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In Ultrathin Film of Coupled Nanocrystals***

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We demonstrate exciton lasing in sub-wavelength coupled nanostructures at ultralow fluence threshold, as probed by femtosecond broadband emission and absorption spectroscopy. The complex spectrotemporal dynamics reveal for the first time an excitonic-to-electron-hole plasma lasing mechanism.

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An exciton is an electron bound to an electronic vacancy, a hole, by Coulombic forces. While the physics of exciton at very low densities is critical for energy-conversion technologies, the complex many-body interactions that emerge with increasing electron-hole pair density offer applications in nonlinear optoelectronic and sensing devices [1]. Here we demonstrate how nanospheres – not quantum-confined but coupled to each other in a solution-processed thin-film – can enhance many-body exciton-exciton and exciton-phonon interactions to yield lasing. Using nanospheres that are highly crystalline and deep sub-wavelength in dimensions to outcompete Auger recombination and reduce scattering losses, respectively, we achieve sub-75 $\mu\text{J}/\text{cm}^2$ lasing-threshold even in the limit of a few-nanospheres-thick film of order $\sim \lambda_{\text{emission}}/4$.

Thin-films were fabricated by spin-coating at 10,000 rpm on a glass substrate a dilute solution of zinc oxide nanospheres, with averaged diameter of about 35 nm that are dispersed in ethanol, and heating the sample at 300 °C on a heating plate to remove the organic solvent [2]. The resulting film was about 120 nm, that is about 3-4 nanospheres thick, as shown in figure 1(a). As control, we also fabricated sets of samples with varying thicknesses, ranging from 80 to 160 nm, and annealed a portion for a short duration (~ 10 minutes). Figure 1 (b-c) display representative results of the sample space studied with lasing (red) occurring only in films greater than 105 nm thick and consisting of the highly crystalline nanospheres. The control experiments (blue), either with thicknesses less than 105 nm or annealed, showed only a linear correspondence between emission intensity and excitation fluence.

Results and discussions

In order to understand the physical mechanisms – which take place on the fs-to-ps timescale – we use a high-efficiency transient emission spectrometer based on the optical Kerr effect to resolve the complex spectrotemporal

Figure 1. (a) Scanning electron micrograph of ZnO coupled nanocrystals. Inset is a cross-sectional SEM of the film and scale bar is 200 nm. (b) Representative results comparing the non-linear emission response of the coupled-nanocrystals with thickness >105 nm to the control ones (films <105 nm or annealed). Here, fluence threshold is $\sim 67 \mu\text{J}/\text{cm}^2$ (c) Kinetic traces at ~ 380 nm, near band-edge emission for the coupled-nanocrystal film (red), for a similar film that undergo rapid annealing (blue) and for nanocrystals that are dispersed in ethanol solution (0.7% volume concentration)(black). Lines are two-exponential fits to the data.

carrier dynamics of the various samples [3, 4]. As readily seen from figure 1(c), a drastic decrease in emission lifetime occurs in the crystalline coupled-nanospheres film (< 5 ps) while both the annealed sample (blue) and that of the dispersed ZnO nanospheres (black) have much longer lifetimes (> 30 ps). This decrease in lifetime is owing to the efficient radiative recombination that efficiently outcompetes the non-radiative recombination processes such as Auger and scattering losses. We note that the rapid anneal affects only the interface as observed in scanning electron micrographs (not shown here), where the overall nanostructure shapes are retained, and more importantly, the fact that the lifetime of the annealed sample shows only a small decrease in lifetime when compared to the dispersed nanospheres in solution, probably due to interfacial defects between the nanocrystals.

Moreover, this optical Kerr gating technique allows us to study for the first time the complex spectrotemporal dynamics of lasing. Critically, since transient emission spectroscopy can probe photoexcited species directly – in contrast to transient absorption that probed the gain lifetime and band gap renormalization – we can also assess subtle changes in the lasing dynamics of the gain material. Figure 2 shows the effect of increasing the excitation fluence on the broadband emission of the crystalline ZnO nanospheres film. Below lasing threshold ($29 \mu\text{J}/\text{cm}^2$), an almost featureless emission dynamics is observed, with decay kinetics similar to the control samples, that is dispersed, annealed and for films with a thickness less than 105 nm. However, at a near threshold of $60 \mu\text{J}/\text{cm}^2$, the first sign of lasing is visible, with “spikes” of intense emission occurring at few-100 fs intervals. For fluences slightly above the threshold, lasing occurs with a decrease in linewidth and accompanied by 3 orders of magnitude change in emission intensity (see Figure 1b as well). Importantly, a temporal red-shift corresponding to p-exciton scattering is seen in Figure 2c. This is due to exciton-exciton scattering with emission occurring in the lower energy emissive states. For higher fluences, this initial exciton scattering mechanism is succeeded by the formation of an electron-hole plasma, which dynamically blue shifts. Fitting these spectrally-evolving data sets confirm this transition from excitonic behavior to an electron-hole plasma mechanism (not shown here), with an accompanied delay of ~ 3 ps in the onset of the emission due to electron-phonon coupling modifications.

In summary, we have demonstrated nonlinear effect in a solution-processed low-dimensional film of ZnO nanocrystals where non-radiative losses are efficiently outcompeted by the few-ps radiative process. This method of using random scattering in nanostructures having dimensions deep in the subwavelength promises a cost-effective approach to tailoring many-body interactions in ultrathin films for novel optoelectronic and sensing technologies.

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Figure 2. Broadband time-resolved emission for the zinc oxide nanospheres ultrathin film at varying fluences: (a) below threshold $29 \mu\text{J}/\text{cm}^2$ (b) around threshold $60 \mu\text{J}/\text{cm}^2$ (c) above threshold $303 \mu\text{J}/\text{cm}^2$ displaying excitonic lasing and (d) above threshold at $607 \mu\text{J}/\text{cm}^2$ displaying lasing due to electron-hole plasma formation. Note that all 2D TRPL graphs have been normalized and plotted on a logarithmic scale.