Unravelling the surface ligand of quantum dots: upgrading the NMR toolbox to see the invisible

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Abstract

Over the last decade, semiconductor nanocrystals -NCs- (also tagged quantum dots -QDs) have emerged as an important class of materials for applications ranging from electronics to biomedicine [1]. Significant achievements have been made possible thanks to the development of procedures leading to nano-objects of controlled-shape, -structure, -composition (homogeneous, graded, core-shell), and surface chemistry (capping ligands) [1]. This latter feature is of key importance for the synthesis of NCs as well as for the optical and the transport properties of individual QDs or ordered-assemblies of QDs. These advances have been also provided by an increased knowledge in the understanding at the molecular scale of the interactions, the bonding modes, the dynamics and the reactivity of the ligands (whether organic or inorganic). However, the monitoring of the surface chemistry requires the development of analytical tools able to probe the composition of NC surfaces. Among the various used methods (that include infrared and X-ray photoelectron spectroscopies), solution nuclear magnetic resonance (NMR) stands out due the possibility (i) to distinguish between free and bound species (ii) to identify and quantify them, and (iii) to monitor the ligand dynamics [2]. Nevertheless, the *in situ* observation of moieties close to the surface as well as short ligands (OCH_3, OH…) are precluded because of resonance broadening due to a distribution of chemical shift and of a manifold of capping ligand-NC bonding environment. This limitation is a major drawback since, for instance hydroxide ligand, which has been suspected but never evidenced, could be at the origin of the deterioration of the optical and electrical properties of PbSe QDs-based films [3]. We will here present a new NMR-based approach (named “Surface”) allowing for the first time the direct observation of ligand moieties and short ligands that are close to the NCs surface. This technique is based on magic angle spinning (MAS) NMR experiment and allows the characterization of ligands which are typically invisible using others classical spectroscopic means. This will be exemplified with Cd_3P_2 QDs coated with hexadecylamine ($CH_3(CH_2)_{15}NH_2$), acetate ($CH3CO_2$) and hydroxyle (HO) ligands (Figure) [4].

References

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Figures