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## Toward the Control of Nonradiative Processes in Semiconductor Nanocrystals

No other chromophore has been scrutinized to the extent of colloidal semiconductor nanocrystals (NCs), also called quantum dots. It is remarkable that the basic photo-physics of these objects are still being examined, even more than two decades since the first high-quality colloidal syntheses in solution were reported.<sup>1–3</sup> Colloidal NCs have several advantages compared to organic chromophores, including an absorption cross section that can be an order of magnitude larger and high photostability. Moreover, the tunability of their optical and electrical properties through size, shape, and composition variations make them particularly unique from a semiconductor science perspective. The degree of complexity is further increased through the engineering of heteronanostructures, which exhibit intriguing physical properties that arise from the combination of the constituent materials. In this editorial, we discuss the nonradiative processes in colloidal semiconductor NCs and, in particular, those that involve surface effects.

**Band Edge versus Surface Trap Emission.** As in epitaxially grown quantum dots, various nonradiative processes occur in these colloidal nanostructures. Nonradiative processes often limit applications based on fluorescence (decrease the photoluminescence quantum yield, PL QY) or charge carrier collection (lower efficiency of photovoltaic cells or detectors). While in bulk semiconductor materials numerous defects are present inside of the crystal lattice itself, the way by which colloidal NCs are synthesized tends to autoexclude volume defects. However, due to the large surface to volume ratio, the electric and optical properties of colloidal NCs are strongly affected by the nature of the surface and its close environment. At the early beginning of this field, it was even proposed that the NC optical properties were dominated by localization of the carriers at the surface rather than the now well-established confinement effect.<sup>4</sup> At that time, poorly passivated NCs exhibited deep trap emission rather than recombination at the band edge. It was later, with better surface passivation by the ligands<sup>5,6</sup> and most importantly the growth of a shell of another semiconductor material, that dangling bonds and thus trap states were significantly reduced and the fluorescence QY was improved.<sup>7,8</sup> In such nanostructures, fluorescence QYs can be close to 100%, in which case, the efficiency of the radiative channels would dominate.<sup>9–11</sup>

**Blinking.** Another consequence of the surface effect on the colloidal NC properties is the photoluminescence intermittency at the single-particle level, known as blinking. This phenomenon presents a strong limitation for the use of NCs as a single-photon source. Whereas some advances have been made<sup>12,13</sup> to overcome its origins,<sup>14–17</sup> blinking is still the source of intensive studies.

**Nonradiative Relaxation.** We still have to keep in mind that important sources of nonradiative channels in colloidal NCs are surface-related and that they compete with radiative deactivation. It has been reported that ligands affect relaxation rates and pathways occurring after absorption of a photon, which can, for

example, result in a “breaking of the optical phonon bottleneck”.<sup>18–20</sup> This plays an important role in photovoltaic applications for high-energy photon harvesting or hot carrier collection. It was even proposed recently that ligands could lead to an intrinsic magnetic field that induces some coupling between the first dark and bright states and thus increase the associated spin-flip rate.<sup>21</sup>

All of these surface effects show how much we need (1) to understand the nonradiative pathways and which carriers they involve and (2) to better characterize the surface. The first point is not a new topic, and various measurements were and are currently performed to study these nonradiative processes, PL quenching,<sup>22,23</sup> temperature-dependent lifetime,<sup>24,25</sup> pump–probe experiments,<sup>26</sup> and so forth. While the first point has been a subject of extensive studies for decades, the investigation of the second one is experimentally more challenging. However, more and more developments have been made to characterize the NC surface and the interface for the case of core/shell structures. Determining the number of ligands per surface area is a tricky measurement (Knittel; et al. Tritium Labeling As Ultra-Sensitive Method for the Quantification of Ligands at the Surface of Nanoparticles. In Preparation), but their nature can be routinely characterized either by infrared spectroscopy<sup>27</sup> or NMR.<sup>28–31</sup> Because it was proposed that the interface (smooth versus sharp) can affect the Auger rate,<sup>32</sup> Raman spectroscopy has become an essential characterization tool for blinking studies.<sup>33–35</sup> (See also, Dzhan; et al. Raman- and IR-Active Phonons in CdSe–CdS Core/Shell Nanocrystals in Presence of Interface Alloying and Strain. Submitted.) In addition, geometrical phase analysis (GPA)<sup>36</sup> can be applied to colloidal NCs<sup>37,38</sup> in order to investigate changes in the band alignment between the core and the shell<sup>39</sup> or crystal asymmetry<sup>38</sup> induced by interfacial strains, which can thus induce a significant modification of the electronic properties. As surface and interface characterization techniques evolve, we expect that nonradiative channels involving trap states or ligand coupling will be clarified.

In this issue of *The Journal of Physical Chemistry Letters*, three Perspectives highlight the importance of nonradiative processes in semiconductor NCs in fundamental and applied research. In their paper, Loomis and co-workers rekindle discussions on the controversial excitation wavelength dependency of fluorescence quantum yields (Hoy, J.; Morrison, P. J.; Steinberg, L. K.; Buhro, W. E.; Loomis, R. A. Excitation Energy Dependence of the Photoluminescence Quantum Yields of Core and Core/Shell Quantum Dots. *J. Phys. Chem. Lett.* **2013**, *4*, 2053–2060). They show that for both CdSe and CdSe/ZnS NCs, the PL QY decreases with the excitation energy. Numerous previous reports have presented conflicting conclusions regarding the excitation energy dependence of the PL QY. In 2004, Chergui and co-workers reported careful measurements and concluded

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that CdSe photoluminescence excitation (PLE) spectra follow those of the absorption when PLE measurements are performed on low optical density samples, below 0.1 at the excitation wavelength, to avoid reabsorption.<sup>40</sup> The small differences were attributed to some scattering signal, as well as population selection. This last effect can be suppressed by performing integrated photoluminescence excitation (IPLE) rather than PLE.<sup>41</sup> These results reported by Chergui<sup>40</sup> thus show constant PL QY as a function of excitation wavelength. However, more recently, several groups have proposed that new nonradiative pathways may occur for high excitation energy, that is, above the band edge.<sup>15,26,42</sup> If these channels are fast enough, that is, comparable in time with the thermalization processes, they should induce a decrease of the PL QY. Interestingly, in the Loomis Perspective, no change was measurable in the photoluminescence lifetime between different excitation wavelength measurements performed at low power excitation (decay time range from <1 to 500 ns). This work reminds us how challenging it is to accurately measure a PL QY and how careful we need to be when performing the experimental measurement<sup>43</sup> and for the interpretation.

Advances in surface characterization, in conjunction with further ultrafast spectroscopy studies, are vital for the elucidation of the surface-related nonradiative processes that occur in colloidal nanostructures.

In their Perspective, Klimov and co-workers discuss the nonradiative channels that compete with carrier multiplication (Stewart, J. T.; Padilha, L. A.; Bae, W. K.; Koh, W.-K.; Pietryga, J. M.; Klimov, V. I. Carrier Multiplication in Quantum Dots within the Framework of Two Competing Energy Relaxation Mechanisms. *J. Phys. Chem. Lett.* **2013**, *4*, 2061–2068). By comparing transient absorption to time-resolved photoluminescence measurements of PbS, PbSe, and PbTe NCs, they showed that Auger recombination is not the only process that should be taken into account as a limitation for multiexciton generation (MEG). For example, they propose that the difference in MEG efficiency between PbS and PbSe is due to phonon emission.<sup>44</sup> In their conclusion, they highlight that their findings will enable the strategic design of nano-heterostructures for specific applications based on carrier multiplication. Despite the ups and downs of research reports on MEG, a recent report by Semonin et al. shows that a solar cell based on a PbSe NC film can have an efficiency of greater than 100% at certain excitation wavelengths, which is a compelling demonstration of MEG in solar energy conversion.<sup>45</sup>

This issue also highlights the work by Cahoon and co-workers on the new design of remarkable silicon-based solar cells, consisting of a horizontal (rather than the traditional vertical direction) array of Si nanowires (Zhang, X.; Pinion, C. W.; Christesen, J. D.; Flynn, C. J.; Celano, T. A.; Cahoon, J. F. Horizontal Silicon Nanowires with Radial p–n Junctions: A Platform for Unconventional Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 2002–2009). In this noncolloidal system, improved efficiency is achieved through the use of optical antennae effects (resonance) that induce an effective increase of the nanowire

cross section. This Perspective emphasizes the importance of the strategy that focuses on the increase of the rate of the desired electronic process (i.e., shorter its characteristic time) rather than eliminating the competing channels that induce losses.

In conclusion, advances in surface characterization, in conjunction with further ultrafast spectroscopy studies, are vital for the elucidation of the surface-related nonradiative processes that occur in colloidal nanostructures.

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### Notes

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