



Review

Quantum dot surface engineering: Toward inert fluorophores with compact size and bright, stable emission



Sung Jun Lim^{a,b}, Liang Ma^{a,c}, André Schleife^c, Andrew M. Smith^{a,b,c,*}

^a Micro and Nanotechnology Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

^b Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

^c Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

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* Corresponding author at: Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA. Tel.: +1 217 300 5638.
E-mail address: smi@illinois.edu (A.M. Smith).

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ABSTRACT

The surfaces of colloidal nanocrystals are complex interfaces between solid crystals, coordinating ligands, and liquid solutions. For fluorescent quantum dots, the properties of the surface vastly influence the efficiency of light emission, stability, and physical interactions, and thus determine their sensitivity and specificity when they are used to detect and image biological molecules. But after more than 30 years of study, the surfaces of quantum dots remain poorly understood and continue to be an important subject of both experimental and theoretical research. In this article, we review the physics and chemistry of quantum dot surfaces and describe approaches to engineer optimal fluorescent probes for applications in biomolecular imaging and sensing. We describe the structure and electronic properties of crystalline facets, the chemistry of ligand coordination, and the impact of ligands on optical properties. We further describe recent advances in compact coatings that have significantly improved their properties by providing small hydrodynamic size, high stability and fluorescence efficiency, and minimal nonspecific interactions with cells and biological molecules. While major progress has been made in both basic and applied research, many questions remain in the chemistry and physics of quantum dot surfaces that have hindered key breakthroughs to fully optimize their properties.

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1. Background

Quantum dots (QDs) are nanoparticles composed of crystalline semiconductors that are among the most widely studied class of nanoscale materials [1–4]. The most useful attributes of these tiny crystals are their tunable optical and electronic properties. By precisely controlling the QD size, shape, composition, and structure, one can modulate the wavelengths of light absorption and fluorescence emission and tune the mobility and location of electronic charge carriers [5]. These particles have been widely applied as functional materials for light absorption and light emission across diverse fields, from electronics to biomedical imaging. They have been particularly useful as fluorescent probes for imaging biological molecules and cells because their bright emission, high stability, and wavelength tunability provide exceptionally high detection sensitivity, stable signals, and multiplexed molecular analysis [1,2]. QDs are also used in light-emitting devices and displays to improve color purity and reduce power consumption due to their narrow bandwidths and high quantum yield [3,6,7]. In addition, they are used to improve energy harvesting in solar cells due to efficient formation of multiple electronic charges from a single photon, a process called multiexciton generation [4,8,9].

The success of these applications critically depends on the properties of the QD surface [10–13]. Due to their small sizes compared with bulk solids, a large fraction of the constituent atoms in a QD crystal (often 10–50%) are on their surfaces. These atoms are not bonded fully within the crystalline lattice, and thus their electronic configuration is dissimilar from the atoms within the crystal. It is critical to control these surface atoms because their distinct electronic energy states can trap electrons, quench fluorescence emission, and reduce charge transfer rates. Indeed, for nearly all applications, these surface atoms must be bonded to coordinating ligands. The ligands further dictate how the QD interacts with the surrounding medium, whether it is an electronic device or biological fluid. However the atoms and molecules comprising the surface remain poorly understood due to the difficulty of accurately

measuring their subtly unique electronic properties and their heterogeneous and dynamically changing structure [14–16].

In this review article, we describe the current understanding of the QD surface and discuss recent and ongoing experimental and theoretical advances. We primarily focus on ionic CdSe-based materials synthesized as colloids dispersed in liquids, and coated with a variety of chemisorbed ligands. As depicted in Fig. 1, we discuss important molecular interactions and state-of-the-art engineering principles from the inside-out, describing the inorganic crystal structure, crystal facets, the chemistry of ligand coordination, ligand-dependent optical properties, and ligand designs for interfacing with biological systems. Our engineering goals are driven by applications in biomedical imaging and sensing, such that small sizes, high quantum yield, high stability, and inert behavior are desired and largely determined by the surface. The engineering of QD surfaces is an ongoing effort for which basic studies are still needed to reveal critical structure–function relationships.

2. Quantum dot crystal facets

The QD surface is a chemically heterogeneous interface between atoms of a crystalline solid and ligands coordinated to the surface atoms. Although QDs are often nearly spherical in shape, when examined closely, their surfaces are typically locally flat regions of truncated crystalline planes [5,18]. The types of facets on the surface are initially defined during synthesis, dictated by the crystal phase and the ligands that bind to surface atoms and modulate interface energies. The ligand layer is usually considered to be dynamically chemisorbed [19] due to relatively weak bond energies (20–40 kJ mol⁻¹, or 0.2–0.4 eV) and can be modified through post-synthetic ligand exchange to adjust the QD properties for specific applications. Here we summarize key attributes of QD surface facets to establish how ligands bind to these surfaces, as deduced from a combination of empirical and theoretical studies of inorganic crystal facets over the past two decades.

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