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Dye-Activated Hybrid Organic/Inorganic Mesostructured Titania Waveguides

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The development of optically activated hybrid organic/inorganic mesostructured silica composites has led to a number of advanced optical applications,[1] such as optical switches and sensors[2] and low threshold waveguide microlasers.[3] However, the low refractive index of silica composites ($n = 1.43$) requires that the optically active layer be supported by an ultralow refractive index layer[3b] for waveguiding to occur.[3] This obstacle could be overcome by using a higher refractive index inorganic component, and recently, Vogel et al. reported amplified spontaneous emission (ASE) from mesostructured titania films.[4]

Here we present a new synthetic approach for high refractive index, dye-activated, hybrid mesostructured materials utilizing a fluorocarbon-stabilized titania precursor. These titania composites can readily be processed into solid, optically transparent, crack-free fibers and planar waveguides several hundred nanometers to tens of micrometers in thickness and a surface roughness between 0.4 and 1.3 nm RMS as measured by AFM on various film surface locations (25 μm^2 area). The dye-doped composites display a high effective refractive index n_{eff} of 1.8 ± 0.2 in photoluminescence (PL) waveguide mode studies (see below)[5] enabling low threshold ASE without the need of an ultralow refractive index support.

Successful fabrication of hybrid organic/inorganic mesostructured composite materials by evaporation-induced self-assembly (EISA)[6] requires controlling the chemistry of the structure directing surfactant and the framework-forming inorganic species simultaneously in the precursor solution. The inorganic species should be soluble over an extended period of time to allow for surfactant-directed mesophase assembly, and the precursor solution must be highly processable to allow patterning and shape control of the composite. Most importantly, the precursor should form a solid glasslike material at room temperature to stabilize the desired morphology. Previously reported synthetic routes based on EISA use, or generate in situ, strong inorganic acids to solubilize titania precursors and require heat treatment to form a stable solid material.[7] This approach is not suitable for fabrication of hybrid mesostructures since heat treatment decomposes the organic components. To circumvent these obstacles, we have developed a synthetic approach utilizing strong fluorinated organic acids, such as trifluoroacetic acid (TFA). Because carboxylic acids are known to be chelating agents for molecular titanium species,[8] it is likely that upon solvent evaporation the complex-forming nature of TFA prevents extended three-dimensional (3D) cross-linking of the molecular titania units and enables the room-temperature formation of this new highly ordered glassy composite.

In a typical synthesis, 55.5 mg of the organic laser dye rhodamine 6G (R6G; Acros Organics) was added to a solution of 2.3 g of poly(ethylene oxide)$_{20}$-poly(propylene oxide)$_{70}$-poly(ethylene oxide)$_{20}$ nonionic surfactant (Pluronic P123, BASF) in 10 g of ethanol and stirred until the dye is fully dissolved. Separately, 3.9 mL of titanium(IV)ethoxide (Aldrich) were reacted under heavy stirring
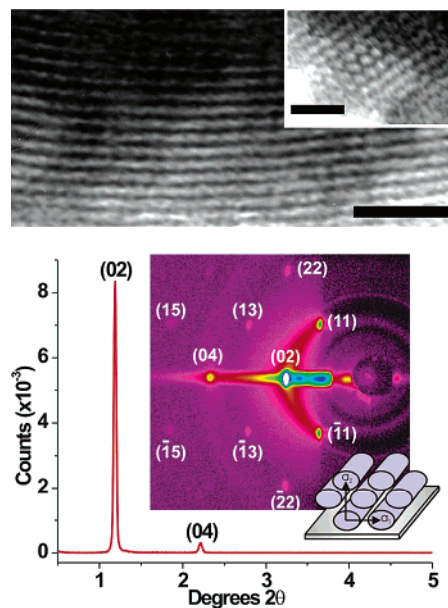

Figure 1. (Top) TEM images of the channel structure and 2D-hexagonal packing (inset). Scale bars are 50 and 30 nm (inset). (Bottom) 1D-XRD and 2D-SAXS (inset) patterns showing high mesostructural order. 2D-SAXS pattern (collected at an incident angle of 0.4°) is shown on a false-color log scale. The transmitted beams are blocked by the substrate.

with a mixture of 2.0 mL of trifluoroacetic acid (Merck) and 0.7 mL of hydrochloric acid (12.1 M).[9] After 5 min this solution was combined with the ethanolic surfactant/dye solution and further stirred for at least 10 min. Films of variable thickness were prepared by dip- or spin-coating onto clean glass slides at various speeds and stored at ~70% relative humidity. Additionally, the high processability of the precursor solutions allows for the fabrication of optically transparent fibers (see Supporting Information) and should allow for the fabrication of microstructures using soft lithography as already demonstrated for mesostructured silica composites.[3b,d]

The mesostructural order of the film samples was investigated by transmission electron microscopy (TEM) using a FEI Tecnai G2 Sphera microscope operated at 200 kV. Typical micrographs taken along different zone axes show a hexagonally ordered channel structure (Figure 1 top).

One- and two-dimensional X-ray diffraction (1D-XRD and 2D-SAXS) patterns of the samples are given in Figure 1 (bottom). 1D-XRD was performed on a Scintag PAD X2 powder diffractometer, and 2D-SAXS measurements were performed on a custom-built diffractometer, both using Cu Kα radiation. The 2D-SAXS results reveal a distorted hexagonal structure corresponding to the plane group $C2m$ with lattice constants $a_1 = 11$ nm and $a_2 = 16$ nm. No wide-angle diffraction peaks were observed, supporting the glasslike nature of this hybrid material.
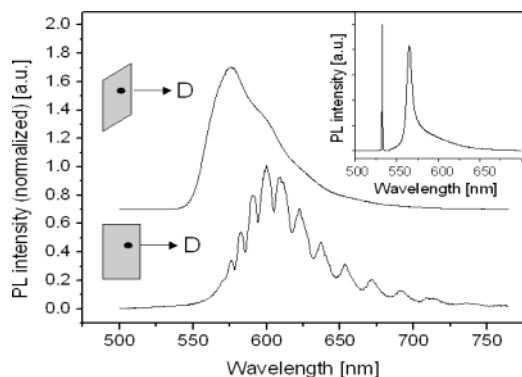
Figure 2. PL emission spectra of a 10-μm thick rhodamine 6G doped hybrid mesostructured titania film recorded in different film orientations (see schematics at left) to distinguish between "normal" emission (top) and waveguided emission (bottom). (Inset) Fully gain-narrowed ASE peak after increasing the excitation pump pulse energy above threshold. The sharp line at 532 nm is scattered light from the Nd:YAG excitation laser.

The defined organic/inorganic domain separation in this mesostructured titania material is of great importance for doping with organic dyes, since the hydrophobic organic nanodomains created by the block copolymer provide a chemically ideal environment for the organic dye. The dye molecules are homogeneously dispersed and less aggregated into nonluminescent dimers, yielding higher PL quantum efficiencies and lower optical gain thresholds.[1b,10]

To study the PL and optical gain properties, the film samples were excited at a position 5−10 mm away from the cleaved edge of the film by the focused output of a frequency-doubled Q-switched Nd:YAG laser (532 nm, 10 ns pulse width, 10 Hz repetition rate). The emitted light was collected in a 90° angle, focused onto the entrance slit of a spectrometer, dispersed by a grating (150 grooves/ mm), and detected by a CCD camera.

Figure 2 shows the PL emission spectra of a 1.5 wt % R6G-doped 10-μm thick film recorded in two film orientations (see left-hand insets in Figure 2). In "normal" 45° orientation of the film the typical broad R6G emission peak centered at around 585 nm is observed (top spectrum). However, in a 90° film orientation, where primarily waveguided emission is collected by the detector, the R6G emission peak is strongly modified and split into several well-defined modes with a spacing of 280 ± 30 cm^{-1} (bottom spectrum). In general, the mode spacing obtained from different samples depends strongly on the film thickness (see Supporting Information) and follows the theoretical formula for the free spectral range between adjacent waveguided modes, $\nu_{fsr} = c/n_{eff}2t$,[11] where c is the speed of light and t is the thickness of the waveguiding film. The observed red-shift of the waveguided emission of about 15 nm results from reabsorption of the emitted light as it travels through the film.

The waveguiding ability of our hybrid titania mesostructured films can be utilized for mirrorless lasing applications such as ASE—a phenomenon that occurs due to high-gain amplification of the spontaneously emitted light by stimulated emission as it travels along a waveguide containing the gain medium.[12] For these measurements the excitation spot was moved closer to the film edge (1−2 mm) and the excitation power was slowly increased. While at low pump pulse energies, typical multiple-mode emission spectra were obtained; increasing the pump pulse energy over a certain threshold resulted in mode competition and the collapse of the multiple-mode structure into a single, fully gain-narrowed mode (fwhm of around 8 nm)—a typical signature of ASE.[12] We measured

ASE pump pulse energy thresholds ranging from 0.8 to 15 mJ for different films deposited directly onto glass slides. It should be emphasized that the lower values are comparable to those obtained from mesostructured silica films supported by an ultralow refractive index layer.

In summary, we have developed a new fluorocarbon-based synthesis route for hybrid organic/inorganic titania mesostructured optical materials. These solid and optically transparent titania composites have all the desired properties of their silica analogues, including nanoscopic domain separation and ease of patterning of the precursor solution, with the important added advantage of a higher refractive index—making possible planar waveguiding via one-step deposition onto simple glass substrates. These combined properties were exploited by demonstrating low threshold mirrorless lasing of dye-activated samples without an ultralow refractive index support layer.

Supporting Information Available: Synthesis procedure of fibers, SEM and optical photographs of fibers and films, waveguided PL emission spectra of films with different thicknesses. This material is available free of charge via the Internet at http://pubs.acs.org.

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