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Luminescence of PbS quantum dots spread on the core surface of a silica microstructured optical fiber

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ABSTRACT

The broadband luminescence spectra, in the region from around 1000 to 1650 nm, of lead sulphide (PbS) quantum dots (QDs) spread onto the dual core surfaces of silica microstructured optical fibers (MOFs) (core diameters of ~2.5 and ~5.0 μm) are reported. For this purpose, colloidal solutions of PbS QDs of different sizes with luminescence bands around 877 (PbS877), 1160 (PbS1160), and 1474 nm (PbS1474) were injected and then spread onto the dual core surfaces of silica MOFs using a nitrogen gas pressure system. The PbS QDs were excited (via evanescent field effect) by the light of a continuum wave semiconductor laser or a Ti:sapphire laser (at 785 nm) guided through the MOF cores. As an important result, blue-shift and the band broadening behaviors in the luminescence spectra of these PbS QDs were observed.

1. Introduction

Quantum dots (QDs) are nanocrystals, with diameters ranging, typically, from 1 to 20 nm, synthesized from metal or semiconductor materials. They are usually grown within glass matrices or as colloidal solutions [1–3]. The quantum confinement effects, associated with the nanometric size, give rise to a number of important and interesting optical and electronic properties that have been exploited for photonic applications, including optical amplifiers, lasers, sensors and solar cells [4–9]. In the last few years, lasers and optical fiber amplifiers working in the 1.5 μm optical communication window were produced by putting together planar waveguides, fiber couplers or photonic crystals and either PbS or PbSe QDs [10–17]. More recently, devices based in the integration of QDs and photonic crystal fibers (PCFs) were obtained as active optical sources due to their long optical paths and strong light-material interactions [8,13].

In this work, broadband luminescence spectra of PbS QDs spread onto the core surfaces of a microstructured optical fiber (MOF) are reported. For that, a silica MOF was manufactured to increase the QD-laser pump interaction via evanescent field effect. Differently from Y-shaped fiber structures previously proposed [18,19], large holes with different diameters surrounding the two solid cores, were designed to allow easy QD filling only into selected air channels. As a result, PbS QD nanolayers could be homogeneously spread onto some of the hole surfaces by using a nitrogen gas pressurized system. Since the PbS semiconductor has much higher refractive index than silica (>4 in the 500 to 3000 nm wavelength range [20]), optical losses caused by modal-field confinement effects were avoided by keeping the PbS QD nanolayers thinner than 100 nm.

2. MOF fabrication and QDs film coating

Silica microstructured optical fiber were designed and fabricated by using the stack-and-draw technique [21] and two preform drawing stages. An image of the preform stage can be seen in Fig. 1(A), with four capillaries of two different diameters and two rods stacked inside a silica tube. Fig. 1(B) shows the cane with a structure that is already similar to the desired MOF. To enhance the air filling fraction into the final MOF structure and, therefore, increase the core surfaces sensibility to materials placed in the air holes, this structured cane was pressurized with nitrogen gas (a maximum pressure of 150 mbar) during the MOF final pulling process. MOFs with external diameters of ~110 μm (MOF110, core diameter of 2.5 μm) and ~200 μm (MOF200, core diameter of 5.0 μm) were obtained from similar preforms. Fig. 1(C) presents a picture of the final structure of the MOF110, where two sets of air holes and two cores are clearly defined.

The filling process requires pressurizing the fluid (in this case PbS-core QDs immersed in a toluene solution) into the MOF holes using a nitrogen gas pressurized system (pressure from 200 to 800 mbar). Toluene was chosen as the carrier liquid due to its high and broad light transmittance between 400 and 2000 nm when compared to other

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Fig. 1. Cross section images showing different stages of the MOF manufacturing process: (A) preform stage with four capillaries and two rods stacked inside a silica tube (before air evacuation of interfaces); (B) a cane with a structure similar to that of the desired MOF; and (C) final structure of the MOF, with ~110 μm external and ~2.5 μm core diameters.

solvents. During the process, PbS-core QDs with emission bands around 877 nm (PbS877 — 700 to 1050 nm, diameter 2.3 nm), 1160 nm (PbS1160 — 950 to 1380 nm, diameter 3.4 nm), and 1474 nm (PbS1474 — 1200 to 1900 nm, diameter 5.2 nm) were used.

To selectively fill just the MOF larger holes with the colloidal solution, low pressure (200 mbar) was initially applied. A 0.01-ml solution containing PbS QDs was injected into the MOFs, typically 150 cm long, during approximately 30 min and then maintained under atmospheric pressure (without external pressure) for another 60 min until the remaining solution was removed. It is important to point out that two different types of solutions were prepared, one of them having only PbS1474 and the other a mixture of PbS877, PbS1160, and PbS1474.

To remove the remaining solution, keeping just a thin nano-thick QD layer, a 400 mbar N_2 pressure was applied to the fiber until gas bubbles appeared at the free end of the MOF. Thereafter, the pressure was increased to 800 mbar and then kept at this level for more than 24 h. The procedure to remove the remaining solution was repeated till white light guided by the MOF core could be seen via an optical microscope.

3. Optical characterization

Cross section scanning electron microscope (SEM) images of the MOF110 (A) and MOF200 (B) are shown in Fig. 2. In particular, both MOF samples were injected with a mixture of PbS QDs (PbS877, PbS1160, and PbS1474). Fig. 2 also presents electromagnetic field intensity distributions calculated by using a code based in the Finite Element Method (FEM). The SEM images were used to prepare the fiber model and five optical modes at 1550 nm were simulated. The field pattern as well as the respective effective refractive indice mode (ranging from the fundamental mode with $n = 1.370176$ to a higher order mode with $n = 1.199044$ for MOF110 and from 1.429653 to 1.338184 for MOF200) is shown in the same figure. From this analysis it is possible to conclude that both MOFs are multimode at 1550 nm. For the MOF200, it can also be seen in Fig. 2(B) that the membrane connecting both cores can support guided modes. This behavior is expected since this membrane is thicker than that of the MOF110. Finally, at bottom region of Fig. 2(A) and (B), infrared camera (IR, MicronViewer model 7290A) images of the intensity distributions of the guided core modes after pumping at 785 nm are shown. The intensity distributions of these optical modes are similar to those calculated using FEM analysis.

A second step towards the characterization of the MOF was to realize optical attenuation spectrum measurements. Firstly, MOF110 and MOF 200 samples without PbS QDs were experimentally analyzed. To do that, the cut-back method was employed along with a Photon Kinetic spectrophotometer (PK2500 model). In this case, the attenuation spectrum was obtained from the spectrometer itself after measurements of two different lengths of the same MOF sample coupled with white light from the spectrometer. At Fig. 3 (left-hand *y* axis) the optical attenuation spectra for MOF200 (a) and MOF110 (b) can be seen. As expected, OH^- ion absorption bands (indicated by dotted-arrows at 950, 1250, and 1383 nm) associated with the OH^- ions concentration present in the silica material (used to fabricate the MOFs) can be observed.

The optical attenuation spectrum of the PbS QDs MOF was obtained from optical transmittance spectrum measurements. In this case, due to the presence of the QDs, the absorption was expected to increase significantly in such a way that the sample lengths had to be shortened to allow detectable light intensity at the output fiber tip, making it impossible to accurately use the spectrometer. Thus, both ends of a 14-cm long MOF110 with a mixture of PbS QDs (PbS877, PbS1160 and PbS1474) were spliced (using a Vytran splice instrument, FFS 2000 model) to two silica single mode fiber (SSMF — core diameter 8 μm and external diameter 125 μm) pigtails. The transmittance spectrum was obtained after connecting one end of the SSMF to a white light source (Advantest TQ8111 model) and the other to an optical spectrum analyzer (OSA — Yokogawa AQ-6315A model). The attenuation spectrum is shown in Fig. 3(c) (right-hand *y* axis). The curve shows two broad absorption bands around 870 and 1200 nm, as well as an OH^- ion absorption band around 1380 nm. The high optical attenuation (>30 dB) of this sample along the measurement band could be related to the expected high splicing losses and the PbS QDs intrinsic absorption.

To characterize the luminescence spectra of PbS QDs (PbS1474 and a mixture of PbS877, PbS1160, and PbS1474) MOFs, a 785 nm pump laser (semiconductor laser of 95 mW or Ti:sapphire of 485 mW) was coupled into the MOF samples (at one of the MOF ends) by using a 40× objective lens, while the output light that emerges from the fiber was collected through a conventional silica multimode fiber (SMMF, of core diameter 62.5 μm and external diameter 125 μm) pigtail connected to the an OSA. Optical filters (F) were introduced in the optic path between the MOF and SMMF ends in order to suppress unwanted laser lines and to avoid the dynamic range effect of the OSA. The luminescence spectra were recorded sequentially for tens of hours using the optical analyzer in the high sensitivity mode and with a 10 nm bandwidth resolution.

The first luminescence experiments that were conducted involved PbS QDs with only one size and, therefore, one main emission band. Due to the spectral proximity of its emission band and the bandwidth of photonic applications in optical communications, the PbS1474 QD became a logical candidate for the first experimental analysis and reference. Fig. 4 shows the luminescence spectra (semiconductor laser pump) of a 138-cm long MOF200 containing only PbS1474 QDs spread onto the core surfaces. The spectra were collected over a period of 315 min. Following the initial spectrum (curve 1, black), after 36 min of pumping, the amplitude of the band around 1460 nm increases considerably (curve 2). As time elapses, the amplitude of this band decreases, while new bands can be observed around 1160 and 895 nm.