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Enhanced Luminescence of Mo³⁺ Doped β -NaREF₄ Nanowires Prepared via Coprecipitation-Solvothermal Ion-Exchange Method And Their Application in Upconversion Polyurethane Composite

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Abstract

A variety of 0-20 mol% of molybdenum ions (Mo³⁺) doped sodium Rare-Earth (RE) fluoride upconversion nanowires (UCNW) were prepared by Coprecipitate-Solvothermal Ion-Exchange (CSIE) method. In this study, the Mo³⁺ doped rare-earth hydroxide [*RE*Mo(OH)₃] precursors were synthesized by the coprecipitation-solvothermal method. Following, the hexagonal phase of the Mo³⁺ doped sodium rare-earth fluoride (β -NaGdF₄: Yb³⁺/Tm³⁺/Mo³⁺) nanowires were successfully prepared by ion-exchange reaction, and checked by XRD data analysis. As shown in the EDS results, Mo³⁺ was uniformly distributed in the β -NaGdF₄: Yb³⁺/Tm³⁺/Mo³⁺. The controlled diameter (20-50 nm) and aspect ratio (20-500) values of β -NaGdF₄: Yb³⁺/Tm³⁺/Mo³⁺ nanowires strongly depend on the amount of Mo doping according to TEM images. The upconversion luminescence intensity (UC) of 10 mol% Mo³⁺ doped β -NaGdF₄: Yb³⁺/Tm³⁺/Mo³⁺ nanowires was increased by one order of magnitude under the 980 nm near-infrared (NIR) excitation in regard to the undoped sample. One-dimensional (1D) upconversion nanowires (UCNW) with 10 mol% Mo³⁺ doping gives the upconversion polyurethane (UCPU) excellent luminescent performance and about 99 % of enhanced tensile strength.

Keywords: Photoluminescence; NaGdF₄; NaREF₄; Ion-Exchange; Upconversion

1. Introduction

Lanthanides ions in luminescent materials such as NaYF₄¹, LiYF₄², BaYF₅³ present unique anti-Stokes optical properties called APTE at first ⁴ in the early age and then upconversion (UC). This fascinating property leads to wide applications in luminescent nanodevices including lasers⁵, photovoltaics⁶, detectors⁷, optical memories⁸, and biomolecules.⁹ Sodium rare-earth fluoride (NaREF₄) UC nanocrystals can be successfully prepared via sol-gel, coprecipitation, solvothermal method, etc.¹⁰ However, considering the problematic preparation process and the high price of rare-

earth (RE) chemicals, it is crucial to decrease the concentration of rare-earth ions required in the devices and if possible to increase the upconversion luminescence efficiency. Then a possible strategy proposed within this work is to replace part of the RE cations by more accessible and cheaper metal cations doping¹¹.

Although several strategies have been reported to improve luminescence of RE based nanocrystals,¹² both the luminescence intensity and high price still strongly limit the applications of rare-earth fluoride in one-dimensional (1D) materials, such as nanowires and nanotubes, which play an essential role to interconnect functional components in the manufacturing of nanoelectronics and optoelectronic devices¹³. At present, in the field of low-dimensional luminescent nanomaterials, the central research direction is toward wide-bandgap emission in semiconductors such as Si¹⁴, Ag¹⁵, GaN¹⁶, InAs¹⁷, InP¹⁸, and ZnO¹⁹. Some other works report on the preparation of nanowires using rare-earth nitrates²⁰. However, there are few studies on rare-earth chlorides to prepare NaREF₄ nanowires, especially the Mo³⁺ doped β -NaREF₄. It is particularly important to enhance UC and reduce the RE content simultaneously. In case of success, enhanced luminescence and lower price devices could facilitate the development of 1D materials as cheap, flexible display and inexpensive wearable optical devices.

In order to solve the above problem and further promote the development and application of rare-earth fluoride in one-dimensional (1D) materials, we designed and prepared ytterbium, thulium and molybdenum ions (Yb³⁺/Tm³⁺/Mo³⁺) co-doped hexagonal phase sodium gadolinium fluoride (β -NaGdF₄: Yb³⁺/Tm³⁺/Mo³⁺, or abbreviated as β -NaREM₂OF₄) nanowires via Coprecipitation-Solvothermal Ion-Exchange (CSIE) method. This study differs from the numerous works on UC nanoparticles such as for instance on sodium yttrium fluoride (NaYF₄)^{12g}. In the present work, MoCl₃ was used as Mo source for the preparation of co-doped precursor [Gd(OH)₃:Yb/Tm/Mo, abbreviated as REM₂(OH)₃]. The hexagonal phase of the β -NaREM₂OF₄ nanowires was successfully synthesized by an in-situ ion-exchange reaction²¹. The morphology and UC luminescence intensity of the β -NaREM₂OF₄ nanowires can be tunable by controlling the doping ratio of Mo³⁺. To the best of our knowledge, this is the first study on Mo³⁺ doped β -NaREF₄ nanowires and their application on upconversion polyurethane (also called UCPU).

2. Experimental Methods

2.1. Preparation of Mo³⁺ doped rare-earth hydroxide precursors²⁰.

RE₂O₃ (high purity, 99.99%) was heated to achieve complete dissolution in excess of hydrochloric acid and then transferred to a vacuum system for evaporation to give solid RECl₃. 5.0 mL of 0.8 M stoichiometric ratio of rare-earth chemical aqueous mixed with ethanol (volume ratio of water: ethanol, 2:1). Then 5.0 mL of 0.08 M of MoCl₃ (variable concentration further used

determined by the Mo^{3+} doping amount), dissolved in ethanol by ultrasound, was added dropwise to RECl_3 solution and stirred for 30 minutes. After that, a certain amount of the mixture of 30 wt% NaOH aqueous solution and absolute ethanol (volume ratio of water: ethanol, 1:1) was added dropwise to the above solution within RECl_3 and MoCl_3 until the solution reached pH 14, and a white precipitate was obtained. The colloidal precipitate was transferred to a stainless steel Teflon-lined autoclave (40 mL) and heated at 120 °C for 12 hours. After cooling to room temperature, the product was collected, washed with deionized water and ethanol, and dried in vacuum at 80 °C for 3 hours.

2.2. Synthesis of rare-earth fluoride nanowires.

In a typical synthesis, 0.38 g of NaF and 1.36 g of HCl (35 wt%) were dissolved in 25 mL of deionized water and stirred for 30 minutes, and then 0.3 g of the $\text{REMo}(\text{OH})_3$ precursors as-synthesized was added to the mixture. Finally, the mixture solution was transferred to a stainless steel autoclave and heated at 120 °C for 12 hours. After cooling, the powder samples were washed several times with deionized water and ethanol and dried in an oven at 80 °C for 2 hours.

2.3. Synthesis of upconversion polyurethane composite (UCPU).

The polyurethane is synthesized by a prepolymer method. First, $\beta\text{-NaREMoF}_4$ and polybutylene glycol (PTMG) were mixed into a three-necked flask with fast stirring for 30 minutes, then heated to 110 °C with slow stirring, and dehydrated for 2 hours. Second, the mixture was cooled down, a quantitative amount of toluene diisocyanate (TDI) was added into the mixture, and heated again to 85 °C for 3 hours. Third, a quantitative amount of oxazolidine was added to the mixture and defoamed under vacuum for half an hour. Finally, the prepolymer was coated on a PTFE mold panel to form a 1 mm thick film.

2.4. Characterizations.

X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni filtered Cu KR radiation (0.15418 nm, 40 kV, 40 mA). Transmission electron microscopy (TEM) measurements were performed on a JEOL 2011 microscope operating at 200 kV. All samples were first dispersed in ethanol and then collected using a copper grid covered with a carbon film for measurement. Energy-dispersive X-ray spectroscopy (EDS) of the samples was performed on a JEOL 2010 EDS instrument during high-resolution transmission electron microscopy (HRTEM) measurements in order to obtain the samples elemental composition. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was performed using a Perkin Elmer 7300DV apparatus. Scanning electron microscope (SEM) images were taken with a Philips XL30 electron microscope operating at 20 kV. Prior to this characterization, a gold film was sprayed onto the sample. The upconversion luminescence spectrum was measured on a spectrum analyzer (ANDO AQ6317, Japan). The sample was placed in a 1.0 cm path length support was excited with a 980 nm CW

semiconductor diode laser (Pmax 800 mW, 1000 mA). The upconversion luminescence spectrum were collected on the spectrophotometer by a multimode fiber having a core diameter of 0.6 mm. The distance between the top of the fiber and the sample is approximately 2 mm. Fourier transform infrared spectroscopy (FTIR) was used to identify the characteristic groups of UCPU. Measurements were carried out on a Thermo Nicolet Nexus 670 FTIR spectrometer, with a resolution of 4 cm⁻¹ and scanning range from 800 to 4000 cm⁻¹.

3. Results and Discussion

3.1. XRD analysis

Various compositions of 0-20 mol% of Mo³⁺ doped *REMo(OH)₃* precursors (figure 1-a) and β -Na*REMoF₄* nanowires (figure 1-c) were prepared by coprecipitate-solvothermal ion-exchange (CSIE) method²². XRD results (figure 1-a, i-v and vi-x) of the Gd(OH)₃ and *REMo(OH)₃* precursors with x mol% Mo³⁺ doping (x=0, 5, 10, 15, 20), give the characteristic peaks of *REMo(OH)₃*, similar to that of Gd(OH)₃ at different x values. The enlarged area of the main diffraction peak (201) shows that the diffraction peak shifts towards larger angles as the concentration of Mo³⁺ ions increases up to 10 mol%, and moves toward reverse angles for Mo³⁺ ion concentrations of 10–20 mol%. The peak shifting indicates that Mo³⁺ ions can be doped into the host lattice through substitution or occupation of the interstitial sites below 20 mol%^{12g}. XRD data analysis indicate that *REMo(OH)₃* has a lattice constant similar to pure Gd(OH)₃ (*a*=*b*= 6.329 Å and *c*=3.631 Å, <*α* = *β* = 90.0, *γ* = 120.0>), (PDF 83-2037). On the other hand, it appears that Mo³⁺ cations have more obvious influences than Tm³⁺ and Yb³⁺ cations closer for their atomic radius values to Gd³⁺.

The successful ion-exchange could be ascribed to the two similar phase structures of the hexagonal Gd(OH)₃ (figure 2-p) and hexagonal NaGdF₄ (figure 2-q), including the spatial distance, coordination number, and symmetry of the local RE³⁺ local sites, and the spatial arrangement of RE³⁺. There is a minimal crystal structure reorganization which is different from classical crystallization that usually occurs by dissolution-renucleation processes. The ion-exchange system in hydrochloric acid environment could be understood as the following process: when HCl and NaF diffuse into *REMo(OH)₃* nanowires, there is a three-step process: (1) H⁺ ion can first combine with OH⁻ ions, (2) Cl⁻ ions can substitute OH⁻ ions, and (3) then F⁻ ions replace Cl⁻ ions almost immediately to interact with RE/(Mo)³⁺ ions to form the more stable β -Na*REMoF₄* phase. Furthermore, because in the hexagonal Na*REMoF₄* crystals, Na⁺ ions are randomly dispersed in different sites. Therefore, they can be easily trapped into the crystals to form a more stable β -Na*REMoF₄* phase under the thermodynamic driving force effect²¹. As a result, the cation sites in the structure of β -NaREF₄ are of three types: (i) a one-fold site fully occupied by RE³⁺, (ii) a one-fold site randomly occupied by 1/2 RE³⁺ and 1/2 Na⁺, and (iii) a two-fold site occupied by Na⁺ or

vacancies stochastically. The process and results of the ion-exchange reaction are revealed by typical diffraction peaks of $REMo(OH)_3$ precursors (i), middle-product (ii, iii, iv), and β - $NaREMoF_4$ nanowires (v) in figure 1-b. The ion-exchange takes place over time. After reacting at 120 °C for 3 h, the characteristic peaks of $Gd(OH)_3$ and $NaGdF_4$ appeared in the XRD spectrum of the product at the same time; the characteristic peak of $Gd(OH)_3$ disappeared after 12 h of reaction, which was shown by figure 2-e. This phenomenon indicates that the $REMo(OH)_3$ precursors can entirely be converted to β - $NaREMoF_4$ at 120 °C for 12 h. That is, under the reaction conditions, the reaction rates of the ion-exchange systems were determined to be similar in the hydrofluoric acid environment and the hydrochloric acid environment ²¹. Besides, 0-20 mol% of Mo^{3+} doping has no negative impact on the *in-situ* ion conversion process.

As shown in figure 1-c, XRD results demonstrated that β - $NaGdF_4$ and β - $NaREMoF_4$ with Mo^{3+} doping mol% (0, 5, 10, 15, 20) nanowires were successfully synthesized, which the typical structure of the β - $NaGdF_4$ ($a=b= 6.02$ Å and $c =3.601$ Å, $\alpha = \beta = 90.0$, $\gamma = 120.0^\circ$) (PDF 27-0699). This is further correlated to the electron diffraction (ED) pattern (figure 2 k and l) which indicates that the Mo^{3+} doping does not influence the crystalline phase of the nanocrystals.

Fig. 1 XRD of (a): precursor $\text{Gd}(\text{OH})_3$ and $\text{REMo}(\text{OH})_3$. (b): Evolution of $\text{REMo}(\text{OH})_3$ to $\beta\text{-NaREMoF}_4$ with reaction time (c) $\beta\text{-NaGdF}_4$ and $\beta\text{-NaREMoF}_4$ for various Mo^{3+} compositions. All compositions are indicated in the graph. The XRD references patterns are also indicated. In inserts are presented the variation of a selected XRD peak versus Mo^{3+} composition (see comments in the text).

3.2. Composition and morphologies of the nanowires

SEM and TEM images show that $\text{REMo}(\text{OH})_3$ precursors are uniform with a smooth faceted surface. TEM images (figure 2 b-e) clearly show that the diameter of nanowires becomes smaller than that without Mo^{3+} doping, and the aspect ratio increases (20 - 500), with increasing concentration (0-15 mol%) of Mo doping. The $\text{REMo}(\text{OH})_3$ precursors with 15 mol% Mo doping show the smallest diameter (~ 20 nm) and the largest aspect ratio (~ 500), and with uniform linear shape. With 20% Mo doping, thicker and shorter nanowires appear. HRTEM images show the interlayer spacing measured to be 0.51 and 0.33 nm corresponding to the $(10\bar{1}0)$ and (0001) planes of $\text{REMo}(\text{OH})_3$ precursor (figure 2-g). The electron diffraction (ED) pattern (figure 2 g and n) recorded perpendicular to the long axis of the single nanowires can be indexed to the $[01\bar{1}0]$ zone axis of the hexagonal $\text{Gd}(\text{OH})_3$ structure with single-crystal feature. XRD patterns of as-synthesized $\text{REMo}(\text{OH})_3$ nanowires further indicated that the products are $\text{Gd}(\text{OH})_3$ hexagonal phase (space group of $P6_3/m$) with lattice constants ($a=b= 6.329$ Å and $c=3.631$ Å, $\alpha = \beta = 90.0$, $\gamma = 120.0^\circ$), (PDF 83-2037).

The morphology of NaREMoF_4 nanowires (figure 2 h-l) prepared at 120°C under solvothermal conditions for 12h is very similar to that of $\text{REMo}(\text{OH})_3$ precursors, which deduces from in-situ chemical reaction process²¹. The nanowires with 15 mol% Mo^{3+} doping show the smallest diameter (~ 20 nm) and the largest aspect ratio (~ 500), and it maintains an uniform linear shape. A typical interlayer spacing of NaREMoF_4 (NaGdF_4) with a d-spacing of 0.49 and 0.32 nm, corresponding to the $(10\bar{1}0)$ and (0001) lattice of the hexagonal phase NaGdF_4 (figure 2-m). The electron diffraction (ED) pattern (figure 2 g and n) recorded perpendicular to the long axis of the single nanowires can be indexed to the $[01\bar{1}0]$ zone axis of the hexagonal $\text{Gd}(\text{OH})_3$ structure with single-crystal feature. XRD patterns of as-synthesized $\text{Gd}(\text{OH})_3$ nanowires further indicate that the products are NaREMoF_4 hexagonal phase (space group of $P6_3/m$) with lattice constants ($a=b= 6.02$ Å and $c = 3.601$ Å, $\alpha = \beta = 90.0$, $\gamma = 120.0^\circ$), (PDF 27-0699). As shown by energy-dispersive X-ray spectroscopy (EDS), all of the involved elements including Gd, Yb, Mo, Na, F, can be detected (in figure 2-o), confirming that the Mo^{3+} ions were successfully doped in the $\beta\text{-NaREMoF}_4$ nanowires. The similar intensity of Mo characteristic peaks as shown in their EDS result at different positions on a single nanowire (similar to figure 2-o), indicates that Mo^{3+} ions are uniformly present in the matrix lattice of the nanowires, which means there is no obvious concentrated distribution. This was

as reported with other 1D structure an important step of the characterization ²³.

The actual concentration of Mo^{3+} ions within the UCNW was verified by ICP-AES results (in Table 1). The measured mass percentages of Mo^{3+} ions in the materials were 2.32%, 4.49%, 6.34% and 8.48% respectively, corresponding to the stoichiometric mole percentages of Mo^{3+} ions of 5%, 10%, 15% and 20%, and stoichiometric mass percentages of 2.66%, 5.50%, 8.65% and 11.5%, respectively. The measured values are lower than the theoretical values, indicating that a proportion of the Mo^{3+} ions is lost during the doping process ^{12g}.

As given by the similar change regulation on the morphology of $\beta\text{-NaREMoF}_4$ nanowires and $\text{REMo}(\text{OH})_3$ precursors, Mo^{3+} dopant ions inhibit the growth of $\beta\text{-NaREMoF}_4$ and that growth and faceting of $\beta\text{-NaREMoF}_4$ depend on the concentration of Mo^{3+} doped precursor ²⁴. The nanowires with 15 mol% Mo^{3+} doping show the smallest diameter (~ 20 nm) and largest aspect ratio (~ 500).

Fig. 2 (a-e) TEM images of $\text{REMo}(\text{OH})_3$ precursor with 0-20 mol% Mo^{3+} dopants. (h-l) TEM images of the NaREMoF_4 nanowire with 0-20 mol% Mo^{3+} dopants. (f, m) The HRTEM image of the part marked by yellow squares in (d, k) respectively. (g, n) Selected area electron diffraction pattern taken in $[01\bar{1}0]$ formation of the $\text{REMo}(\text{OH})_3$ precursor and NaREMoF_4 nanowire respectively. (o) EDS of NaREMoF_4 nanowire. (p, q) Schematic presentation of the hexagonal phase $\text{REMo}(\text{OH})_3$ precursor and NaREMoF_4 nanowire. Scale bars are 200 nm for panels (a-e) and (h-l), 100 nm for illustration in (k), and 2 nm for panels (f) and (m).

Table 1 Results of ICP – AES of NaREM₄F₄ nanowires (data from NaREM₄F₄ dissolved in 5 wt% nitric acid solution)

Sample	Con / mol%	Gd	Mo	Yb	Tm
NaREM ₄ F ₄	ppm	41.5135	0.0000	11.5080	0.2644
	mol %	79.50 %	0.00 %	20.00 %	0.50 %
NaREM ₄ F ₄ :5%Mo	ppm	45.9443	0.8445	13.1191	0.3014
	mol %	77.18 %	2.32 %	20.00 %	0.50 %
NaREM ₄ F ₄ :10%Mo	ppm	51.3504	1.8795	15.0869	0.3467
	mol %	75.01 %	4.49 %	20.00 %	0.50 %
NaREM ₄ F ₄ :15%Mo	ppm	60.6015	3.2112	18.2552	0.4194
	mol %	73.16 %	6.34 %	20.00 %	0.50 %
NaREM ₄ F ₄ :20%Mo	ppm	75.4216	5.5066	23.4041	0.5378
	mol %	71.02 %	8.48 %	20.00 %	0.50 %

3.3. Optical properties

In the study of the Tm³⁺ upconversion luminescence mechanism that occurs in the codoped Yb³⁺ / Tm³⁺ samples under excitation at 980 nm, blue and ultraviolet emission are more emphasized. The characteristic peaks of Tm³⁺ ions in the up-conversion emission spectrum are exhibited in figure 3-a. UV emission at ~292 nm, ~345 nm, and ~362 nm correspond to the emission corresponding the ¹I₆→³H₆, ¹I₆→³F₄, and ¹D₂→³H₆ Tm³⁺ transitions, respectively. The visible emissions at ~450 nm and ~475 nm originate from the ¹D₂→³F₄ and ¹G₄→³H₆ transitions. In the Yb³⁺ / Tm³⁺ co-doping systems, Yb³⁺ ions are first excited ²F_{7/2}→²F_{5/2} (Yb³⁺) under 980 nm irradiation from semiconductor infrared laser pumped, and then through multisteps (up to five in the case of Tm³⁺) upconversion or addition of photons could occur, until the upconversion emission from the thulium upper level ¹I₆ at 292 nm. Briefly, and as presented in figure 4-a in the first step: Tm³⁺ cations could reach the ³H₅ manifold (³H₆→³H₅), and either rapidly relax non-radiatively to the ³F₄ level (³H₅→³F₄) (or the second step could directly occur from the ³H₅ level if there is a possible resonant level, but not in that case as presented in figure 4-a). In the second step, Tm³⁺ cations in the ³F₄ level are excited to the upper ³F₂ level and rapidly relaxed non-radiatively toward the ³H₄ level (³F₄→³H₄). Following, in the third and fourth steps, population of ¹G₄ and ¹D₂ levels is achieved. For the five-photon process, the population ¹I₆ level is reached through the non-radiative relaxation from the ³P₂ manifold. Notice that the center wavelength of the strongest emission peak is at 345 nm (¹I₆→³F₄, Tm³⁺). The doping of Mo³⁺ with different concentrations does not affect the position of the UC luminescence emission peaks. The luminescence intensity enhanced with the doping concentration of Mo³⁺ increases from 0 to 10 mol% (figure 3-a and 3-b). However, when the concentration of Mo³⁺ was increased up to 20 mol%, the luminescence intensity strongly decreased. figure 3-a shows that when the concentration of Mo³⁺ is between 0 and 10 mol%, the intensities of UV and blue emission follow the same trend. This is also the case for the decrease observed for higher Mo³⁺

content (up to 20 mol%). In brief, it appears that the intensity of blue emission is about 10 times higher than in free-Mo³⁺ sample when the doping amount of Mo³⁺ is 10 mol%.

In order to better understand the variation of the UC luminescence, the effects of Mo³⁺ doping on the UC mechanism were investigated. The UC luminescence intensity vary according to the following formula ^{25, 26} :

$$I_{up} \propto (I_p)^n \text{ (Eq 1)}$$

$$\text{or } \ln(I_{up}) \propto n \cdot \ln(I_p) \text{ (Eq 2)}$$

Where n is the number of photons, I_{up} is the upconversion (UC) luminescence intensity, and I_p is the pump laser intensity. As given in figure 3-c and 3-d, the slopes (n values) obtained are 4.57 and 3.44 for the 345 and 450 nm emissions in the NaREMof₄ UCNW samples when introducing 10 mol% Mo³⁺, which are slightly smaller than the n values (4.75 and 3.62 for 345 and 450 nm, respectively) for the NaREMof₄ nanocrystals, indicating that the ultraviolet and blue emissions are five-, four- and three-photon processes for the samples with and without Mo³⁺ ions. The same behavior was observed in other samples (ESI, Fig. 1-3). The n values change slightly with the change of Mo³⁺ ions concentration and are smaller than that of the NaREMof₄ UCNW without Mo ions. It was reported that a realistic upconversion system that produces detectable upconversion luminescence would exhibit an intensity-*versus*-power dependence, which is less than the assumed I_p^n . Competition between the upconversion process and linear decay by luminescence to the ground state or relaxation into the next lower-lying state for the depletion of the intermediate excited states results in a significantly reduced slope ²⁷. A larger upconversion rate should correspond to a smaller n value, or reduced slope as the efficiency decreases with the increase number of photons. Introducing Mo³⁺ ions can increase the upconversion rate leading to the enhancement of upconversion luminescence ²⁸ to reach an optimal Yb³⁺/Mo³⁺ ratio. This phenomenon can be interpreted as a softly synergistic resonant effect on the multiphoton process in upconversion luminescence (figure 4-a for the scheme of the Mo³⁺/Yb³⁺ energy diagram), which also explains the simultaneous enhancement and attenuation of emission peaks. Another way to present the possible mechanism is that Mo³⁺ surrounding give an help to reach the upper levels but in excess the effective energy transfer processes (Yb³⁺ / Yb³⁺-Mo³⁺ → Tm³⁺) are reduced. Indeed, the enhancement of UC luminescence could be related to change in the Tm³⁺ surrounding environment with Mo³⁺ of the absorption rate of Yb³⁺ / Yb³⁺- Mo³⁺ pair under 980 nm excitation. This can explain the observed enhancement for UCNW with 10% Mo³⁺ doping, the other being the relative change in the RE content or RE (Yb³⁺/Tm³⁺ pairs) with the Mo³⁺ doping (in Table 1).

Fig. 3 (a) Upconversion luminescence of NaREMof4 UCNW doped with different Mo³⁺ concentrations (0-20 mol%) under 980 nm laser excitation; (b) The emission intensity at a specific UV/blue wavelength (292, 345, 362, 450, 475 nm) based on different Mo³⁺ doping concentrations under the same 980 nm NIR irradiation; (c) pump power dependence of the 292, 345, 362, 450 and 475 nm emission doped with 10 mol% Mo³⁺ (the others like c and d with different concentrations 5, 15 and 20 mol% of Mo³⁺ dopant ions were shown in supporting Information).

3.4. Toward applications.

For the applications we consider flexible UCNW embedded in polyurethane composite, as the non-isotropic nature of the 1D material makes it a primary candidate as reinforcement in the elastomer in addition to their optical properties. UCNW is added at first as a reinforcement tool in the process of synthesizing the polyurethane elastomer, and the UCNW reinforced polyurethane composite (UCPU) could further give excellent light-induced upconversion luminescence properties. Table 2 gives the (wt%) combination of the UCNW and polyurethane respectively. The UCPU (1-5) samples were prepared with different UCNW contents from 0 to 0.8 wt%) and was

further reworked into a wearable bracelet that showed a visible blue emission under 980 nm excitation, as shown in figure 4c (i-x). Again in the UCPU composites, sample containing 10 mol% Mo^{3+} -doped UCNW as a reinforcement UCPU shows (fig 4-c viii) more than 10 times stronger UC luminescence, which is similar to that shown in figure 3 (a-b) but with better visualization. Obviously, such UCPU could be used for security control or light source in future portable display devices. On the other hand, the tensile strength of the polyurethane material to which UCNW is added improved significantly. As shown in figure 5, when the content of NaREF_4 UCNW is 0.8 wt%, the tensile strength is about 17 MPa, which increases about 2 times compared with the polymer without UCNW as additive. The elongation at break also presented in figure 5 reaches 277%, which corresponds to an increase of 25.34%. This result indicates that UCNW imparts give bimodality as improvement of tensile strength coupled with luminescent properties.

Table 2 Content (wt%) of the UCNW and polyurethane

Sample \ Content	PU(wt%)	UCNW(wt%)
UCPU(1)	100	0
UCPU(2)	99.8	0.2
UCPU(3)	99.6	0.4
UCPU(4)	99.4	0.6
UCPU(5)	99.2	0.8

Fig. 4 (a) the energy level diagram of NaREMof_4 UCNW and the process of photoelectron transition; (b) Actual photos of UCPU composites; (c) Photos of UCPU(5) (0.8 PU wt%) where UCNW were doped with 0-20 mol% Mo^{3+} (i-v) and their upconversion luminescence in the dark under 980 nm NIR irradiation (vi-x).

Fig. 5. Tensile strength and elongation at break of UCPU compositions with (0-0.8 wt%) NaREMof_4 content.

To complete the analysis, the FTIR spectrum of UCPU (1-5) samples were measured and presented in (figure 6). The -NCO groups have completely reacted as there is no obvious characteristic -NCO stretching vibration at $2280\text{-}2240\text{cm}^{-1}$. Interestingly, free N-H stretching vibration should appear at about 3500 cm^{-1} , and hydrogen-bonded N-H should be observed at about $3300\text{-}3327\text{cm}^{-1}$. In UCPU (1-5) samples) prepared in our experiments, we observed bands at about 3304 cm^{-1} (see figure 6), this demonstrates that hydrogen bonds are formed at N-H groups. The free C=O stretching vibrations in urethane and in urea bonds are expected at $1730\text{-}1740\text{cm}^{-1}$ and $1670\text{-}1689\text{ cm}^{-1}$, respectively. However, hydrogen-bonded C=O vibrations should move to $1702\text{-}1729\text{cm}^{-1}$ and $1630\text{-}1669\text{ cm}^{-1}$.²⁹ FTIR spectrum in figure 6 also demonstrated that hydrogen bonds are formed at C=O in urethane and urea bond. The C-N stretching vibration (at 1532cm^{-1}), benzene ring skeleton (at 1600 cm^{-1}), symmetrical and asymmetric C-H (at 1851cm^{-1} and 2925cm^{-1}), C-O-C (at 1104 cm^{-1}) all these expected vibrations indicate that UCPU has the characteristic structure of polyurethane material.

Fig. 6 FTIR spectrum of UCPU with different UCNW contents

Hydrogen bonding could affect structural and mechanical properties of PU materials. According to the stretching vibration of N-H (at 3306 cm^{-1}) and that of C=O (at 1703 cm^{-1}) in 0.8 wt% UCNW content embedded in UCPU, hydrogen-bonded N-H and C=O are the interface forces between UCNW and PU. As expected with such low doping content; no clear variation is observed on the FTIR spectrum with increasing UCNW content from 0 to 0.8%. On the other hand, the stretching vibrations of other groups (such as C-H, C-O-C) did not show significant shifts either, even in the case of adding different UCNW content, which proves that the molecular structure of UCPU will not be apparent due to the addition of UCNW Variety.

4. Conclusions

Various contents in the range 0-20 mol% of molybdenum ions (Mo^{3+}) doped sodium rare-earth (RE) fluoride $\beta\text{-NaREMof}_4$ RE being trivalent Gd/Yb/Er nanowires (UCNW) were prepared by coprecipitate-solvothermal ion-exchange (CSIE) method and present upconversion properties. As main results, one observe that Mo^{3+} was uniformly doped into the $\beta\text{-NaGdF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mo}^{3+}$ lattice at 120 ° C without the need for higher temperatures preparation. 10 mol% Mo^{3+} -doped $\beta\text{-NaGdF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mo}^{3+}$ upconversion nanowires (UCNW) exhibit significant enhanced UC luminescence at 345 and 450 nm. We also notice that the aspect ratio of the $\beta\text{-NaGdF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mo}^{3+}$ UCNW can be controlled by adjusting the injection amount of molybdenum source. For a morphological point of view, shortest diameter (~ 20 nm) and largest aspect ratio (~ 500) were both obtained for 15 mol% Mo^{3+} doped UCNWs. In addition $\beta\text{-NaGdF}_4\text{:Yb}^{3+}/\text{Tm}^{3+}/\text{Mo}^{3+}$ nanowires could be used as reinforcement in a so-call composite to give for 0.8 wt% of $\beta\text{-NaREMof}_4$ nanowires embed in PU

about 99% enhancement of tensile strength and 25.34% of increased elongation at break and excellent luminescence performance.

This work proposes the use of Mo^{3+} doping strategy to enhance the luminescence intensity of lanthanide-doped nanowires. Mo^{3+} doped UCNW elaborated via the CSIE method broaden application prospects for 1D rare-earth fluoride.

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