

## A Solvent-Stable Nanocrystal-Silica Composite Laser

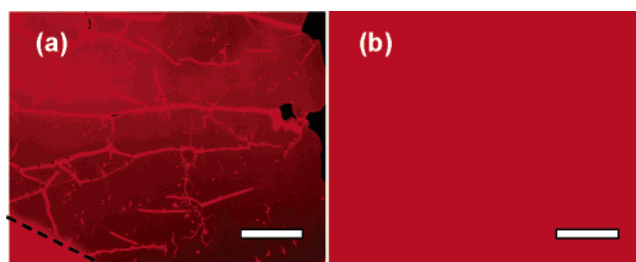
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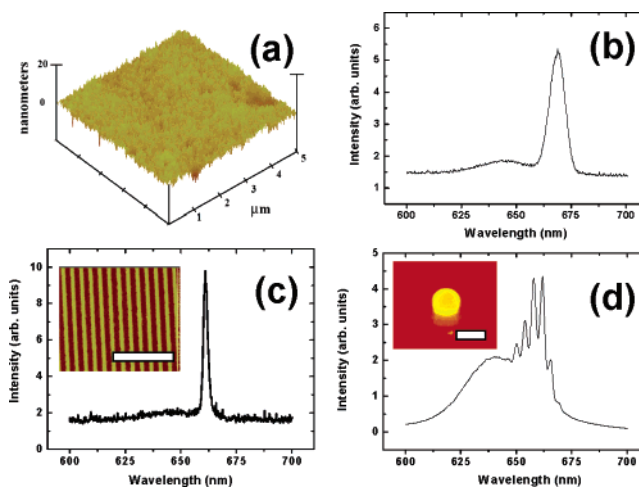
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Colloidal semiconductor nanocrystals (NCs) incorporated into sol-gel derived titania matrixes have been exploited as optical gain media, exhibiting amplified spontaneous emission (ASE) that is tunable and microcavity lasing at room temperature.<sup>1</sup> The microscale dimensions of these photostable NC-based lasers should make them ideal for integration with microfluidic networks, facilitating the interaction of liquids with the laser on a miniaturized scale. This would provide the potential of dynamically tuning<sup>2</sup> the optical properties of the laser, enabling possible applications such as nonlinear optical chemosensing<sup>3</sup> at small length scales. However, although sol-gel derived titania provides a host structure that is thermally resilient<sup>1a</sup> to the intense optical excitation required to achieve gain in NCs, exposure to water and short-chain alcohols results in rapid structural and photophysical degradation of the NC-titania composite, as shown in Figure 1a. The extensive cracking observed may be attributed to a dramatic syneresis<sup>4</sup> of the titania matrix, which incorporates unreacted titanium butoxide moieties as a result of a necessarily low annealing temperature.<sup>1b</sup> This makes NC-titania matrices unsuitable as robust NC-based lasers within a microfluidic framework. Indeed, such a device requires a composite that (i) does not suffer from any significant structural and photophysical degradation when exposed to polar solvents, (ii) incorporates NCs in high volume fraction to achieve optical gain, and (iii) has the versatility to be coupled to a microcavity, facilitating room-temperature lasing in the presence of solvents. We present in this communication the development of a NC-silica composite that addresses all of the above requirements.

Previous efforts to chemically incorporate CdSe NCs into sol-gel derived silica resulted in composites with a relatively low volume fraction of NCs,<sup>5</sup> insufficient to exhibit ASE.<sup>6</sup> We overcame this problem by first modifying the surface of CdSe/ZnS NCs with 5-amino-1-pentanol (AP) to impart ethanol solubility before introducing 3-aminopropyltrimethoxysilane (APS) as the silica precursor. The amino group on APS presumably binds to the NC surface, allowing the NCs to be incorporated in high volume fraction into the silica network. Due to the affinity of the amino group on APS for the NC surface, however, sole use of APS resulted in some displacement of AP, causing a slight aggregation of the NCs in ethanol. This yielded composites with a rough surface morphology (~8 nm RMS). We circumvent this complication by replacing a small amount of APS with (triethoxysilyl)propyl isocyanate (TSPI), a silica precursor reactive enough to co-condense with APS without the need for acid catalysts that are detrimental to the optical properties of NCs. Since the isocyanate group has a much lower affinity for the NC surface than primary amines, displacement of AP is minimized, rendering the NCs more dispersible in ethanol. Use of TSPI as the only silica precursor, however, resulted in very smooth films but with a low volume fraction of NCs. This is expected since TSPI, lacking a functional group with good affinity for the NCs, cannot assist in the incorporation of NCs into the silica matrix. A judicious choice of the relative amounts of APS and TSPI

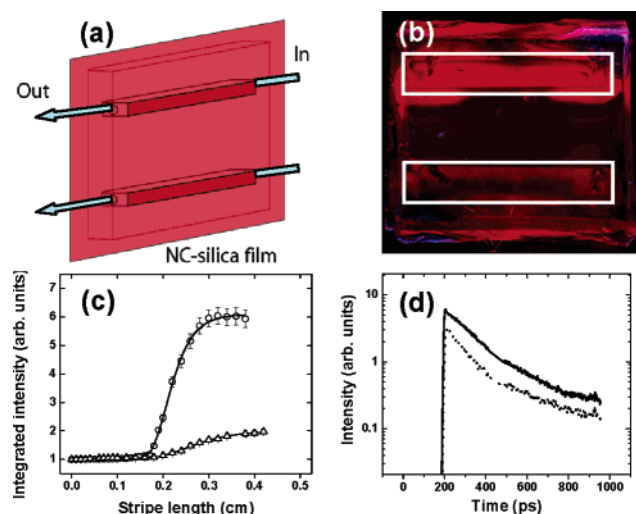


**Figure 1.** (a),(b) Fluorescence microscope images of a NC-titania (left) film and a NC-silica film (right) that have been exposed to water. The films were left to dry in air before the image was taken. The dotted line in (a) separates the area on the NC-titania film that did not come into contact with water. Darkening of the areas exposed to water may be attributed to a loss of capping ligands tethering the NCs to the titania matrix as a result of its rapid collapse. No structural or photophysical degradation of the NC-silica film in (b) was observed. The scale bar is 30  $\mu\text{m}$  in both images.



**Figure 2.** (a) AFM image showing a  $5 \times 5 \mu\text{m}$  area of a typical NC-silica film. (b) ASE from a NC-silica slabguide in air. (c) Lasing from a NC-silica film embossed with a 360-nm grating. The inset is an AFM image showing the high fidelity of the pattern transfer. The scale bar is 2.5  $\mu\text{m}$ . (d) WGM lasing in methanol from a silica microsphere coated with a NC-silica composite film. The inset is a fluorescence microscope image of the construct. The scale bar is 20  $\mu\text{m}$ . All ASE and lasing spectra shown were taken at room temperature.

used afforded silica films with a high volume fraction of NCs (~12%) that did not structurally degrade when exposed to water, as evidenced in Figure 1b. Surface analysis of the film via atomic force microscopy (AFM) revealed a roughness (RMS) of ~1.4 nm, as depicted in Figure 2a, and suggests a uniform dispersion of NCs within the silica matrix. These morphologically smooth NC-silica composites therefore incorporate a high volume fraction of NCs and in addition have an enhanced structural resilience over NC-titania composites that is achieved because APS and TSPI are less susceptible toward hydrolysis or alcoholysis than titanium butoxide.



**Figure 3.** (a) Device structure for liquid flow experiments. The NC-silica film is between a glass substrate and a PDMS block. (b) The NC-silica film excited using a UV-lamp. The upper channel was exposed to 0.1 M AH, while the lower channel was exposed to pure water. (c) The PL plotted as a function of excitation stripe length for a NC-silica film in 6-amino-1-hexanol (○) and in water (△). (d) Streak camera lifetime measurements using a 1-ns time window on a NC-silica film exposed to water (dotted line) and AH (solid line). The decays are dominated by biexcitonic emission, with a lifetime of  $\sim 150$  ps. An increase in the biexciton quantum yield from water to AH is seen by comparing the areas under their respective PL decay curves.

The NC-silica composites readily exhibited ASE under ambient conditions upon excitation using a frequency-doubled Ti:Sapphire laser with a 60-fs pulse width at 1 kHz, as illustrated in Figure 2b. We utilize the versatility of these NC-silica composites to couple them to various feedback structures, achieving lasing at room temperature and, more importantly, while submerged in solution. Figure 2c shows distributed feedback (DFB) lasing in water from a NC-silica film embossed with an  $\sim 360$ -nm periodicity grating pattern via soft lithography.<sup>7</sup> The AFM image in the inset illustrates the uniformity of the periodicity and modulation depth ( $\sim 45$  nm) of these NC-silica films. Figure 2d shows whispering gallery mode (WGM) lasing in methanol from a NC-silica composite coated onto the surface of a 20- $\mu$ m-diameter microsphere via a simple spin-coating process.<sup>1c</sup> Lasing in the presence of water and short-chain alcohols from these composites was stable over hours ( $\sim 10^6$  laser shots). The development of these robust, solvent-stable CdSe/ZnS NC-silica microcavity lasers not only allows for integration with microfluidic devices for potential applications, but also presents a platform in which to study the nonlinear optical properties of NCs as a dynamic function of their environment. We demonstrate this dynamical response by studying the effect of adding primary amines to the solution under lasing conditions.

While amines have been shown to increase the single exciton quantum yield in CdSe NCs, it was not clear that they should have any effect on the optical gain, which is due to biexcitons.<sup>6</sup> We utilize the porosity and solvent stability of the organoalkoxysilane-derived NC-silica films to investigate their modal gain in the presence of 6-amino-1-hexanol (AH) in water. The films are first interfaced with a block of poly(dimethylsiloxane) (PDMS) containing two isolated channels, each bearing an inlet/outlet duct to facilitate liquid flow, as illustrated in Figure 3a. Upon exposure to AH, a dramatic increase in the single exciton intensity was found, as shown in Figure 3b. Variable stripe length (VSL) measurements on a silica

film incorporating 4.1-nm CdSe/ZnS NCs were analyzed according to a previously described procedure,<sup>8</sup> yielding a modal gain that increased from  $\sim 32$   $\text{cm}^{-1}$  in water to  $\sim 62$   $\text{cm}^{-1}$  in the presence of 0.1 M AH, as depicted in Figure 3c. Care was taken to ensure that the area of excitation as well as the excitation intensity was the same in both cases. Streak camera measurements on the PL intensity of a similar film, shown in Figure 3d, revealed that the biexciton quantum yield was also increased upon optical excitation in the presence of AH. This suggests that AH plays a role in neutralizing charged NCs that are known to have extremely fast nonradiative relaxation pathways,<sup>9</sup> rendering them available for lasing. This also suggests that a charged biexciton has a nonradiative lifetime that is significantly faster than a charged exciton. The increase in the population of neutral NCs subsequently contributes to the increase in both the single and biexciton quantum yield upon optical excitation, consistent with the observed increase in modal gain. We thus see in this exemplary experiment that it is possible for certain amines to play a role in enhancing both the linear and nonlinear optical properties of NCs.

In summary, we have produced a NC-silica based laser that is robust under different chemical environments, making it suitable for integration with a microfluidic network. Conclusions from the VSL measurements indicate that the nonlinear optical properties of the NC-silica composite can be a dynamic function of its local environment. While optimized strategies are required to impart specificity and sensitivity to NC-silica composites to realize their utility as nonlinear optical chemosensors, these preliminary results suggest that such an outlook is promising.

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**Supporting Information Available:** Schematic of the incorporation process of NCs into silica. Detailed procedures for the incorporation of NCs into silica films, embossing of the films with a DFB pattern, as well as the fabrication of NC-silica coated microspheres for WGM lasing. Effect of AH on lasing in NC-silica DFB structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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