

CdSe Semiconductor Nanocrystals: The Surface and the Core

Frédéric Blanc

Department of Chemistry, Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, L69 7ZD, U.K.

Highly resolved and sensitive ^{113}Cd NMR spectra provide insights into the surface and core of CdSe quantum dots and nanoplatelets.

Disruptive, new and improved existing technologies with the potential to address some of the significant environmental challenges faced by our society are urgently needed, particularly in the area of renewable clean energy. One approach to achieving this goal is to revolutionize materials science and nanotechnology using rational design of new materials, which includes control over materials' function and a step change in their physical properties. Semiconductor nanocrystals (NCs) have attracted considerable research interest as they may play an important role in this revolution. Successful applications of NCs in optoelectronic devices, including application in photovoltaics and photocatalysis, have already resulted in their broad commercialization.

NCs show size-dependent, optical and electronic properties that differ from those of larger particles.^{1,2} This phenomenon arises from the quantum confinement effect that is observed when the particle size is smaller than the wavelength of the electron. The shape, surface, and coating of NCs are all important in defining their physical and chemical properties. Fabrication of materials in the form of colloidal suspension provides exceptional control over their size, dispersity, and shape. In particular, the individual entities of the NCs (crystalline cores, surface atoms, and surface ligands, Figure 1a) and their interdependence play a key role in defining the properties of these nanomaterials. Therefore, detailed understanding of all these components and interfaces, especially the semiconductor NCs surfaces, is important for the discovery of new materials with improved properties and the delivery of the revolution.

In an exciting paper that represents an important step toward providing atomistic description of NCs and strengthening characterization methods based on nuclear magnetic resonance (NMR), Kovalenko, Copéret, and co-workers³ demonstrated that the core and surface atoms of core/shell quantum

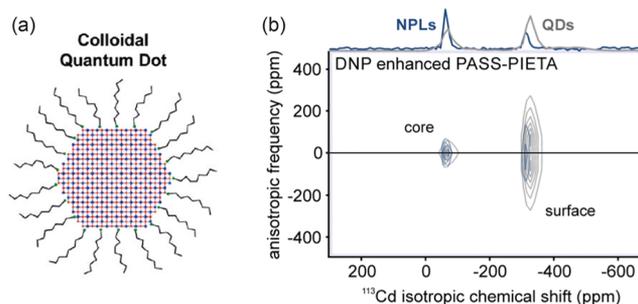


Figure 1. (a) Schematic representation of a colloidal quantum dot that contains a crystalline core, a surface covered with atoms of a specific element, and capping organic ligands. Reprinted with permission from ref 1. Copyright 2010 American Chemical Society. (b) Overlaid two-dimensional nuclear magnetic resonance ^{113}Cd isotropic anisotropic spectra of quantum dots (gray) and nanoplatelets (blue). The core and surface signals appear around -60 and -320 ppm, respectively. The horizontal black line centered at 0 ppm represents the position of the center band spectrum that is the high-resolution isotropic spectrum. Reprinted with permission from ref 3. Copyright 2018 American Chemical Society.

dots and core/crown nanoplatelets can be effectively discriminated with specific spectral fingerprints obtained from both the effect of the core crystal structure and the shape of the NCs. The significance of this work is further emphasized by the fact that the developed approach is applicable to multicomponent complex systems in a range of chemical forms (crystalline, amorphous, colloid, etc.) and, more

This NMR approach enables gathering structural information at the atomic level by achieving sufficient resolution and sensitivity while using very small amounts of nanoheterostructured materials.

importantly, to materials that are only accessible in small quantities (a typical synthesis of NCs is on the $1\text{--}2$ mg scale) and are intrinsically very dynamic.

Published: August 23, 2018

The ^{113}Cd NMR resonances of colloidal CdSe NCs cores and surfaces⁴ are usually broad due to the wide distribution of chemical shifts (positions of bands in a spectrum) and the large anisotropic broadening, which dramatically challenges the acquisition of high-resolution spectra by standard NMR methods. The authors were able to resolve ^{113}Cd resonances by exploiting a robust NMR method based on separation of spinning sidebands (artifacts that often accompany main bands in NMR spectra)⁵ augmented with a surface enhanced NMR approach that they previously developed,⁶ using dynamic nuclear polarization (DNP),^{7–9} to increase the signals from the NCs surfaces. The developed NMR approach is arguably one that can provide the most comprehensive understanding of all NCs components.

Isotropic properties are constant irrespective of the direction of measurement, while anisotropic properties change depending on the direction. Two-dimensional ^{113}Cd NMR spectra separating and correlating the isotropic and anisotropic chemical shifts were recorded (Figure 1b). The high-resolution spectrum containing the isotropic chemical shift only is obtained at the center band position (0 ppm in the vertical dimension, Figure 1b), which enables a very significant gain in resolution from previous work where only a standard NMR acquisition method was used.⁴ The spectrum in the vertical dimension (Figure 1b) provides access to the anisotropic component of the chemical shift, which is challenging to obtain in standard NMR experiments, and provides a breadth of information regarding the NCs shapes and defects.

The high-resolution isotropic ^{113}Cd NMR spectrum of quantum dots with cubic-type crystal core (zinc blend) shows two well-defined resonances and is significantly less crowded than the one obtained for quantum dots with a hexagonal-type crystal core (wurtzite), where a number of resonances are observed (Figure 2). Although both materials display the same optical quality, the differences in NMR spectra indicate the increased atomic complexity of the quantum dots with hexagonal-type crystal core. It is worth pointing out that these results cannot be deduced from the regular NMR data only as the ^{113}Cd spectra are dominated by an extensive manifold of broad spinning sidebands that prevent achieving high resolution (Figure 2), which validates the advanced data acquisition strategy.

The success of these experiments relies on ensuring homogeneous dispersion of the electron-polarizing agent (stable radical) and elimination of NCs aggregation to maintain a colloidal state. This is achieved in a two step process by first dispersing the NCs in the solution of the radical followed by impregnation of the NCs-radical solution in mesoporous silica.⁴ Achieving reproducibility

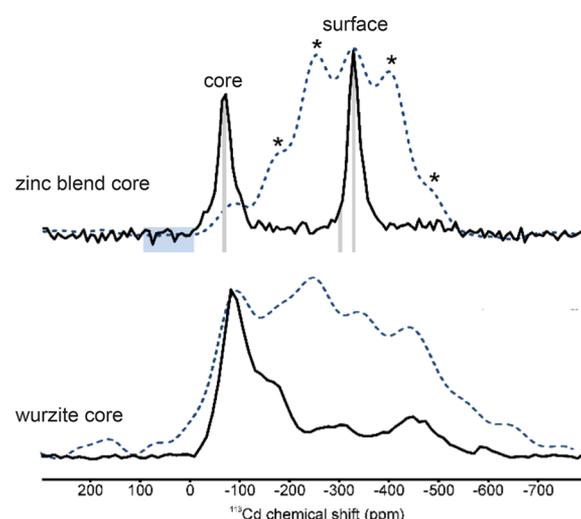


Figure 2. Stacked plot of the high-resolution isotropic ^{113}Cd NMR spectra of CdSe quantum dots with cores that have a different crystal structure. Both the conventional NMR spectra (dashed lines) and high-resolution isotropic spectra (black, see Figure 1b) are shown. Asterisks denote spinning sidebands. Reprinted with permission from ref 3. Copyright 2018 American Chemical Society.

of the formulation of this matrix is the key to future characterization of many materials. Further consideration into matrix-free sample preparation and NMR experiments at room temperature, which are both important research directions being currently pursued, would enable the study of the NCs in their native state.

In summary, the authors harnessed NMR approaches to characterize, at the atomic level, the core and surface of a range of colloidal CdSe quantum dots and nanoplatelets. The judicious exploitation of selective and sensitive NMR methods that yield highly resolved and receptive data enables advances in semiconductor nanocrystals.

Author Information

E-mail: frederic.blanc@liverpool.ac.uk

ORCID

Frédéric Blanc: 0000-0001-9171-1454

Notes

The author declares no competing financial interest.

REFERENCES

- (1) Smith, A. M.; Nie, S. Semiconductor Nanocrystals: Structure, Properties, and Band Gap Engineering. *Acc. Chem. Res.* **2010**, *43*, 190–200.
- (2) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chem. Rev.* **2010**, *110*, 389–458.
- (3) Piveteau, L.; Ong, T.-C.; Walder, B. J.; Dirin, D. N.; Moscheni, D.; Schneider, B.; Bär, J.; Protesescu, L.; Masciocchi, N.; Guagliardi, A.; Emsley, L.; Copéret, C.; Kovalenko, M. V. Resolving the Core and the Surface of CdSe Quantum Dots and Nanoplatelets Using Dynamic Nuclear Polarization Enhanced PASS-PIETA NMR Spectroscopy. *ACS Cent. Sci.* **2018**, DOI: 10.1021/acscentsci.8b00196.
- (4) Piveteau, L.; Ong, T.-C.; Rossini, A. J.; Emsley, L.; Copéret, C.; Kovalenko, M. V. Structure of Colloidal Quantum Dots from

Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy. *J. Am. Chem. Soc.* **2015**, *137*, 13964–13971.

(5) Dixon, W. T. Spinning-sideband-free and Spinning-sideband-only NMR Spectra in Spinning Samples. *J. Chem. Phys.* **1982**, *77*, 1800–1809.

(6) Lesage, A.; Lelli, M.; Gajan, D.; Caporini, M. A.; Vitzthum, V.; Miéville, P.; Alauzun, J.; Roussey, A.; Thieuleux, C.; Mehdi, A.; et al. Surface Enhanced NMR Spectroscopy by Dynamic Nuclear Polarization. *J. Am. Chem. Soc.* **2010**, *132*, 15459–15461.

(7) Overhauser, A. W. Polarization of Nuclei in Metals. *Phys. Rev.* **1953**, *92*, 411–415.

(8) Carver, T. R.; Slichter, C. P. Experimental Verification of the Overhauser Nuclear Polarization Effect. *Phys. Rev.* **1956**, *102*, 975–980.

(9) Hall, D. A.; Maus, D. C.; Gerfen, G. J.; Inati, S. J.; Becerra, L. R.; Dahlquist, F. W.; Griffin, R. G. Polarization-Enhanced NMR Spectroscopy of Biomolecules in Frozen Solution. *Science* **1997**, *276*, 930–932.