C_2O_3)_4$ photosensitizer on their surfaces), the latter were re-dispersed in water to form a corresponding colloidal solution.

4. Determination of up-conversion luminescence energy yield

Visible range up-conversion luminescence spectra, used for calculations of corresponding energy yields, were recorded with the instruments described in [43]. The latter included redesigned Avantes integrating sphere, LESA-01 Biospec spectrometer, and 1 W/974 nm continuous radiation laser. The aforementioned Avantes integrating sphere (internal diameter-50 mm) had a SMA port under its optical gate. The setup of this apparatus was modified so that the hole through which exciting radiation was introduced into the sphere (via fiber), was oriented perpendicularly with respect to both the SMA port and the sample inside the sphere. The absorption of exciting radiation by the optical fiber was accounted for by control measurement of the radiation power at the fiber output with a power meter. Radiation, scattered inside the sphere (including up-conversion luminescence), was collected and delivered via SMA/SMA fiber to LESA-01 Biospec spectrometer. Spectra acquisition and analysis were carried out by UnoMomento (Biospec) software. The spectra were normalized to the instrument function of the spectrometer and an integrating sphere.

Spectra acquisition and analysis were carried out by UnoMomento (Biospec) software specifically designed to account for effects of spectrometer hardware and integrating sphere (e.g, background, etc.). The optical scheme of the spectrum analyzer allowed the simultaneous recording of both luminescence and scattered radiation spectra within the same dynamical intensity range.

The up-conversion luminescence energy yield was calculated as follows:

$$QY = \frac{P^{Sample}_{emitted}}{P^{Sample}_{974\_absorbed}} = \frac{P^{Sample}_{emitted}}{P^{Reference}_{974\_scattered} - P^{Sample}_{974\_scattered}} \quad (1)$$

where $P^{Sample}_{974\_absorbed}$ is the output laser power, absorbed by the sample. This value is equal to the difference of the scattered

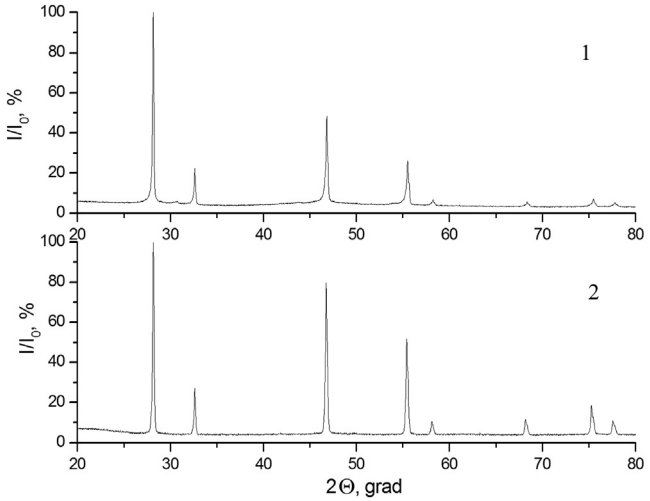

Fig. 1. X-Ray diffraction patterns for $NaY_{0.78}Yb_{0.2}Er_{0.02}F_4$ specimen before (a = 5,4856(2) Å) (1) and after (a = 5,4968(7) Å) (2) annealing at 600 °C.