Microring Lasing from Dye-Doped Silica/ Block Copolymer Nanocomposites

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For a considerable time,[1] sol−gel glasses have been known to be excellent hosts for the encapsulation of organic dyes. Above all, laser dyes and molecules for nonlinear optical effects (second and third harmonic generation) have been incorporated into oxide glasses.[2−4] Some important aspects of sol−gel chemistry for the generation of useful optical materials are the low-temperature chemistry which can be employed (usually below 100 °C), the reported high dispersion and reduced dimerization of the encapsulated dyes, and the high processibility of the sol−gel precursor solution into a desired geometry (thin films, monoliths, and waveguides).

Sol−gel chemistry can also be combined with surfactant or block copolymer templating to derive ordered mesoporous and mesostructured materials with a structural ordering on the nanometer scale. These materials are currently attracting interest for optical and electronic applications.[5−14] For example, mesoporous compounds are promising candidates for next-generation low-*k* dielectrics due to the high porosity of these materials after surfactant removal. Clearly, the refractive index also is comparably low ($n \sim 1.15-1.3$, depending on the structure and porosity), which makes these materials interesting for low-refractive-index supports.[5] On the other hand, for as-synthesized mesostructured compounds, i.e., mixed nanostructured arrays of an inorganic wall and surfactants or block copolymers, the inorganic−organic co-assembly of these materials allows one to dope dye molecules in high concentrations into these structures[5,15] by simultaneously ensuring high dye dispersion and reduced dye aggregation. Previously, we have combined these properties to create mesostructured waveguide patterns by soft lithography. These waveguides exhibit low-threshold amplified spontaneous emission (∼10 kW cm^{-2}) when optically pumped.[5] In this process, spontaneously emitted light is amplified by stimulated emission as it propagates along the waveguides.

Mesostructured silica/block copolymer composites have been shown to be advantageous over sol−gel glasses because they further reduce dye dimerization (dimers do not emit strongly). Also, the investigation of rhodamine 6G (R6G)-doped mesostructured waveguides revealed a good photostability with a half-life of about 2500 pulses when pumped to give a fully gain-narrowed output.[16] However, there is no feedback in these waveguides, and the emission line width of the amplified spontaneous emission (ASE) is limited to a full width at half-maximum (fwhm) of about 7−8 nm. It would be desirable to have spectrally more narrow emission.

Introducing the necessary feedback for lasing can be achieved by patterning the material in a disc or ring. While direct patterning would be one choice, we have been interested in the goal of microlasers on solid supports that are easy to handle and that might be integrated in, for example, sensing devices. Optical fibers are well-suited for this purpose since the mesostructured materials can be coated on them. We employed a weakly acidic sol−gel route using the block copolymer P123 [poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), $(PEO)_{20}(PPO)_{70}(PEO)_{20}$; BASF] to derive homogeneous mesostructured coatings. The precursor solution had a molar composition of tetraethyl orthosilicate/P123/H_2O/HCl/ethanol/R6G = $1/1.0 \times 10^{-2}/2.65/2.3 \times 10^{-4}/13.2/2.5 \times 10^{-3}$. To ensure waveguiding in the ring structure, the optical fiber (from which the cladding was removed) was coated two times with the precursor solution. After being dried, the fiber was calcined, giving a low-refractive-index support on the fiber. In the next step, the fiber was coated several times with the R6G-containing solution. Finally, the fibers were usually dried for 1 day. We also investigated, however, fibers that had been dried for about 5 min after coating with the dye-containing solution and observed the same effects described below.

Although the dip-coating technique works very well for producing thin films on supports such as silica glass and polished silicon wafers[10,17] and the dipping speed can be chosen variably,[18] the coating of the optical fibers proved to be difficult. By employing high dipping speeds of about 150 cm/min we could derive homogeneous coatings on the optical fibers. Significantly lower dipping speeds did not lead to a wetting of the fiber surface and

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(1) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956.
(2) Lebeau, B.; Sachez, C. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 11.
(3) Reisfeld, R. *Struct. Bond.* **1996**, *85*, 215.
(4) Avnir, D. *Acc. Chem. Res.* **1995**, *28*, 328.
(5) Yang, P.; Wirnsberger, G.; Huang, H. C.; Cordero, S. R.; Scott, B.; McGehee, M. D.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Buratto, S. K.; Stucky, G. D. *Science* **2000**, *287*, 465.
(6) Marlow, F.; McGehee, M. D.; Zhao, D.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1999**, *11*, 632.
(7) Dag, Ö.; Ozin, G. A.; Yang, H.; Reber, C.; Bussiere, G. *Adv. Mater.* **1999**, *11*, 474.
(8) Wirnsberger, G.; Stucky, G. D. *Chem. Phys. Chem.*, in press.
(9) Zhou, H. S.; Honma, I. *Adv. Mater.* **1999**, *11*, 683.
(10) Zhao, D.; Yang, P.; Melosh, N.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 1380.
(11) Zhou, H. S.; Sasabe, H.; Honma, I. *J. Mater. Chem.* **1998**, *8*, 515.
(12) Baskaran, S.; Liu, J.; Domansky, K.; Kohler, N.; Li, X.; Coyle, C.; Fryxell, G. E.; Thevuthasan, S.; Williford, R. E. *Adv. Mater.* **2000**, *12*, 291.
(13) Huo, Q.; Zhao, D.; Feng, J.; Weston, K.; Buratto, S. K.; Stucky, G. D.; Schacht, S.; Schüth, F. *Adv. Mater.* **1997**, *9*, 974.
(14) Melosh, N. A.; Lipic, P.; Bates, F. S.; Wudl, F.; Stucky, G. D.; Fredrickson, G. F.; Chmelka, B. F. *Macromolecules* **1999**, *32*, 4332.
(15) Ganschow, M.; Wöhrle, D.; Schulz-Ekloff, G. *J. Porphyrins Phthalocyanins* **1999**, *3*, 299.
(16) Wirnsberger, G.; Yang, P.; Huang, H. C.; Scott, B.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Stucky, G. D. *J. Phys. Chem. B*, in press.
(17) Lu, Y.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W.; Guo, Y.; Soyez, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364.
(18) Typically, the dipping speeds are in the range of 10 cm/min.

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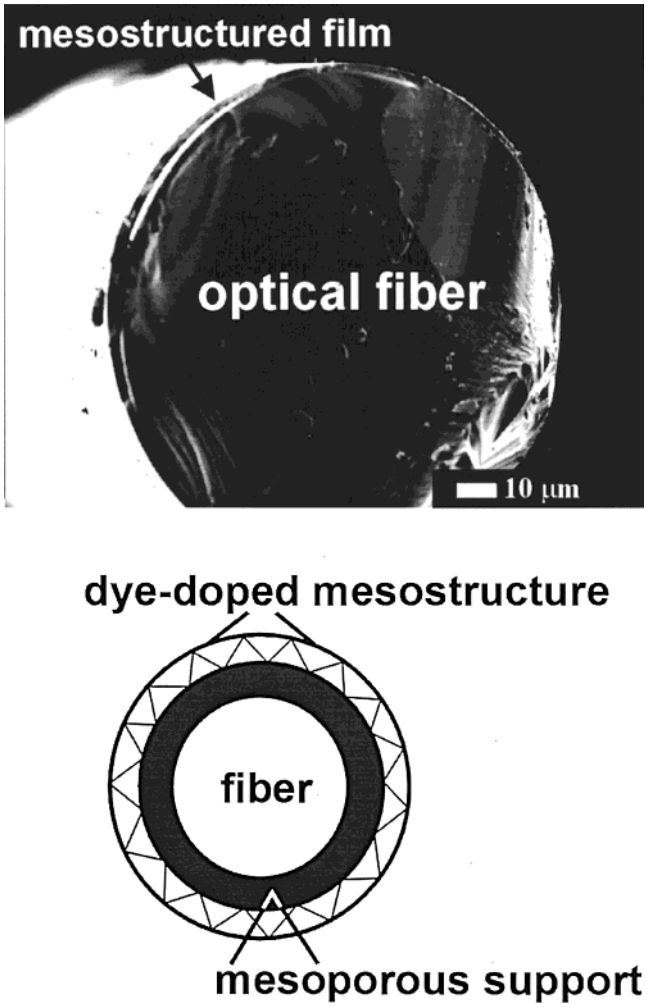

Figure 1. Scanning electron microscopy image of the cross section of the fiber and the mesoporous/mesostructured coating. On the bottom, a schematic picture of the cross section is given, depicting the waveguiding in the mesostructured coating enabled by the mesoporous support.

no coatings were deposited. Once deposited, however, the films had a smooth surface and a relatively homogeneous thickness of ~2 μm (Figure 1). Transmission electron microscopy was employed to investigate the degree of mesostructural order. As commonly found for both bulk samples[19] and thin films[10] synthesized with P123, the composite coating has a 2-D hexagonal channel structure with *p6mm* symmetry.

To observe lasing from this ring configuration, mesostructure-coated fibers were optically pumped by the second harmonic light of a Q-switched Nd:YAG laser (532 nm, ~10 ns pulse width, 10 Hz). The pump light intensity was adjusted with neutral density filters, passed through a slit, and focused by a cylindrical lens to a stripe of 1 × 0.4 mm. The angle between the pump light and the collected emission was 90° (see Figure 2 inset). At low pump intensities (<1 kW cm^{-2}), the emission spectra exhibit a broad luminescence with a full width at half-maximum (fwhm) of ~60 nm and a peak maximum at 580 nm, characteristic of R6G incorporated in SBA-15 type materials.[5,16] However, when a certain threshold was reached, narrow lines

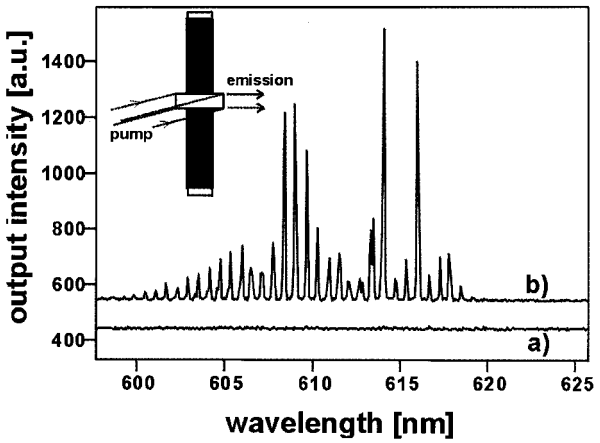

Figure 2. (a) Photoluminescence spectra at low pump intensity (<1 kW cm^{-2}) and (b) above the threshold (6 kW cm^{-2}) showing lasing modes. The inset depicts the measurement geometry.

began to grow out of this broad luminescence, indicative of microring lasing.[20−24] The threshold for the onset of lasing modes to appear consistently was found to be in the low range 1.4−4.5 kW cm^{-2}. In comparison to ASE observed in patterned waveguides having the same dye concentration,[16] the threshold for lasing is about 1 order of magnitude lower (1.4 vs 16 kW cm^{-2}).[25]

The lasing modes are spectrally narrow with a fwhm of 1.5 Å, limited by the spectrometer resolution. Due to the thickness of the optical fiber (125 μm), there are a large number of modes. These modes are due to the waveguiding and hence feedback within the mesostructured film. From the relation $\Delta\nu = c/d\pi n_{\text{eff}}$ (where d is the optical fiber diameter), we extract a theoretical spacing ($\Delta\nu$) of 17.8 cm^{-1}, assuming the coating to have an effective refractive index similar to that of patterned waveguides ($n_{eff} \sim n = 1.43$). Thus, the experimental spacing (16.7−18.0 cm^{-1} at the blue and red end of the spectra, respectively) agrees well with the theoretical value and shows that the light is effectively confined to the dye-doped cladding layer.[26] The Q value was evaluated to be on the order of ~3.5 × 10^3, which is in the range to those values reported for other ring microlasers.[21] The waveguided modes are modulated, as is clearly visible in Figure 2. We attribute this to a resonant modulation of the waveguided modes by whispering galley modes; we note that there is no

(19) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(20) Frolov, S. V.; Shkunov, M.; Vardeny, Z. V.; Yoshino, K. *Phys. Rev. B* **1997**, 56, 4363.

(21) Frolov, S. V.; Fujii, A.; Chinn, D.; Vardeny, Z. V.; Yoshino, K.; Gregory, R. V. *Appl. Phys. Lett.* **1998**, *72*, 2811.

(22) Frolov, S. V.; Vardeny, Z. V.; Yoshino, K. *Appl. Phys. Lett.* **1998**, *72*, 1802.

(23) Kawabe, Y.; Spiegelberg, C.; Schülzgen, A.; Nabor, M. F.; Kippelen, B.; Mash, E. A.; Allemand, P. M.; Kuwata-Gonokami, M.; Takeda, K.; Peyghambarian, N. *Appl. Phys. Lett.* **1998**, *72*, 141.

(24) Kuwata-Gonokami, M.; Jordan, R. H.; Dodabalapur, A.; Katz, H. E.; Schilling, M. L.; Slusher, R. E.; Ozawa, S. *Opt. Lett.* **1995**, *20*, 2093.

(25) In ASE experiments, the threshold is not defined uniquely. In most cases, the onset of the gain narrowing or the decrease of the fwhm to half (or 1/*e*) of the value of the usual photoluminescence spectrum is taken. In our studies,[5,16] we took the latter value, and it should be noted that the energies for a fully gain-narrowed ASE output are somewhat higher than the thresholds.

(26) This is also evident from the far-field pattern in ASE experiments, in which we pumped the fibers along the long axis. The patterns consist of a dark center (corresponding to the fiber core) and bright ASE light scattered out from the edges of the coated film.

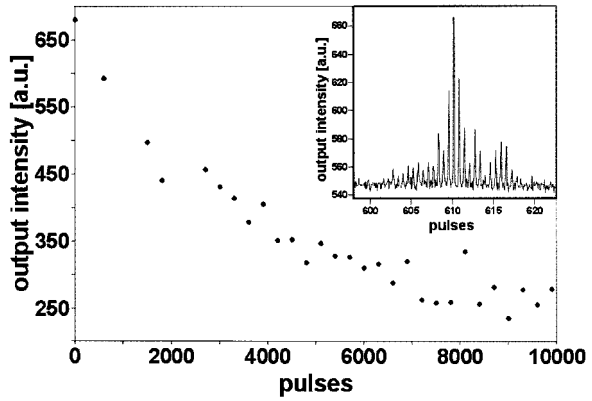

Figure 3. Decay of the integrated output versus the number of pump pulses. The data were acquired at 6 kW cm^{-2} and with a repetition rate of the pump pulses of 10 Hz. The inset shows the spectrum after 25 000 pulses, still giving narrow-line width lasing output. The sample was kept under ambient conditions during measurements.

structure due to quantum electrodynamic confinement below the threshold. From the spectra above the threshold, a further substructure of the bands is evident, which is attributed to the presence of TE and TM modes in these 2 μm thick films.[27]

Due to the low threshold, the ring lasers can be pumped at low intensities, hence increasing the lifetime of the optically active species. Although R6G is a relatively labile molecule with respect to photostability, the integrated output intensity reduces only to half of the initial value after 6000−7000 pulses at a pumping frequency of 10 Hz (Figure 3). As the decay is roughly exponential, we could observe lasing even after several thousand pulses. Hence, the low threshold obtained is also promising with respect to long-term operation.

In conclusion, we have shown for the first time that very low-threshold multimode lasing can be achieved by mesostructured microring lasers deposited on a mesoporous support which itself coats an optical fiber. Since the energies required to have lasing output are relatively low, the material can be optically pumped for comparably long times and still give lasing emission, thus making these materials interesting for applications. These materials could find applications in sensing devices where the lasing output is tuned by the presence of molecules that diffuse into the mesostructured composite. In this respect, in further synthetic improvements, it might be interesting to obtain single-mode lasers by coating fibers with smaller diameters and utilizing other optical configurations. Other configurations more directly related to sensing applications are currently under investigation.

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(27) Knight, J. C.; Driver, H. S. T.; Hutcheon, R. J.; Robertson, G. N. *Opt. Lett.* **1992**, *17*, 1280.