Nanofibers coated with Rare-Earth complexes

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Abstract

Crystals and fibers doped with Rare Earth (RE) ions provide the basis to most of today’s solid-state optical systems, from the laser and telecom industries, to emerging potential quantum applications such as quantum memories and optical to microwave conversion. The two platforms, doped crystals and doped fibers, seem nearly mutually exclusive, each having their own strengths and limitations – the former providing high homogeneity and coherence, and the latter offering the advantages of robust optical waveguides. Here we present a hybrid platform that does not rely on doping but rather on coating the waveguide - a silica nanofiber - with a monolayer of RE complexes. We describe the synthesis and assembly of the complexes’ monolayer, as well as the characterization, and their application to tailor-fabricated nano-fibers. We present
optical measurements with Yb-coated nanofibers at 300K, exhibiting fluorescence times of 0.9 ms similarly to doped inorganic crystals, and spectral linewidth of 6 nm. This scheme is general to all RE ions and oxygenated surfaces, which renders its feasibility to many applications of photonics, quantum optics and microwave.

Introduction

Rare-earth (RE) ions, or Lanthanides (Ln), are one of the major backbones of today’s laser and amplifier systems, and are the enabling platform of a wide variety of applications and industries. The partially-filled 4f shell of all the RE$^{+3}$ ions is shielded from the environment by the outer 5s and 5p shells, thereby reducing the influence of the host lattice on intra-shell f-f transitions. As a result, RE ions exhibit sharp absorption and emission spectral lines even when located inside a solid-state matrix or a complex, with f-f transition wavelengths ranging from microwave to optical and UV. Accordingly, RE-doped crystals are the key building block in most solid-state lasers and amplifiers, and RE-doped fibers provide the basis for practically all fiber lasers, leading to a wide range of applications from telecommunications, to laser designators and radar systems (LIDARs). Notably, the two major platforms for interfacing RE ions with light rely on doping the host material – either crystals or fibers. Each of these platforms exhibits its own physical properties and advantages. While RE-doped crystals can enable low inhomogeneity and high coherence, RE-doped fibers offer the efficiency and practicality of a confined optical waveguide. Efforts to reconcile the two approaches have proved to be nontrivial. The amorphous silica of optical fibers exhibits large inhomogeneity and spectral diffusion due to dynamic charges and two-level systems that do not freeze even at 100 mK, leading to large inhomogeneity and low coherence times. Fabrication of waveguides based on RE-doped crystals requires Focused Ion beam (FIB) milling and similar techniques. Fabrication of waveguides from doped crystals is possible by the introduction of a secondary dopant into the lattice for instance. This process reduces memory time in comparison to a bulk doped crystal due to the additional strain. The
effort of coherently incorporating RE ions into a single-mode waveguide platform is perhaps mostly significant in the field of quantum information, where RE-doped crystals were already harnessed to demonstrate quantum optical memories,\textsuperscript{13-17} and are also the basis for optical-to-microwave qubit conversion proposals.\textsuperscript{18} One of the most advanced platforms in this direction is a nano-photonic cavity fabricated in a YVO\textsubscript{4} crystal doped with Nd\textsuperscript{+3} ions exhibiting long coherence time and narrow inhomogeneous broadening,\textsuperscript{19} which has been harnessed to demonstrate a quantum memory,\textsuperscript{20} a cavity protected interface between RE and photonic qubits,\textsuperscript{21} and a readout of photonic qubit stored in a single ion in a single shot measurement.\textsuperscript{22} Purcell enhancement was demonstrated with a ring resonator fabricated in Yb-doped silicon nitride.\textsuperscript{23,24} Other approaches to develop material qubits such as doped nanocrystals\textsuperscript{25} and nanoparticles\textsuperscript{26,27} have been investigated as well, including molecular complexes of transition metals\textsuperscript{28-30} and lanthanides.\textsuperscript{31-34} In particular, lanthanide complexes proved useful for many other applications including probes,\textsuperscript{31,33} immuno assay,\textsuperscript{34,35} OLED,\textsuperscript{36} MRI labels,\textsuperscript{37} and NIR fluorophores.\textsuperscript{38,39} Lanthanide deposition via vapor deposition,\textsuperscript{40} and Self-Assembled Monolayers (SAMs) of lanthanide complexes have been reported as well.\textsuperscript{41-43} Most recently, lanthanide complexes have been considered also for and coherent light-spin interfaces and photonic quantum technologies.\textsuperscript{44,45}

Here we present an alternative approach based on tapered optical silica fibers, an approach which is applicable to all RE ions and does not involve doping the raw material or custom-fabrication process of the waveguide. Tapered nanofibers are optical fibers that were stretched to a sub-wavelength waist diameter, thereby enabling coupling light to emitters within their evanescent field. In particular, such nanofibers have already been used to couple light to crystals of molecular dyes addressing a single dye molecule.\textsuperscript{10}

Specifically, we functionalize the surface of a nanofiber tapered from a commercial fiber with a monolayer of self-assembled complexes, each containing a single RE ion. The device proposed here is depicted in Figure 1.
Results and discussion

Our RE complex

The device explored in this study is composed of a tapered optical fiber coated with a monolayer of organic complexes (Fig. 1), each encapsulating a single RE ion. A suitable complex for this purpose must have intrinsic quantum yield approaching unity and long coherence times. Both can be achieved by surrounding the RE ion with a carefully tailored environment, thus eliminating non-radiative decay channels common to organo-lanthanide complexes, as well as sources of decoherence such as adjacent nuclear spins.\textsuperscript{47} Despite their shielded shell, intra 4f transitions exhibit coupling to high-energy vibrations such as C-H, O-H, and N-H which are common in organic ligands, thereby efficiently quench the excited state,\textsuperscript{48} particularly for NIR transitions, which occur at relatively low energy. For high intrinsic quantum yield, H atoms must not be adjacent to the ion. In order to suppress non-radiative decay, several methods have been carried out including deuteration, fluorination, and encapsulation. An example of such a family of Ln complexes is the metallacrown which was first synthesized by Pecoraro et al.\textsuperscript{49} These novel complexes consist of rings formed by heavier atoms – a metal (such as Zn$^{+2}$, Cu$^{+2}$, and Mn$^{+2}$), oxygen, and nitrogen similar to
crown ethers. As a result, hydrogen atoms are absent from the central Ln$^{+3}$ ion vicinity, thus non-radiative decay channels are well suppressed.\textsuperscript{50} Moreover, the crowded 3D cage structure in the metallacrown Ln complexes prevents the approach of solvent molecules to reach the first coordination sphere of the Ln ion.

In this work, a particular metallacrown complex was used, based on the quinoxaline hydroxamic acid (QXA).\textsuperscript{51} Not only does this specific ligand form a large volume metallacrown complex which defines a specific distance between two adjacent Ln$^{+3}$ ions thus limiting dipole-dipole interaction between them, but it also imposes a hydrogen-free environment near the Ln$^{+3}$ ion in vacuum, leading to higher intrinsic quantum yield of the intra 4f transitions. The synthetic procedure is provided in the supplementary information and follows a slightly modified procedure from reference.\textsuperscript{50} To demonstrate the paradigm, we chose Yb$^{+3}$ which has a convenient NIR transition at approximately 976 nm, and a relatively simple energy level structure. This complex forms an iso-structure as Yb$^{+3}$[Zn(II)$_{MC}$ (QHA)] (Fig 2.), which was previously shown as an efficient NIR fluorophore.\textsuperscript{50}

**Monolayer formation**

To avoid clustering and random orientations, and minimize inhomogeneity in general, the complexes should form an ordered monolayer on the surface of the nanofiber. The interface between the silica and the RE metallacrown complex is generated utilizing a bi-functional layer, sililated on one end and possessing a pyridyl moiety on the other, thus acting as a template layer. Such template layers were previously obtained on SiO$_2$ substrates, mostly by two step reactions.\textsuperscript{52,53} Our main substrate, the tapered optical fibre, is frail; hence any additional step, as well as temperature change undermines its mechanical stability and optical properties. Therefore, we chose a straightforward template layer with commercial silane reagent. The substrate's surface was functionalized according to scheme 1. Starting with a silane reagent with pyridyl end group (a), the complex was then deposited on the surface
Figure 2: Ligand (A), and (B) ORTEP presentation of crystal structure Yb$^{3+}$[Zn(II)$_{MC}$ (QXA)]. Thermal ellipsoids are in 50% probability and Hydrogens are omitted for clarity using an intermediate layer of zinc salt (triflate or acetate) (b), which then binds to the quinoxalyl nitrogen of the complex to the surface’s pyridyl group (c) (Scheme 1).

This method is applicable to other substrates such as alumina, and can be extended to a multilayered structure by alternately repeating layers (b) and (c). As the waist of the tapered fiber is submicron sized, the direct characterization of the deposited layers is difficult. Therefore, the layer is monitored by Si chips which undergo the same procedure in parallel. It is characterized by AFM for thickness and homogeneity (See supporting information).

**Optical measurements**

The heart of the experiment is a tapered nanofibre, which had been previously functionalized with a monolayer of the above complex. It was placed in vacuum to remove adsorbed solvent
Scheme 1: Deposition of metallacrowns on silica: The surface was functionalized with a silane containing a pyridyl end group (a), an intermediate layer of zinc triflate (or acetate) (b) was used to bind the complexes via the additional nitrogen of the ligand (c). molecules (and mounted on a cryostat).

The Yb$^{+3}$ ions were excited by optical pulses created from an external cavity laser diode (NewFocus Velocity TLB-6700), in the spectral range of 945-985 nm, chopped using an Acousto-Optic Modulator (AOM) in a double-pass configuration. Fluorescence was collected by Single-Photon Counting Modules (SPCMs) in the backward direction and any parasitic reflection was gated using a second AOM in a single-pass configuration (see Fig. 3).

Yb$^{+3}$ has 13 electrons in the 4f shell which leads to a transition between $F_{7/2}$ and $F_{5/2}$. Due to the ligand field, both levels are split into 4 and 3 degenerate pairs respectively (Kramer doublet). By applying a magnetic field, this degeneracy can be further lifted. In figure 4 (inset) a level diagram is depicted. The transition at approximately 976 nm originates from the lowest level (labeled as 0) in the ground state manifold to the lowest level (labeled as 0’) in the excited state manifold.

The photoluminescence excitation spectra of Yb$^{+3}$ at room temperature is depicted both in ambient atmosphere (i.e. without special drying procedure) and in vacuum of approximately
Figure 3: Optical setup: pulses are generated from a tunable laser (945-985 nm) by an AOM and sent to the tapered fiber. Fluorescence is collected on SPCMs in the backward (BW) direction and is separated from parasitic laser reflections using a second AOM serving as a gate.

1·10⁻⁷ mbar. The main peak is assigned to the 0-0' transition. An additional shoulder at 970 nm is attributed to the 0-1' transition. We observe a shift of the main transition from 978 nm in ambient atmosphere to 976 nm in vacuum. Fluorescence collected on resonance in ambient atmosphere exhibits a lifetime of a few µs, whereas in high vacuum a dramatic increase in signal and extension of the lifetime by more than two orders of magnitude to over 0.9 ms occur as shown in Fig. 5. To the best of our knowledge, the longest reported lifetime in Yb-based NIR organic fluorophores is 0.7 ms via sensitization.[5] Yb doped inorganic crystals which do not have H atoms present in them typically exhibit lifetime of approximately 1 ms,[54,56] with slight variations depending on the crystal. Those have already proved as good candidates for quantum applications due to their long coherence times. As we have a comparable lifetime, we conclude an efficient suppression of non-radiative decay channels in our system resulting in high intrinsic quantum yield.
Figure 4: Photoluminescence excitation spectra for different samples of fibers coated with a monolayer (thin film) of Yb$^{+3}$[Zn(II)$_{MC}$ (QXA)]. Sample 1 was measured at atmospheric pressure (black dots) and fitted (black solid line). Two samples were measured after over a week in vacuum (blue circles and triangles) and fitted (blue solid line). The black curve was multiplied by a 100 for better visibility. The bi-Gaussian fit shows a main resonance at 978 nm and 976 nm (at atmospheric pressure and in vacuum respectively) and additional component at 970 nm. As seen in the Yb level diagram (inset), excitation from the ground state occurs to the three levels of the excited state manifold. We attribute the 970 nm component to the 0 → 1$'$ transition, whereas the main peak at 978 nm corresponds to the 0 → 0$'$ transition, and shifts to 976 nm in vacuum due to the removal of ligating solvent molecules which changes the symmetry of Yb ion.
Conclusions

In conclusion, we present a new interface between Ln$^{+3}$ ions and photonic devices, based on organo-lanthanide complexes with low non-radiative loss, i.e. high intrinsic quantum yield. We observed optical coupling of a thin film (monolayer) of complexes on a tapered fiber at 300 K with $T_1 = 0.9$ ms, which confirms the efficient suppression of non-radiative decay channels. This platform, which is generally applicable to all RE ions and can be applied on photonic devices made of oxygenated substrates such as Si, glass or Al$_2$O$_3$, enables enhanced coherent coupling to Ln$^{+3}$ ions by tailoring their immediate (nm) environment and evanescently coupling them to waveguides and whispering-gallery-mode resonators, potentially opening the path towards a large number of optical and quantum-optical applications.
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Supporting Information Available

Synthetic procedure for the ligand and complex, HNMR, CNMR, MS, crystal structure .cif file, Functionalization procedure, and AFM scan picture are available, Raman spectrum of a crystal of Yb$^{3+}$[Zn(II)$_{MC}$ (QXA)].

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