

The (Dynamic) Surface of Colloidal Quantum Dots

Carlo Giansante ¹

¹Dipartimento di Matematica e Fisica “E. De Giorgi”, Università del Salento, Italy

Materials at the nanometer size scale show inherently large surface-to-volume ratio. This feature confers pivotal role to the study of surfaces and interfaces in nanomaterials. Here we pursue description and control of the surface of semiconductor nanomaterials obtained by colloidal synthetic methods, which permit to obtain highly monodisperse nanocrystals in large quantities free-standing in solution phase.

As-synthesized colloidal quantum dots (QDs) are constituted by nanometer-sized crystallites of inorganic semiconductor materials surrounded by organic molecules and/or metal complexes as ligands that coordinate the core surface preventing aggregation and ensuring solubility. The ligand/core (organic/inorganic) interface exerts a relevant role in the synthetic control of QD size and shape, [1] markedly affects the electronic structure of colloidal QDs, [3] and mediates QD non-covalent bonding interactions with other QDs or different chemical species [4].

A thorough description of the organic/inorganic interface towards control is therefore essential for the development of refined synthetic strategies and for the effective application of QDs in (opto)electronic devices and as luminophores, among others, to which aim metal chalcogenides are the most employed colloidal QD systems.

Although frequently represented as discrete entities stably dispersed in liquid phase, the static depiction of metal chalcogenide QDs and of their surface chemistry is fallacious: indeed, the QD growth mechanism implies a dynamic organic/inorganic interface at high temperatures [1] whereas the room temperature effect of extra added Lewis bases has led to indirectly infer the lability of neutral ligands at the core surface, either as electron-donor organic species [4] and as electron-acceptor metal complexes [5].

Here we provide direct evidence that archetypal PbS QDs, synthesized according to the most widely employed procedure [6] exist in solution-phase as equilibrium mixtures with their ligand and core components in response to the QD surroundings. Both organic molecules and metal

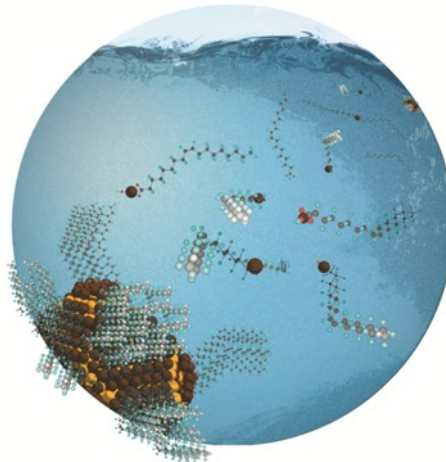


Figure 1. Depiction of colloidal PbS quantum dots existing in solution-phase as equilibrium mixtures with their (metal-)organic ligand and inorganic core components.

complexes as ligands in mutual exchange are demonstrated to undergo dynamic equilibrium with the PbS core surface. Such interfacial equilibria depend on the solvent polarity and on QD concentration and size, prevalently involving specific nanocrystal facets.

We thus remark the hybrid organic/inorganic character of colloidal QDs and the importance of conceiving them as inherently dynamic chemical species rather than as discrete entities, thus showing equilibrium structures that largely depend on the QD surroundings [7]. The ligand/core dynamic equilibrium may have relevant implications for the design of novel synthetic paths by tuning the affinity of reaction precursors for specific QD facets during nanocrystal growth. In addition, this notion can prompt refined (asymmetric) post-synthesis QD surface chemical modification procedures in solution-phase by exchanging native ligands under thermodynamic control, towards defect-free conductive QD solids for efficient (opto)electronic applications.

REFERENCES

1. Y. Yin, A. P. Alivisatos, Nature 2005, 437, 664-670.

2. K. Katsiev, A. H. Ip, A. Fischer, I. Tanabe, X. Zhang, A. R. Kirmani, O. Voznyy, L. R. Rollny, K. W. Chou, S. M. Thon, G. H. Carey, X. Cui, A. Amassian, P. Dowben, E. H. Sargent, O. M. Bakr, *Adv. Mater.* 2014, 26, 937-942; P. R. Brown, D. Kim, R. R. Lunt, N. Zhao, M. G. Bawendi, J. C. Grossman, V. Bulović, *ACS Nano* 2014, 8, 5863-5872; C. Giansante, I. Infante, E. Fabiano, R. Grisorio, G. P. Suranna, G. Gigli, *J. Am. Chem. Soc.* 2015, 137, 1875-1886.
3. J. J. Choi, C. R. Bealing, K. Bian, K. J. Hughes, W. Zhang, D.-M. Smilgies, R. G. Hennig, J. R. Engstrom, T. Hanrath, *J. Am. Chem. Soc.* 2011, 133, 3131-3138; C. Giansante, L. Carbone, C. Giannini, D. Altamura, Z. Ameer, G. Maruccio, A. Loiudice, M. R. Belviso, P. D. Cozzoli, A. Rizzo, G. Gigli, *J. Phys. Chem. C* 2013, 117, 13305-13317; R. Li, K. Bian, T. Hanrath, W. A. Bassett, Z. Wang, *J. Am. Chem. Soc.* 2014, 136, 12047-12055; A. C. Balazs, T. Emrick, T. P. Russell, *Science* 2006, 314, 1107-1110; C. Giansante, R. Mastria, G. Lerario, L. Moretti, I. Kriegel, F. Scotognella, G. Lanzani, S. Carallo, M. Esposito, M. Biasiucci, A. Rizzo, G. Gigli, *Adv. Funct. Mater.* 2015, 25, 111-119.
4. X. Ji, D. Copenhaver, C. Sichmeller, X. Peng, *J. Am. Chem. Soc.* 2008, 130, 5726-5735; A. Hassinen, I. Moreels, C. de Mello Donegá, J. C. Martins, Z. Hens, *J. Phys. Chem. Lett.* 2010, 1 (17), 2577-2581.
5. N. C. Anderson, M. P. Hendricks, J. J. Choi, J. S. Owen, *J. Am. Chem. Soc.* 2013, 135, 18536-18548.
6. M. A. Hines, G. D. Scholes, *Adv. Mater.* 2003, 15, 1844-1849.
7. D. Grisorio, D. Debellis, G. Gigli, G. Suranna, C. Giansante, *Angew. Chem. Int. Ed.* 2016, 55 (23), 6628-6633.