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Comment on “Spin-Flip Limited Exciton Dephasing in CdSe/ZnS Colloidal Quantum Dots”

In the Letter by Masia *et al.* [1], a four-wave mixing technique is used to probe the dephasing time of the optical coherence and in turn the homogeneous linewidth of the zero-phonon line (ZPL) of the lowest bright exciton in an ensemble of CdSe/ZnS nanocrystals (NCs). The authors claim that the rapid ZPL dephasing time ($T_2 \approx 100$ ps) is determined by phonon-assisted spin flip from the lowest bright state to the dark exciton state of the band-edge exciton fine structure. Furthermore, they claim that this result explains the previously reported high-resolution linewidth measurements of single NCs of these same materials [2]. However, the four-wave mixing technique used by Masia *et al.* studies ensembles of heterogeneous materials, which confounds the interpretation of the dephasing time. This is particularly relevant, as the commercial NCs used have significant shape variation [see TEM Fig. 1(a)], which leads to different fine structure states [3] [see Fig. 1(b)] with multiple relaxation rates. Furthermore, the band-edge exciton fine structure of these NCs is crowded, as the crystal field splitting is compensated by the shape anisotropy. In this regime, all the optically allowed band-edge transitions lie within a 4 meV span, complicating the analysis of any ensemble response generated using a femtosecond laser that excites the entire band-edge manifold of energy levels.

The authors use NCs with a peak emission at 655 nm at room temperature in order to make meaningful comparisons with prior work. Much of their analysis rests on a high spin-flip rate (~ 10 ns $^{-1}$), based on the lifetime measurements of Labeau *et al.* [4]. However, this spin-flip rate is inappropriate, as the latter work was dedicated to different NCs with a smaller size, which exhibit single ZPL emission spectra at 2 K [4]. For the NCs used by Masia *et al.*, several studies [2,3,5,6] have reported spin-flip rates γ_0 at least an order of magnitude lower than the dephasing rate measured in Ref. [1]. In fact, the simultaneous observation of both bright and dark state spectral lines at low temperature indicates slow spin relaxation, as is the case for the 10 μ eV linewidth measured in Ref. [2].

At low temperatures where we can neglect thermal pumping, the ratio of the bright and dark state emission is $\gamma_B/(\gamma_B + 2\gamma_0)$ [2,5]. As exemplified in the inset of Fig. 1(c), the significant contribution of the bright state emission in the photoluminescence spectrum at 2 K is consistent with values of $\gamma_0 < 1$ ns $^{-1}$ for these NCs. In Fig. 1(c), we provide a direct measurement of the bright exciton lifetime from the biexponential decay of a NC at 2 K. The well-resolved short decay time of 2 ns indicates a low spin-flip rate according to $\gamma_0 + \gamma_B = 1/2$ ns $^{-1}$. The concurrent detection of both the lifetime and spectrum

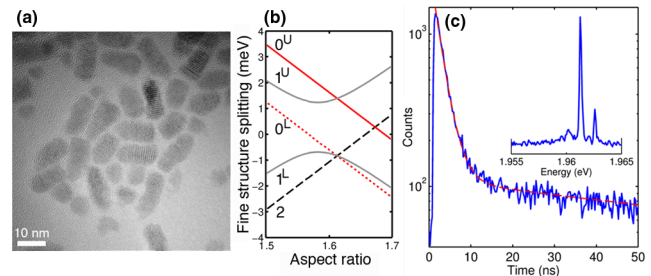


FIG. 1 (color online). (a) High-resolution TEM image of 655 NCs similar to those used by Masia *et al.* (b) CdSe fine structure versus aspect ratio for NCs with a 7 nm width [3]. (c) Single NC decay at 2 K with biexponential fit. (Inset: emission spectrum of this NC recorded during the luminescence decay acquisition.)

provides independent and mutually compatible measurements of slow spin relaxation, ruling out any systematic bias. Thus, ZPL linewidths of ~ 10 μ eV are *not* spin-flip limited in these materials.

In summary, we believe the four-wave mixing photon echo signal of Masia *et al.* does not reflect an intrinsic property of the NCs, but merely reflects an ensemble response where the observed decay is dominated by sample heterogeneities. In fact, based on single NC measurements, we come to the conclusion that these ensemble measurements obscure the dephasing mechanism. Thus, the long-standing question of the physical origin of the ZPL broadening in CdSe/ZnS quantum dots is not yet resolved.

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