Characterizing the Organic Shell Structure and Composition of Hydrophobic CdSe-ZnS Quantum Dots using NMR Spectroscopy

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We have combined several advanced solution phase NMR spectroscopy techniques, namely ^{1}H, ^{31}P, heteronuclear single quantum coherence (HSQC), and diffusion ordered spectroscopy (DOSY), to probe the composition of the organic capping layer on colloidal CdSe-ZnS core-shell quantum dots; the nanocrystals have been grown using the common "hot injection" route. Combining solution phase ^{31}P and ^{1}H NMR with DOSY, we are able to distinguish between ligands that are free and those coordinated onto the QD surfaces. Furthermore, when the NMR data are complemented with matrix assisted laser desorption ionization (MALDI) measurements, we find that the organic shell of the as-prepared QDs consists of a mixture of tri-n-octylphosphine oxide TOPO), tri-n-octylphosphine (TOP), alkyl amine, and alkyl phosphonic acid (e.g., n-hexylphosphonic acid); the latter are usually added during growth at a rather small concentrations to optimize the quality of the prepared nanocrystals. However, data collected from QD dispersions subjected to two or three rounds of purification prove that the organic shell composition on the QDs is essentially dominated by n-hexylphosphonic acid (HPA), along with small fractions of surface-coordinated or self-assembled (via hydrogen-bonding) with hexadecyl amine and TOP/TOPO. This is true even though large excesses of TOP and TOPO surfactants are used during QD growth. This finding proves that n-hexylphosphonic acid exhibits substantially higher coordinating affinity to the QD surfaces, compared to other phosphorus containing surfactants such as TOP and TOPO. Finally, we test the effectiveness of DOSY NMR to provide accurate data on the translational diffusion coefficient and hydrodynamic radius of QDs as well as feely diffusing ligands in a sample. This proves that this this technique is highly effective for charactering such small size colloids and organic surfactants where dynamic light scattering tends to reach its limit.

Keywords: semiconductor core-shell quantum dots, fluorescence, organic ligands, surface characterization, MNR spectroscopy

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