

Photoluminescence Dynamics of Broadband Emission from Cadmium Sulfide (CdS) Quantum Dots

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Motivation—CdS quantum dots typically have a narrow bandwidth emission that is accompanied by a photoluminescent lifetime on the order of a few ns. This fast decay is attributed to direct electron-hole recombination. Both the emission bandwidth and the PL lifetime can increase dramatically upon the addition of surface ligands. The nature of the decay can also become strongly non-exponential, and these three characteristics are thought to be due to the formation of surface trap states. Surface functionalized CdS QDs can be made following the reverse micellar synthesis developed by Lianos and Thomas. The surfactant dioctyl sulfosuccinate sodium salt (AOT) acts as the surface ligand, and the resulting 2 nm QDs have nearly white emission. Our interest is in characterizing and understanding the decay dynamics of this complex emission and how this is affected by UV photolysis. Our goal is to determine whether the PL lifetime can be controlled in such a way that QDs can be used as taggants that have both emission color and lifetime as identifying characteristics.

Accomplishment—CdS quantum dots were prepared in reverse micelles in heptane and were purified by cooling to -30°C and cold-filtering out the ice that formed. The purified solutions were then photolyzed with UV light, which is known to increase the emission intensity. Both the quantum yield (QY) and the PL lifetime were monitored during photolysis. Significantly, the emission spectrum is only slightly changed by photolysis. The QY was found to increase with photolysis, reaching a maximum value of 24%. This high value, which is twice that reported in the literature, is due to the purification before photolysis. The

PL lifetime was found to increase in proportion to the quantum yield, Fig. 1, demonstrating that control of the lifetime is possible without altering the emission color. The proportionality of the lifetime and QY can be explained by a simple model of parallel radiative and non-radiative decay channels, where the non-radiative lifetime increases with photolysis. Studies at -70°C show that the quantum yield and the lifetime increase to more than twice their ambient values, which is consistent with trap state emission. Further evidence of trap states comes from the form of the PL decay, which is well described by a stretched exponential with an exponent of 0.5, Fig. 2. This decay is consistent with an exponential distribution of lifetimes, which is expected for trap states. Finally, the lifetime and the quantum yield were found to decrease significantly with the addition of alkane thiols, with only a modest red-shift in the emission, so the addition of these ligands can be used to control the lifetime.

Significance—In understanding the trap state emission in quantum dots we have shown that it is possible to control the PL lifetime independently of emission color. Lifetime control can be accomplished by photolysis or by the addition of surface-active ligands, such as alkanethiols. This discovery demonstrates that QDs can be used as two-dimensional taggants, which greatly increases the number of distinguishable taggants that can be synthesized. With the development of UV LEDs it is now possible to make a compact device for measuring the PL lifetime, based on the phase-shift method, so lifetime tagging may become a practical reality.

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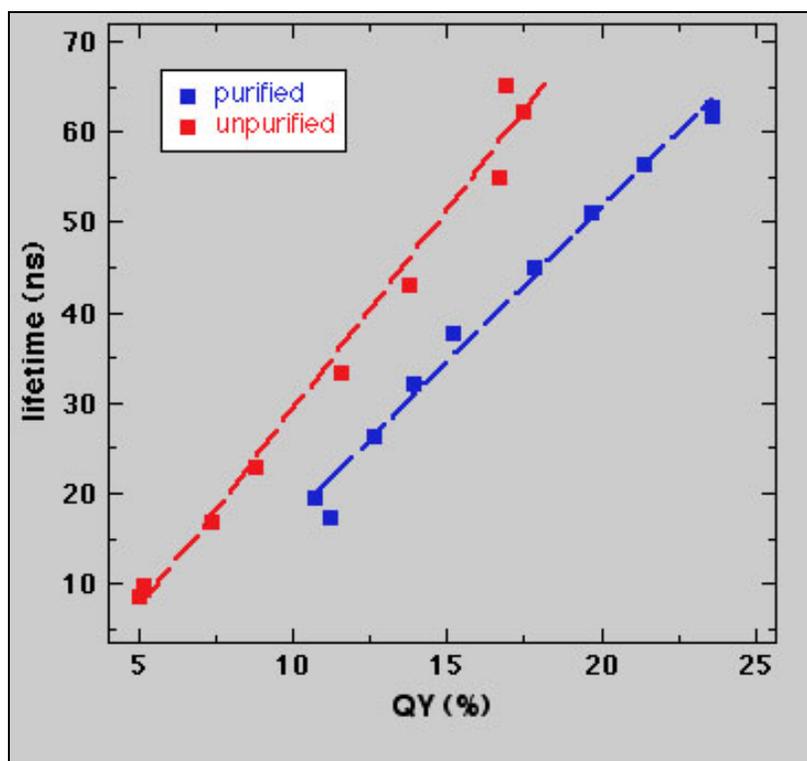


Figure 1. For both purified and unpurified CdS samples the lifetime is proportional to the quantum yield, although the purified sample has a considerably larger QY. The QY increases with photolysis.

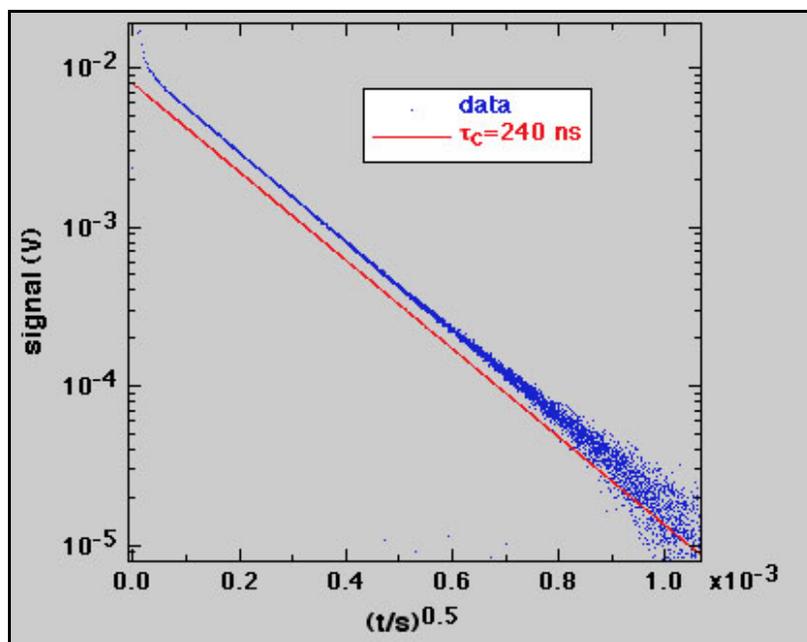


Figure 2. The PL decay of broadband-emitting CdS quantum dots is well described by a stretched exponential decay with an exponent of 0.5. This is consistent with a broad, exponential distribution of lifetimes. The characteristic time of this decay is 240 ns.