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Up-converting ALD/MLD thin films with Yb³⁺,Er³⁺ in amorphous organic framework

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Abstract

Near-infrared to green and red up-conversion is reported for a new type of hybrid (Yb,Er)-IR-806 films prepared using the atomic/molecular layer deposition (ALD/MLD) thin-film fabrication technology. These amorphous films can be realized in controllable nanothicknesses and they show an exceptionally wide absorption band in the near-infrared region. The films exhibit a highly local upconversion excitation process, which suggests strong potential for use as e.g. temperature sensors with Ångström scale surface resolution.

Keywords

upconversion luminescence; inorganic-organic hybrids; thin films, atomic/molecular layer deposition

Introduction

Up-conversion is a special case of luminescence where lower energy photons are piled up to create higher energy emission [1]. Materials showing this property are currently intensively studied for bioanalytic applications to be used in e.g. assays [2], photoactivation [3], microscopy [4], nanoscopy [5] and imaging [6]. For these applications it is crucially important that the excitation can be realized within the transparency window of tissue [7], i.e. with near-infrared (NIR) radiation. Also, once the excitation occurs in the NIR range, the excitation and detection are well separated in the energy scale and thus there are no autofluorescence effects [8] that need to be accounted for. Another highly important prospective field of application for the NIR-to-visible up-converters is in photovoltaics [9], because a major part of the sun's spectrum on earth's ground level is in the infrared region, which cannot be utilized by the present solar cells. If this part of radiation could be taken to use for energy production the performance of the solar energy conversion devices could be considerably enhanced. Some advances have been reported in this field (see e.g. [10–14]), but the efficiency of present up-converters still needs to be improved to enable practical applications in solar energy conversion.

In order to enhance the efficiency in bioanalytics, the emitting sites in the up-conversion systems should be brought as close as possible to the analytes' active sites. This is difficult with the current state-of-the-art inorganic up-converters, as they have only a fraction of their emitters on the crystal surface while a considerable fraction of the emitters is in the bulk of the crystal, even in nanocrystals. An obvious way to overcome these limitations would be to use molecular up-converters, where the organic ligands would function as a short bridge between the up-converting ion and the analyte. In an optimal case the ligands could additionally act as antennas to enhance the absorption of the excitation radiation [11]. However, the problem with conventional molecular metal-organic up-converters is that the

organic ligands have a strong tendency to quench the up-conversion via multiphonon de-excitation [15]. Despite this, there are reports of up-conversion in molecular compounds [16]-[21].

Recently we demonstrated exciting luminescence and up-conversion properties for lanthanide (Ln) based inorganic-organic hybrid materials fabricated by the currently strongly emerging atomic/molecular layer deposition (ALD/MLD) thin-film technique [22]-[24]. Through ALD/MLD it is possible to realize novel hybrid materials with molecular assemblies and bonding schemes not necessarily accessible with other synthesis techniques [25]-[27]. This technique is derived from the state-of-the-art industrial-scale gas-phase thin-film deposition technique, *i.e.* ALD (atomic layer deposition), mostly utilized for growing high-quality thin films of simple inorganic materials [28]. In ALD for the binary inorganic thin films the two gaseous/evaporated/sublimated precursors are sequentially pulsed into the reactor; these precursor pulses are separated by an inert gas pulse to achieve self-saturated gas-surface reactions and the atomic-level control of the growth of the thin film. The MLD (molecular layer deposition) technique is an analogous way to ALD to produce purely organic thin films [29]. For the combined ALD/MLD technique for the inorganic-organic thin films ALD cycles are combined with MLD cycles [30]-[33]; this enables the atomic/molecular layer-by-layer growth of hybrid thin films with high precision for the film thickness and composition. There are several other advantages that are inherent to both ALD and MLD, such as the possibility to use sensitive substrates with complex surface architectures, such as polymers, textiles or biomaterial [34–37].

In this work, we report novel ALD/MLD-grown up-converting ($\text{Yb}^{3+}, \text{Er}^{3+}$)-based hybrid thin films; we employ the so-called IR-806 molecule [10] as a NIR-absorbing organic ligand. Previously, this dye has been reported to enhance up-conversion when attached to $\text{NaYF}_4:\text{Yb}, \text{Er}$ particles [11]. Also, the dye has been successfully used as an antenna to enable

up-conversion from the $\text{Er}(\text{TTA})_4(\text{IR-806})$ ($\text{TTA} = 2\text{-thenoyltrifluoroacetone}$) complex [17]. Here we show for the first time that IR-806 can be directly coupled to Yb^{3+} and Er^{3+} ions to construct an up-converting system.

Experimental Section

Thin-film depositions: The thin films were deposited from the in-house prepared precursors of $\text{Yb}(\text{DPDMG})_3$, $\text{Er}(\text{DPDMG})_3$ ($\text{DPDMG} = \text{N,N}'\text{-diisopropyl-2-dimethylamido}$ guanidinato) and IR-806, see Figure 1 for the schematic molecule structures. $\text{Er}(\text{DPDMG})_3$ was prepared as reported earlier [38], and $\text{Yb}(\text{DPDMG})_3$ was synthesized with the same procedure; both syntheses were scaled up to a batch size of 10 g. IR-806 was obtained from a reaction of 2-[2-[2-chloro-3-[(1,3-dihydro-3,3-dimethyl-1-propyl-2*H*-indol-2-ylidene)ethylidene]-1-cyclohexen-1-yl]ethenyl]-3,3-dimethyl-1-propylindolium iodide and 4-mercaptobenzoic acid as reported earlier [10]. Before their use in the depositions, the two Ln precursors were mixed into a homogeneous mixed powder, with the atomic Yb/Er ratio of 98/2. This Yb/Er ratio was chosen to ensure effective NIR absorption (high Yb content) and restrain the probability of concentration quenching (low enough Er content).

Figure 1. Schematic structures of the precursor molecules used in this work: $(\text{Yb,Er})(\text{DPDMG})_3$ (left) and IR-806 (right).

The depositions were carried out on silicon(100) substrates in a commercial ALD reactor (F-120 by ASM Microchemistry Ltd.). During the depositions, both the (Yb,Er)(DPDMG)₃ and IR-806 precursor powders were kept in glass crucibles inside the reactor, at the elevated temperatures of 130 and 245 °C, respectively, for an efficient sublimation. During the depositions the pressure inside the reactor was kept within 2–4 mbar and nitrogen (>99.999%; Schmidlin UHPN 3000 N₂ generator) was used as a carrier and purging gas. Note that we carried out a thermogravimetric (TG) measurement under vacuum conditions (Perkin Elmer TGA7; pressure 4 mbar, heating rate 2 °C/min) for the IR-806 powder to corroborate the chosen precursor heating temperature; the TG data showed a single sharp evaporation/sublimation step at around 219 °C with a mass residue less than 10 %. With the aforementioned precursor supply temperatures, we then fixed the precursor pulse/purge sequence based on preliminary experiments as follows: 3 s (Yb,Er)(DPDMG)₃ / 5 s N₂ / 3 s IR-806 / 10 s N₂ [39,40]. After testing the temperature range of 250–280 °C, the deposition temperature was fixed to 280 °C for the final depositions.

Finally, since the IR-806 precursor molecule is remarkably heavy (C₄₃H₄₉N₂SO₂I) [10] and thus required a relatively high temperature for the sublimation, there was a concern that it may partially decompose/be fragmented upon the evaporation. In an attempt to address this concern, we carried out preliminary Rutherford backscattering spectroscopy nuclear reaction analyses (RBS/NRA) for the elemental composition (except H) in the hybrid thin films. These experiments confirmed – within the accuracy of the analysis – the expected atomic ratios for C, N, S and I; however, the O and Ln amounts were considerably higher, which could be due to (i) cleavage of the organic molecules from the film surface, (ii) oxidation during the storage of the film in ambient air, and/or (iii) partial fragmentation of the IR-806 precursor.

Characterization techniques: The film thicknesses were determined from X-ray reflectivity (XRR) patterns collected with Panalytical X'Pert MPD Pro Alfa 1 equipment. The same equipment was used for grazing incidence X-ray diffraction (GIXRD) measurements to investigate the film crystallinity. Nicolet Magna-IR Spectrometer 750 was used to collect Fourier transform infrared (FTIR) spectra for the samples; 32 scans with 4 cm^{-1} resolution were applied for each sample. Absorbance measurements were carried out with PerkinElmer Lambda 950 UV/Vis/NIR absorption spectrophotometer for films grown on quartz. For the up-conversion emission spectra and power curves, the emission was excited with an Optical Fiber Systems IFC-975-008 NIR laser operated at 974 nm. The measurements were carried out using an Avaspec-HS-TEC CCD spectrometer. A long-pass filter (edge at 900 nm, Edmund Optics) was used to cut off any higher-energy harmonics from the laser. The emitted light was collected at a 90° angle to the excitation and directed through a short-pass filter (edge at 900 nm, Newport 10SWF-900-B) to remove the scattered excitation radiation. The emission was collected through an optical fiber (600 μm diameter). The up-conversion decay curves were measured using a FLS980 Fluorescence Spectrometer from Edinburgh Instruments. 975 nm continuous wave semiconductor laser diodes (excitation peak width: 4 nm) were used as the excitation source. The diodes were modulated by the spectrometer at a repetition frequency of 300 Hz using an excitation pulse length of 25 μs . The emission arm was supplied with a ruled grating of 1800 lines/mm blazed at 750 nm. The spectral resolution was 0.5 nm. All up-conversion measurements were carried out at room temperature.

Results and Discussion

Our ALD/MLD process based on the sequential pulsing of the (Yb,Er)(DPDMG)₃ and IR-806 precursors yielded visually homogeneous thin films in a highly reproducible manner. In our preliminary experiments we investigated the process at different temperatures to find out

that the films grew in an essentially similar manner independent of the deposition temperature at least in the temperature range investigated, see Figure 2(a). The observed relatively high film growth rate, i.e. the GPC (growth-per-cycle) value of ~ 2.5 Å/cycle, is typical for well-behaving ALD/MLD processes involving large-sized organic components; for example for the ALD processes of purely inorganic lanthanide oxide films the GPC values are typically more than an order of magnitude lower. For the rest of the experiments we fixed the deposition temperature to 280 °C. At this temperature we then confirmed that the film growth is linear as expected for an ALD/MLD process, i.e. the film thickness is precisely controlled by the number of deposition cycles, see Figure 2(b). In the rest of the experiments we used 39 nm thick films grown with 150 ALD/MLD cycles.

Figure 2. Confirmation of the controllability of our (Yb,Er)(DPDMG)₃+IR-806 ALD/MLD process: (a) the essentially constant film growth rate (i.e. growth-per-cycle or GPC value of ~ 2.5 Å/cycle) at different deposition temperatures in the range of 250–280 °C, and (b) the linear dependence of the resultant film thickness on the number of ALD/MLD cycles applied (deposition temperature fixed at 280 °C). The film thickness/GPC values are from XRR data.

All the films yielded from the (Yb,Er)(DPDMG)₃+IR-806 process were found amorphous from the GIXRD examination; this is not unusual, as majority of the ALD and ALD/MLD films are amorphous [32]. The films moreover seemed to be of low density, as expected for

hybrid metal-organic films with spacious organic ligands. We estimated the film densities based on the so-called critical angle in the XRR patterns: the higher the angle the denser the film [41]. While calculating the absolute density values was considered unfeasible, we compared the critical angles observed for the present hybrid films (ca. 0.20°) with that (ca. 0.35°) reported in our earlier study for $(\text{Yb,Er})_2\text{O}_3$ films grown by ALD [42]. The clearly lower critical angle in the present case indeed is an indication of the considerably lower density of our hybrid (Yb,Er)-IR-806 thin films.

For the bonding structure in our hybrid (Yb,Er)-IR-806 thin films, valuable information was obtained from the FTIR spectra. When the hybrid thin film is formed through sequential surface reactions between the two precursors, $(\text{Yb,Er})(\text{DPDMG})_3$ and IR-806, the DPDMG ligands are expected to be removed from the Ln precursor when the IR-806 molecules bind to the (Yb,Er) ions through their functional groups. This is what can be concluded from Figure 3(a), where we show FTIR spectra both for our (Yb,Er)-IR-806 thin-film sample and the $(\text{Yb,Er})(\text{DPDMG})_3$ and IR-806 precursor powders. Firstly, the spectrum for the thin film does not show any indication of the presence of the DPDMG ligand. Secondly, the spectrum for the hybrid thin film shows several ($\text{C}=\text{C}$ benzene skeleton vibration at 1542 cm^{-1} , $\text{C}-\text{H}$ bending vibration at 1422 cm^{-1}) but not all of the features seen for the IR-806 molecule. The most evident difference is the disappearance of the representative peak of IR-806 at around $2800\text{--}3000\text{ cm}^{-1}$ due to the OH group apparently owing to the bonding of the Ln cations to the IR-806 backbone via the oxygen atoms from the OH groups (replacing the protons from these groups). Vibrations observed for IR-806 within the region of $1686\text{--}1697\text{ cm}^{-1}$ are the characteristic absorption bands of $\text{C}=\text{O}$ belonging to the free carboxylic acid ligands of IR-806; these are not seen for the hybrid thin film, while the characteristic feature of COO^- appears at around 1589 cm^{-1} suggesting that oxygen atoms of carboxylate are bonded to Ln. Furthermore, the peak at 1245 cm^{-1} due to the $\text{C}-\text{N}$ stretching vibration in the pure IR-806

dye disappears and a new peak at 1107 cm^{-1} appears upon the (Yb,Er)-IR-806 hybrid formation, which could be taken as an indication that nitrogen is involved as well when the IR-806 molecule is coordinated to the Ln^{3+} cations [43]. Finally the peak at 609 cm^{-1} confirms that the Yb-O and/or Yb-N bonds are formed in hybrid thin films [24].

Figure 3. (a) FTIR spectra for the (Yb,Er)-IR-806 thin film and for the IR-806 and $\text{Yb}(\text{DPDMG})_3$ precursor powders for comparison. (b) Vis-NIR absorption spectra for the (Yb,Er)-IR-806 thin film (specifically grown on a quartz substrate) and the IR-806 precursor.

In Figure 3(b) we also display the UV-vis absorption spectra for both our (Yb,Er)-IR-806 thin film and the IR-806 precursor. A wide absorption band extending from 660 to well above 1000 nm can be observed for the thin film. This can be taken as the combination of absorption from the IR-806 and Yb^{3+} albeit the contribution from Yb^{3+} should be far less because of its much smaller absorption cross-section. It can be seen that the absorption peak seen at 806 nm for IR-806 shifts to 878 nm for the hybrid thin film. Since the length of conjugated polymeric chains affects the absorption energy in such way that the longer is the chain the lower is the absorption energy [44], this shift may be due to the IR-806 in the film being more polymeric than those in the IR-806 precursor.

The NIR absorption band for our (Yb,Er)-IR-806 thin film is far wider than those reported before for samples where IR-806 is coupled e.g. to NaYF₄:(Yb,Er) particles [11] or to an erbium 2-thenoyltrifluoroacetone complex [17]. Therefore, our hybrid thin-film material is in principle a promising candidate for efficient harvesting of NIR radiation. In Figure 4a we display the resultant visible-range up-conversion luminescence spectrum when the film is excited at 973 nm. Indeed, the material shows efficient green and red up-conversion emissions typical for trivalent erbium. These emission peaks correspond to the $^2H_{11/2}, ^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er³⁺, respectively [1].

Figure 4. Up-conversion emission (973 nm excitation) (a) spectrum, (b) excitation power dependence, (c) ETU mechanism, and (d) decay curves for the (Yb,Er)-IR-806 thin film. The insets in (d) show a zoom-in to the rise part in linear intensity scale. Rise curves of the excitation pulse (blue curves) are included, as well.

The power dependence curves (Figure 4b) give slopes of 1.5 (green emission) and 1.8 (red emission) indicating that both emissions involve the stacking of two photons [45]. This two-photon stacking can proceed by two ways in the present materials (Figure 4c): (i) Energy transfer up-conversion (ETU): Yb^{3+} absorbs the first excitation photon through the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition and the energy is transferred to Er^{3+} which thus is excited to the $^4\text{I}_{11/2}$ state. Next, this excited state absorbs a second photon promoting Er^{3+} to the $^4\text{F}_{7/2}$ state. (ii) Ground state absorption followed by excited state absorption (GSA + ESA): The first photon is absorbed directly by Er^{3+} through the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ transition. Then, this excited state absorbs a second photon promoting Er^{3+} to the $^4\text{F}_{7/2}$ state. In both cases, (i) and (ii), the $^4\text{F}_{7/2}$ state relaxes nonradiatively to the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and/or $^4\text{F}_{9/2}$ states, which finally relax to $^4\text{I}_{15/12}$ yielding the green and/or red light emission.

For the red emission in $(\text{Yb}^{3+}, \text{Er}^{3+})$ co-doped systems, a three-photon process is also possible, e.g. in $\text{NaYF}_4:(\text{Yb}, \text{Er})$ crystals [46][47]. The mechanism involves the same two steps as in the two-photon processes; the third photon then raises Er^{3+} to the $^4\text{G}, ^2\text{K}$ manifold (at ca. 385 nm, 26000 cm^{-1}). This is followed by a back energy transfer to the Yb^{3+} ground state $^2\text{F}_{7/2}$ relaxing Er^{3+} at the red-emitting $^4\text{F}_{9/2}$ state. However, our results suggest that there are only two photons involved in this process for the (Yb, Er) -IR-806 thin film.

The decay curves of the up-conversion emission measured at 550 (green) and 660 nm (red) indicate that the overall lifetimes of both emissions lie in the microsecond range that is typical of up-converting ionic inorganic materials [48] (Figure 4d). Both emissions decay in a quite similar bi-exponential fashion with the faster component of 113 μs (44 % amplitude) for green and 109 μs (55 %) for red and slower component of 274 μs (56 %) for green and 323 μs (45 %) for red. The fact that the decays include two components indicates that there

are two different processes or luminescence centers involved in the up-conversion mechanism.

Generally, the lifetime of up-conversion emission initiated via ETU is longer than that involving GSA + ESA [49]. However, previous literature on the up-conversion emission lifetimes in Er^{3+} or $\text{Er}^{3+}/\text{Yb}^{3+}$ containing molecular systems appears to be non-existing thus allowing no comparison with existing data. To get more information on the possible mechanism, we examined also the rise part of the curve. However, the excitation pulse length used in the present work (25 μs) is longer than is typical of all the time constants involved in up-conversion energy transfer. Thus, it is not possible here to use either the rise or decay parts to unequivocally judge the mechanism of up-conversion [49]. We observe that it takes ca. 5 μs to reach saturation in the excitation, which is much slower than the rise of the excitation pulse (Figure 1d, insets). Such a rise time of a few microseconds during the excitation pulse can be associated with both ETU and GSA + ESA in ionic systems as shown by e.g. Francini et al. [50]. However, it must be noted that for ionic Yb/Er systems the ETU rise time can extend up to the millisecond range as shown in e.g. [51–53]. Thus, we conclude that the mechanism may be either one of these or a mixture of them.

Because the f-f transitions are forbidden, the critical distance for non-radiative energy transfer to occur lies within a range of ca. 5–8 Å [54]. The IR-806 ligands can be assumed to be more or less planar because of their extended conjugated bonding, which means that the size of the IR-806 molecule is around 5 Å x 10 Å. We tentatively believe that one IR-806 ligand is bonded to two Ln cations, through the N and O atoms as suggested by the FTIR results, resulting in an interatomic distance below 5 Å for these two lanthanides. Such a structure is in agreement with the presence of the ETU mechanism. Additionally, the large size of the IR-806 molecule in comparison with the 5–8 Å critical distance suggests that each lanthanide pair is separated from the next nearest lanthanide pair by more than this critical

distance. We thus suggest that the absence of the third photon involvement in our (Yb,Er)-IR-806 thin films (i.e. the power dependence slopes are lower than 2) could be due to the formation of such isolated lanthanide pairs in the films; owing to this the energy transfer between Yb^{3+} and Er^{3+} takes place only locally such that the probability for the piling up of a third photon is low. Interestingly, this could possibly be utilized in applications where highly position-sensitive monitoring of NIR radiation is required. For example, it is known that the intensity ratio of the green up-conversion emission peaks is sensitive to temperature and that this ratio can be used as a temperature sensor [55]. Thus, combining the short energy transfer range with the temperature sensitivity of the intensity ratio of the green emission peaks, these materials could be used as thermometers with Ångström scale resolution. This would be an order of magnitude higher resolution than possible with up-converting nanocrystals.

Finally we discuss the possible role of IR-806 in the absorption and energy transfer processes in our (Yb,Er)-IR-806 thin films. As IR-806 absorbs around 800 nm, we tested also if the Er^{3+} up-conversion emission could be obtained through the absorption of the IR-806 ligands and a subsequent energy transfer to the $^4\text{I}_{11/2}$ state of Er^{3+} or the $^2\text{F}_{5/2}$ state of Yb^{3+} as proposed earlier for $\text{NaYF}_4\text{:}(\text{Yb,Er})$ crystals coated with IR-806 [11] and also for a $\text{Er}(\text{TTA})_4(\text{IR-806})$ complex [17]. Here, we do not observe any up-converted emission with excitation at 800 nm for the (Yb,Er)-IR-806 thin film. This implies that there is either no energy transfer from the ligands to the $\text{Yb}^{3+}/\text{Er}^{3+}$ ions or the lifetime of the excited IR-806 is not long enough to allow the stacking of the photons. In the case of $\text{NaYF}_4\text{:}(\text{Yb,Er})$ particles coated with IR-806, it was reported that the optimal center-to-center distance for the IR-806 molecules was 3.4 nm, whereas shorter distances would result in self-quenching within the IR-806 molecules [56]. For our (Yb,Er)-IR-806 thin films, the distance is expected to be much shorter and thus we propose that self-quenching within the IR-806 will be the main

mechanism hampering the excitation of $\text{Yb}^{3+}/\text{Er}^{3+}$ up-conversion at ca. 800 nm. Decreasing the self-quenching will thus be the topic of a future study.

Conclusions

We have presented the successful preparation of (Yb,Er)-IR-806 thin films by using the ALD/MLD technique. This technique allows the growth of hybrid thin films with an atomic/molecular level of control for the film thickness through sequential pulsing of the (Yb,Er)(DPDMG)₃ and IR-806 precursors; from FTIR data the films are shown to grow via Ln(Yb,Er)-O and (Yb,Er)-N bonds between the Ln cations and IR-806 molecules. These unique hybrid materials show a very wide absorption in the red-NIR region indicating high potential for use in harvesting red and NIR radiation. Although direct excitation on the IR-806 molecules does not yield emission, when excited at 973 nm, the films show efficient up-conversion emission that is highly local. We envision that in the future, the films can be used as e.g. thermometers with Ångström scale resolution.

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