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Aggregation-Induced Changes in Optical Characteristics of CdSe/ZnS Quantum Dots

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Extended Abstract

Over the past decades, semiconductor quantum dots (QDs) along with their remarkable size-dependent optical and electrochemical properties have attracted considerable research interest. Modern studies have opened up the possibility of employing these nanomaterials in the variety of applications, ranging from bioimaging and fluorescent labeling [1] to new-generation solar cell and display fabrication [2]. The widespread usage of QDs has led to a necessity of understanding the factors that affect optical properties of these nanostructures. For instance, QDs, as well as colloidal nanoparticles of other types, tend to aggregate upon environmental changes [3–5]. The decrease in interdot distance initiated by the aggregation process promotes efficient QDs interactions and gives rise to the Förster resonance energy transfer (FRET) between proximal dots within the aggregate [6]. The FRET process is considered to be the reason of rapid changes in optical characteristics of aggregated QDs.

The present study is focused on the effect of aggregation on optical properties of colloidal core-shell CdSe/ZnS QDs. The aggregates were formed by adding methanol to the QDs solution in chloroform. To monitor the process of aggregation, hydrodynamic diameters of particles were evaluated by Dynamic Light Scattering (DLS) technique. DLS measurements showed good agreement with the data obtained from scanning electron microscopy.

Optical characterization of QDs was provided by photoluminescence (PL) and UV-VIS spectroscopy. The QD aggregation was accompanied by an 80% decrease in PL intensity and a red shift of the spectral peak by 10 nm, while the PL quantum yield reduced from 10% to 2%. As for the absorption spectra, QDs in both monodispersed and aggregated states were characterized by the same excitonic peak positions. The magnetic circular dichroism (MCD) measurements conducted at magnetic field strengths of +1.5 T and -1.5 T did not reveal any significant changes of MCD spectra upon the aggregation.

The PL kinetics was examined using a time-correlated single photon counting spectrometer Micro-Time100 (PicoQuant). The characteristic PL lifetime was investigated as a function of recording wavelength. We employed 10 nm band-pass filters to selectively detect the emission in a wavelength range corresponding to the PL spectra of QDs. We observed that the QD PL decay time of non-aggregated QDs did not depend on the luminescence wavelength, while the PL lifetime of aggregates increased linearly with increasing the wavelength. Moreover, the slope of observed linear dependance increases, as the degree of QD aggregation becomes higher. We assume that obtained results can be explained by the energy transfer from smaller to larger sized QDs within an aggregate. As the QD colloidal state changes from monodispersed to aggregated, the FRET efficiency value increases up to 40%.

To conclude, we demonstrated that optical characteristics of CdSe/ZnS QDs alters dramatically during the aggregation process. We believe that FRET between QDs of various sizes within the aggregate causes these changes.

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