



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.

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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 $\sim 110\ \mu\text{m}$ external and $\sim 2.5\ \mu\text{m}$ 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 $8\ \mu\text{m}$ and external diameter $125\ \mu\text{m}$) pigtailed. 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 ($>30\ \text{dB}$) 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 $40\times$ objective lens, while the output light that emerges from the fiber was collected through a conventional silica multimode fiber (SMMF, of core diameter $62.5\ \mu\text{m}$ and external diameter $125\ \mu\text{m}$) 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.

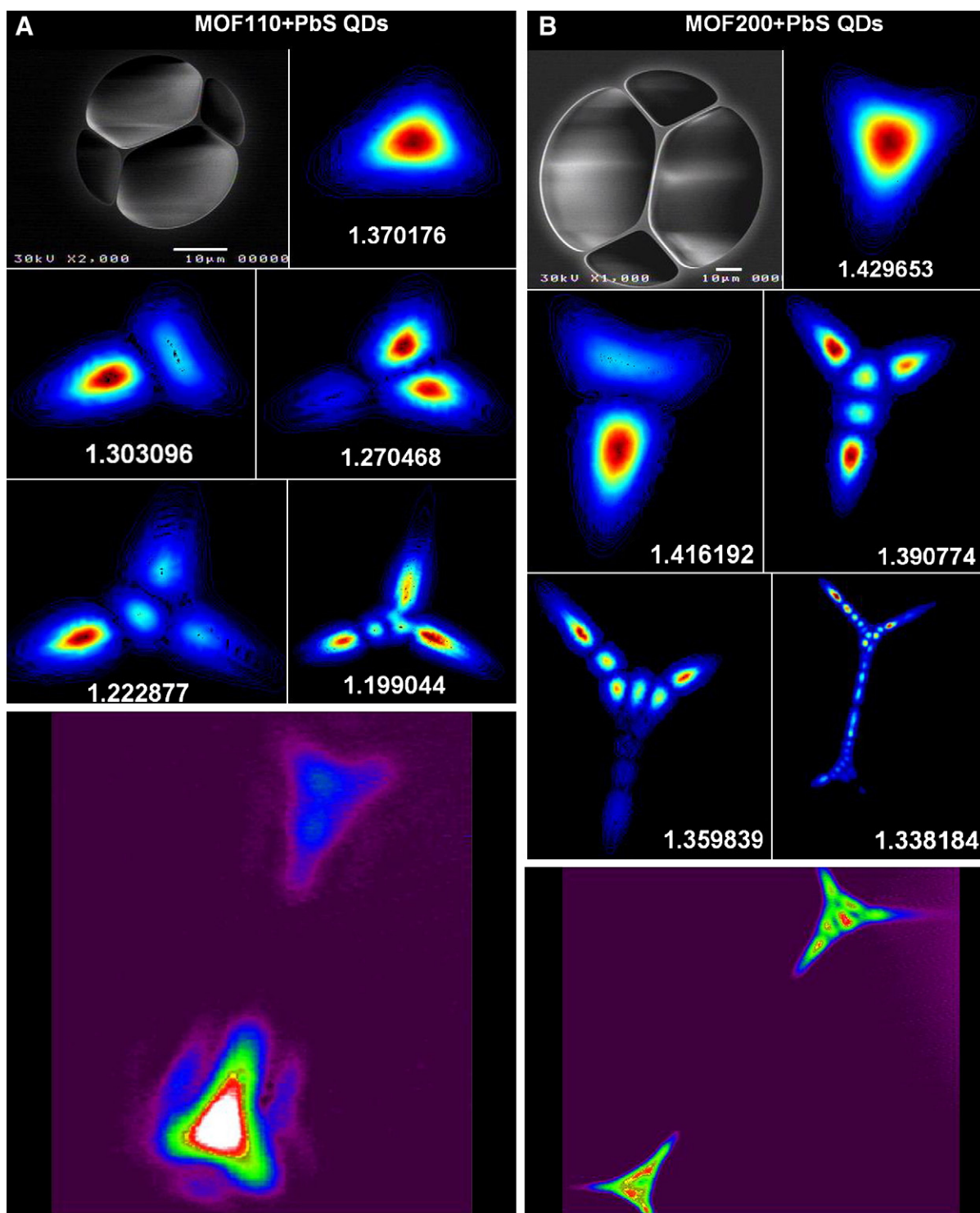


Fig. 2. Cross section images from a scanning electron microscope (SEM) of the MOF110 (A) and MOF200 (B) containing a mixture of PbS877, PbS1160, and PbS1474; intensity distribution (obtained by using FEM) of optical modes guided by the MOFs with their respective effective refractive indices (ranging from 1.370176 to 1.199044 for MOF110 and from 1.429653 to 1.338184 for MOF200); IR images of the light intensity distribution in the cores of MOF110 and MOF200 respectively (bottom region).

There was a significant increase in the new band intensities within 135 and 315 min (curves 3, 4, and 5). As can be observed, as the toluene solution evaporates with time, the luminescence spectra tend to present several secondary bands along the analyzed wavelength span. Similar results were observed for MOFs with different PbS QDs (PbS877 or PbS1160), suggesting that a mixture of QDs could produce a much wider and flatter emission band.

For a potential optical amplification application of MOFs coated with mixed PbS QDs, the luminescence power characterization as

function of the MOF length is also important. Thus, Fig. 5 shows the luminescence spectra of MOF200 samples with different lengths (18 and 88 cm), containing a mixture of QDs (PbS877, PbS1160, and PbS1474) and pumped by a 785 nm semiconductor laser for approximately one week. For the shorter fiber, luminescence around 895 nm and 1160 nm was the most intense, while the luminescence spectrum of the longer MOF200 was broader and flatter, from around 1000 to 1600 nm. The difference between the curves in Fig. 5 could be related to the intrinsic optical attenuation of the MOF200 sample

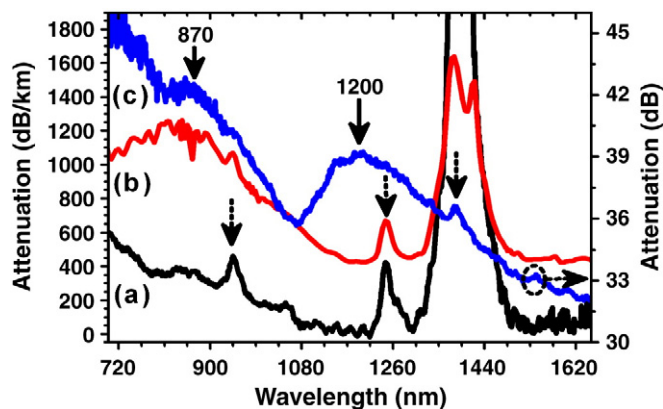


Fig. 3. Optical attenuation spectra of (a) MOF200 and (b) MOF110, both without PbS QDs, and (c) MOF110 containing a mixture of PbS877, PbS1160, and PbS1474 spread onto the core surfaces.

(with the mixture of PbS QDs), energy transfer process between PbS QDs, and re-absorption processes of PbS QDs.

To compare the performance of the two types of MOF with mixed PbS QDs, Fig. 6 presents the luminescence spectra of the (A) MOF200 (38-cm length) and (B) MOF110 (14-cm length), with mixed PbS QDs (PbS877, PbS1160, and PbS1474), having always the time of plot (1) as an initial parameter. The MOFs were pumped by a 785-nm Ti:sapphire laser of 485 mW. After passing through a long pass optical filter to remove the pump signal, the luminescence was measured from 1000 to 1700 nm.

In Fig. 6(A), initially, two high intensity regions centered around 1090 (more intense) and 1470 nm were observed. After a long period of excitation (around 72 h, with a period between measurements of 12 h), the luminescence around 1090 nm remained with practically the same amplitude and that around 1470 nm became more intense. Eventually, the 1470 nm luminescence band was displaced to the region around 1330 nm.

After a long period of excitation (around 48 h, with a period between measurements of 24 h), Fig. 6(B) shows that the luminescence amplitude of the MOF110 sample around 1090 and 1300 nm becomes more intense. Other luminescence spectra (not shown here) obtained after an even longer period of excitation (around 72 h) presented almost similar behavior as that of curve 3 in Fig. 6(B). In this case, the OH⁻ ions absorption band (around 1383 nm) clearly shows very little influence on the luminescence spectra in comparison with that of Fig. 6(A).

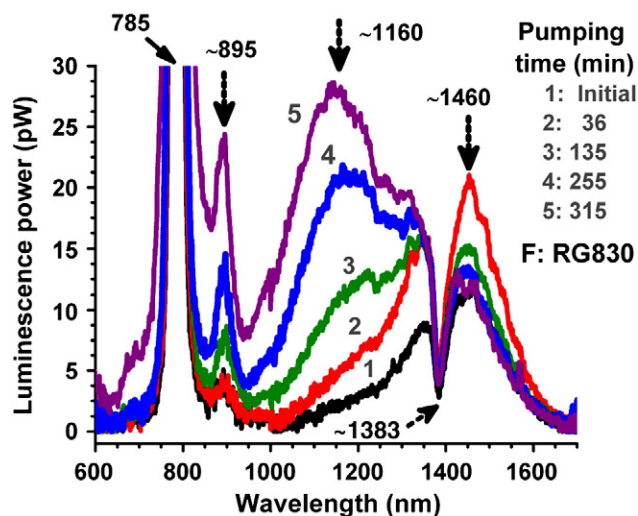


Fig. 4. Luminescence spectra of a 138-cm long MOF200 containing only PbS1474 QDs, having the pump time interval as a parameter.

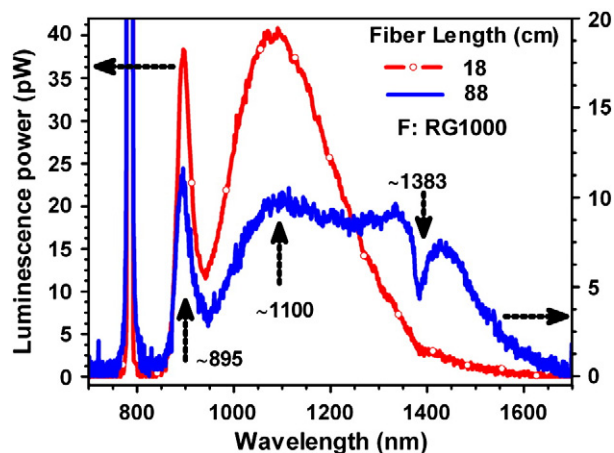


Fig. 5. Luminescence spectra of 18- and 88-cm long MOF200 containing a mixture of PbS877, PbS1167, and PbS1474, having sample length as a parameter.

4. Discussions

The luminescence spectra of PbS QDs shown in Figs. 4–6 reveal important optical characteristics of solid core MOF with internal nanocrystals coating.

First, the luminescence spectra (Figs. 4–6) show that the bands are more intense at 895, 1160 and 1460 nm. Thus, this may suggest a

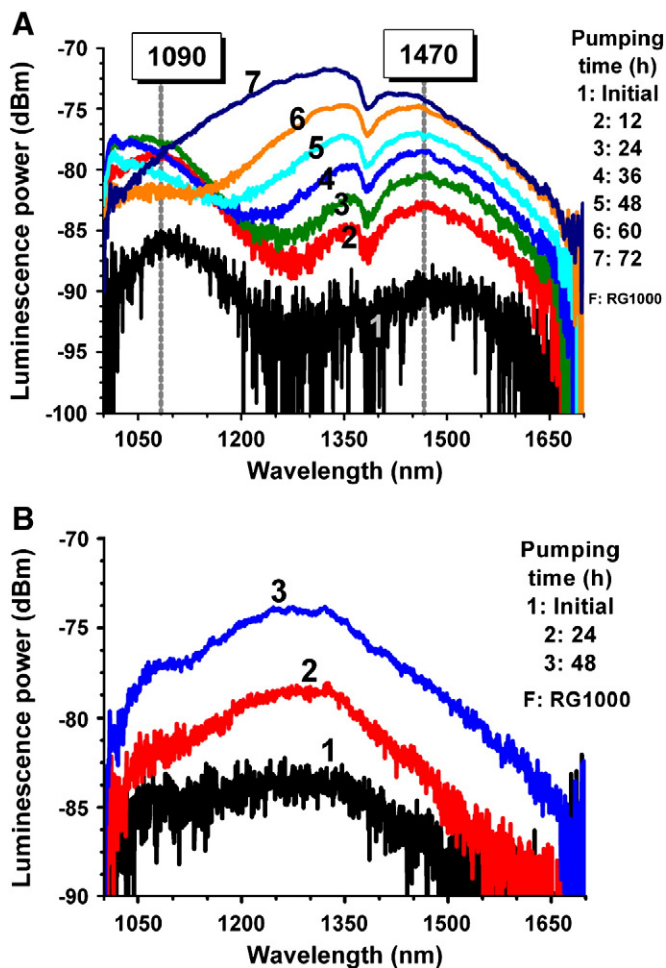


Fig. 6. Luminescence spectra of the (A) MOF200 (38-cm length) and (B) MOF110 (14-cm length), with mixed PbS QDs (PbS877, PbS1160, and PbS1474), having the pump time interval as a parameter and pumped by a 785-nm Ti:sapphire laser of 485 mW.

growth of PbS QDs that depends on the sizes of the QDs. This behavior is apparently independent on the type of QDs used: only the PbS QDs (PbS1474) (Fig. 4) or a mixture of PbS QDs (PbS877, PbS1160 and PbS1474) (Figs. 5 and 6).

Second, blue-shift and band broadening of the PbS QDs luminescence spectra were observed in Fig. 6(A) and (B), after a long period of excitation. The blue-shift effect is clearly observed in Fig. 6(A) when the luminescence band around 1470 nm became the more intense. Eventually, this band was displaced to the region around 1330 nm. The broad luminescence bandwidth (observed in both spectra of Fig. 6) extends to around 300 nm (~ 3 dB below the maximum intensity). The blue-shift and band broadening may be linked to photo-oxidation (PbS QDs – laser pump) and superficial interactions (silica – PbS QDs; air – PbS QDs). Such effects may modify the sizes of the nanocrystals and create trap levels. In addition, the energy transfer of PbS QDs and the re-absorption processes may be considered as luminescence band broadening mechanisms. This is because the luminescence band broadening is dependent on the MOF length, as seen in Fig. 5.

Finally, the PbS QDs luminescence power amplitudes of MOF110 and MOF200 are weak, typically lower than ~ 70 dBm. Efforts are, however, on the way to increase these power levels by optimizing the field-QD overlap while decreasing inserted losses. On the other hand, the maximum measured PbS QDs luminescence power of the MOF110 sample was always less intense than that of the MOF200, as seen in Fig. 6(B) and (A), curves 3 and 7, respectively. Two reasons may be linked to this fact: the higher optical attenuation of MOF110 (see curve c of Fig. 3); and, the smaller core areas of MOF110. In fact, as previously commented, the MOF200 thicker core has a thicker membrane that can also support optical modes, Fig. 2(B), increasing the overlap between the optical mode and the QD film.

5. Conclusions

A new microstructured optical fiber was proposed and manufactured. The silica MOF presents two sets of air channels with different diameters, and two cores linked by a membrane. By changing the MOF dimensions, it was possible to control the presence of guided modes within the membrane.

The luminescence spectra of PbS QDs core-coated MOFs were analyzed when pumping at 785 nm was coupled into the samples. The PbS QDs luminescence spectra reveal blue-shift and band broadening behaviors when increasing the pumping time duration. Broader and flatter luminescence spectra (from around 1000 to 1650 nm) were obtained using a mixture of QDs (PbS877, PbS1167, and PbS1474). By maximizing the signal amplitude MOF with PbS QDs may be used as an active optical device with potential application in optical amplification and sensing.

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References

- [1] A.I. Ekimov, Optical properties of semiconductor quantum dots in glass matrix, *Phys. Scr.* T39 (1991) 217–222.
- [2] A. Mews, A. Eychmueller, M. Giersig, D. Schooss, H. Weller, Preparation, characterization, and photophysics of the quantum dot quantum well system cadmium sulfide/mercury sulfide/cadmium sulfide, *J. Phys. Chem.* 98 (1994) 934–941.
- [3] A.P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, *Science* 271 (1996) 933–937.
- [4] A.V. Malko, A.A. Mikhailovsky, M.A. Petruska, J.A. Hollingsworth, H. Htoon, M.G. Bawendi, V.I. Klimov, From amplified spontaneous emission to microring lasing using nanocrystal quantum dot solids, *Appl. Phys. Lett.* 81 (2002) 1303–1305.
- [5] R.J. Ellingson, M.C. Beard, J.C. Johnson, P. Yu, O.I. Micic, A.J. Nozik, A. Shabaev, A.L. Efros, Highly efficient multiple exciton generation in colloidal PbSe and PbS quantum dots, *Nano Lett.* 5 (2005) 865–871.
- [6] K.K. Zhuravlev, J.M. Pietryga, R.K. Sander, R.D. Schallera, Optical properties of PbSe nanocrystal quantum dots under pressure, *Appl. Phys. Lett.* 90 (2007) 043110.
- [7] A.M. Malyarevich, M.S. Gaponenko, V.G. Savitski, K.V. Yumashev, G.E. Rachkovskaya, G.B. Zakharevich, Nonlinear optical properties of PbS quantum dots in borosilicate glass, *J. Non-Cryst. Solids* 353 (2007) 1195–1200.
- [8] Y. Ruan, E.P. Scharfner, H. Ebendorff-Heidepriem, P. Hoffmann, T.M. Monro, Detection of quantum-dot labeled proteins using soft glass microstructured optical fibers, *Opt. Express* 15 (2007) 17819–17826.
- [9] E. Rodríguez, E. Jimenez, L.A. Padilha, A.A.R. Neves, G.J. Jacob, C.L. César, L.C. Barbosa, SiO₂ / PbTe quantum-dot multilayer production and characterization, *Appl. Phys. Lett.* 86 (2005) 113117.
- [10] R.D. Schaller, M.A. Petruska, V.I. Klimov, Tunable near-infrared optical gain and amplified spontaneous emission using PbSe nanocrystals, *J. Phys. Chem. B* 107 (2003) 13765–13768.
- [11] S. Hoogland, V. Sukhovatkin, I. Howard, S. Cauchi, L. Levina, E.H. Sargent, A solution-processed 1.53 μ m quantum dot laser with temperature-invariant emission wavelength, *Opt. Express* 14 (2006) 3273–3281.
- [12] Z. Wu, Z. Mi, P. Bhattacharya, T. Zhu, J. Xu, Enhanced spontaneous emission at 1.55 μ m from colloidal PbSe quantum dots in a Si photonic crystal microcavity, *Appl. Phys. Lett.* 90 (2007) 171105.
- [13] S. Kawanishi, T. Komukai, M. Ohmori, H. Sakaki, Photoemission of semiconductor nanocrystal quantum dots at 1550 nm wavelength in the core of photonic bandgap fiber, Conference on Lasers and Electro-Optics CLEO 2007, Baltimore, Maryland, paper CTu14, May 6, 2007.
- [14] T. Wang, F. Pang, K. Wang, R. Zhang, G. Liu, Evanescent wave coupled semiconductor quantum dots fiber amplifier based on reverse Micelle method, Proceedings of the 7th IEEE, International Conference on Nanotechnology, Hong Kong, Aug. 2–5, 2007, pp. 819–822.
- [15] J. Yang, F. Pang, Z. Chen, T. Wang, Fabrication and characterization of evanescent wave coupled PbS quantum dots fiber amplifier based on sol–gel method, *Proc. SPIE* 7135 (2008) 71352M1–71352M8.
- [16] F. Wise, Quantum dots call the shots: nanometer-scale structures let designers engineer optical properties, *SPIE OE Mag. Newsroom* (2002) 24–27.
- [17] F. Wise, Lead salt quantum dots: the limit of strong quantum confinement, *Acc. Chem. Res.* 33 (2000) 773–780.
- [18] C.M.B. Cordeiro, M.A.R. Franco, C.J.S. Matos, F. Sircilli, V.A. Serrão, C.H. Brito Cruz, Single-design-parameter microstructured optical fiber for chromatic dispersion tailoring and evanescent field enhancement, *Opt. Lett.* 33 (2007) 3324–3326.
- [19] S.C. Warren-Smith, S. Afshar Test, Theoretical study of liquid-immersed exposed-core microstructured optical fibers for sensing, *Opt. Express* 16 (2008) 9034–9045.
- [20] G. Guizzetti, A. Borghesi, Part II—semiconductors-lead sulfide (PbS), in: E.D. Palik (Ed.), *Handbook of Optical Constants of Solids* vol. 2, Academic Press, Orlando, 1985, pp. 525–534.
- [21] P.St.J. Russell, Photonic crystal fibers, *Science* 299 (2003) 358–362.