Photophysics

Bulk Semiconductor Nanocrystals Transform Solution-Processed Gain Media

Remarkable optical gain performance of bulk-size CdS colloidal nanocrystals shows promise for printable laser diodes.

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The past two decades have witnessed remarkable progress in solution processed optoelectronic materials. The utilization of colloidal semiconductors as building blocks of flexible electronic devices has led to successful developments in printable display technologies,[1,2] photovoltaic cells,[3] and photodetectors.[3] However, achieving a regime where stimulated emission surpasses absorption (or, net optical gain) with solution-processed semiconductors, remains an elusive challenge.[4] This issue has impeded the development of solution-processed lasers, a crucial element in photonic circuits and many flexible electronic devices. The problem stems from the fact that most organic materials degrade under intense optical conditions required for lasing, while colloidal inorganic nanocrystals suffer from a low net gain that cannot compete with a lossy laser cavity. Writing in Nature Nanotechnology, Tanghe et al. [5] now offer a potential solution in the quest for colloidal laser materials by demonstrating surprising advantages of bulk semiconductor nanocrystals (BNCs) over quantum-confined nanostructures in gain media.

The study of Tanghe et al. focuses on CdS colloidal nanocrystals with a particle size range that exceeds the typical quantization diameter for this semiconductor. These nanomaterials exhibit a continuous (non-quantized) density of states and therefore are referred to as bulk colloidal nanocrystals. To gain insights into their properties, the team conducted optical gain measurements using a combination of ultrafast transient absorption spectroscopy and resonant cavity measurements. The latter approach employs both the standard thin film characterization using the Variable Stripe Length technique, as well as measurements of the optical gain in photonic crystal lasers.

The results of this study demonstrate that the optical gain performance of BNCs benefits from the combination of three crucial factors: high gain coefficients (~50,000 cm^{-1}), long gain lifetimes (~3 ns), and low gain thresholds (pump fluence ~10 $\mu J/cm^2$). This blend of desirable characteristics in a single material provides a decisive advantage over previous isolated improvements seen in quantum-confined nanocrystals like core/shell quantum dots[6] and semiconductor nanoplatelets.[7]

The presence of a long-lived, large optical gain in BNCs also leads to a low-threshold broad-band amplified spontaneous emission, evident in solution-processed films of these nanomaterials. Additionally, low-threshold lasing is observed in prototype photonic-crystal devices, showcasing the effectiveness of BNCs under both femtosecond and nanosecond excitation conditions while demonstrating a synergy with the underlying physical principles. Tanghe et al. explains excellent optical gain performance in BNCs using the band gap renormalization model (Figure 1a). This phenomenon, previously unobserved in solution-processed materials, causes a pronounced, 40-80 meV redshift in stimulated emission that surpasses the established benchmarks for quantum dots by an order of magnitude (Figure 1b). Such a red-shifted gain spectrum reduces self-absorption in the cavity, offering a new approach for exploiting bulk photophysics in optoelectronics.

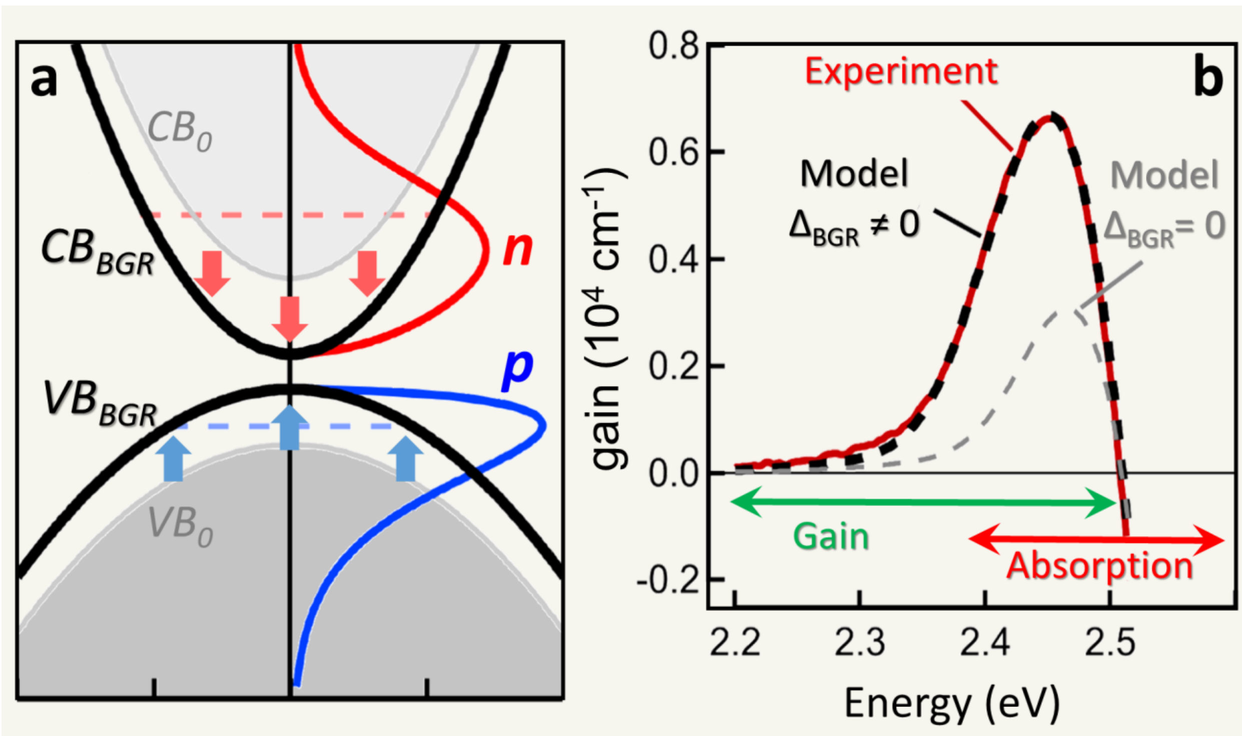

Figure 1. The phenomenon of band gap renormalization in bulk nanocrystals. (a). Quantitative Bulk Gain Model. A bulk valence band (VB) and conduction band (CB) are shown by grey lines, together with the calculated electron (red, n) and hole (blue, p) densities of an excited electron-hole population in 12-nm CdS nanocrystals. The black bands refer to the renormalized gap, CB_{BGR}-VB_{BGR}, which is reduced compared to the corresponding bulk value. (b). Material gain spectrum with (dashed black) and without (dashed grey) band gap renormalization (Δ_{BGR}). Dashed black line adds a BGR of 45 meV. Solid red line indicates experimental data. Panels (a) and (b) were adapted from Tanghe et al,[5] Figures 4a and 4d, respectively.

Another critical aspect of BNCs is their ability to overcome a long-standing limitation of strongly confined nanomaterials - the Auger bottleneck. In bulk nanocrystals, Auger processes become much slower and can no longer compete with the gain, effectively circumventing the Auger losses.

This intrinsic advantage allows for efficient gain without compromising performance, as was evidenced in Tanghe et al through the observation of long-lived optical gain, exceeding 3 ns.

From a broader prospective, the demonstrated performance of BNCs opens the door to reevaluating the advantages offered by bulk photophysics in optoelectronics. In the past, achieving optical gain has been associated with nanocrystals featuring a strong charge confinement regime, but this study challenges that perspective by highlighting the benefits of bulk photophysics. Bulk colloids, exemplified by Tanghe et al. using 12-nm CdS nanocrystals, offer a continuous density of states, large cross sections, and limited non-radiative losses, which have not been fully exploited due to historical limitations in material quality and the inability to confine both light and carriers in bulk materials. While certain challenges persist, such as the limited spectral tuning of bulk nanocrystals, previous studies[8] have demonstrated that alloying techniques can effectively address this issue by providing a general method for expanding the spectral range of bulk materials.

The implications of this study promise a wide range of opportunities in optoelectronics. First and foremost, bulk nanocrystals mark a significant advance in the pursuit of efficient solution processed gain materials capable of operating under realistic device conditions, including electrical pumping.[9] In addition to gain performance, BNCs also leverage the ability for the suppression of Auger decay, which is important for devices that endure high intensity excitation regime or high-energy photon absorption. Prominent examples of such devices include photodetectors, X-ray scintillators, and high-brightness LEDs. Ultimately, this study provides a solid foundation for developing optical gain media and inspires a reevaluation of the possibilities offered by bulk (nano)-materials in the realm of optoelectronics.

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Conflict of interest

The author declares no conflict of interest.

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