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REVIEW

Charge transfer and separation in photoexcited quantum dot-based systems

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Summary Colloidal quantum dots (QDs) are semiconductor nanocrystals which exhibit strong photoluminescence and have a variety of applications in modern nanotechnology. Specifically, QDs may serve as source of photoelectrical response to optical excitation, thus paving the way to development of novel optoelectronic and photovoltaic QD-based systems and devices. QD photoexcitation gives rise to excitons, electron—hole pairs which are bound by Coulomb forces and may dissociate in such a way that the charge carriers leave the nanoparticle and interact with the environment. The surface of inorganic QDs is always covered with organic ligands ensuring their colloidal stability during the synthesis and subsequent processing. The possibility to control the composition of the surface ligands is considered a promising way to modulate different parameters of charge formation and separation in nanoparticles, including the secondary pathways of charge transfer, rates of carrier generation, radiative or nonradiative electron—hole recombination, and some others.

The rates and directions of these processes strongly affect the fundamental photophysical properties of QDs, such as luminescence quantum yield, quenching, bleaching, blinking, and photostability; they also determine the applicability of nanocrystals to specific areas of photovoltaics, photocatalysis, and bioanalysis, as well as fabrication of light-emitting diodes (LEDs) and QD cellular automata (the transistorless computation paradigm).

Abbreviations: (P)ET, (photoinduced) electron transfer; (O)LED, (organic) light emitting diode; CB(E), conduction band (edge); CT, charge transfer; CV, cyclic voltammetry; EL, electroluminescence; ETL, electron transport layer; E_{vac}, vacuum level; FRET, Förster resonance energy transfer; HOMO, highest occupied molecular orbital; (P)HT, (photoinduced) hole transfer; HTL, hole transport layer; IPCE, incident photon to current conversion efficiency; LUMO, lowest unoccupied molecular orbital; MPA, mercaptopropionic acid; NHSs, nanoheterostructures; PEDOT:PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate); PL, photoluminescence; PV, photovoltaics; QD, quantum dot; TA, transient absorption; TOPO, trioctylphosphine oxide; UPS, ultraviolet photoelectron spectroscopy; VB(E), valence band (edge); XPS, X-ray photoelectron spectroscopy.

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In this review we analyze recent advances in controlled charge generation, separation, and transfer in QD-based organic and inorganic systems, with a special emphasis on the role of the surface-stabilizing ligands in the transfer and separation of photogenerated charge carriers. The prospects of development of advanced QD-based photovoltaic and optoelectronic devices employing carefully selected surface ligands that improve the nanocrystal photophysical properties are analyzed in the ''Summary and outlook'' section.
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Introduction

Nanostructured materials have been among the most promising and most intensely studied objects in the past two decades due to their unique properties, which are intermediate between those of bulk materials and molecular species. Quantum dots (QDs), one of the most attractive objects of nanotechnology [1], are semiconductor nanocrystals with the size ranging from 1 to 20 nm, which have some unique characteristics making them outstanding materials for LEDs [2,3], solar cells [4,5], photocatalysis [6,7], and biotechnology [8—10]. The size- and shape-controlled luminescence properties of QDs, high quantum yields and brightness of their photoluminescence, and the stability of QDs against photobleaching are underlain by the quantum confinement effect [11]. Furthermore, QDs have narrow luminescence bands with large Stokes shifts, which allows effective coupling of the emitted light to other fluorophores via Förster resonance energy transfer (FRET) and the use of QDs as light-harvesting antennae in hybrid materials [12,13] even in the two-photon mode [14]. QDs have large absorption cross-sections and, in contrast to organic fluorophores, may be excited by light with any wavelength corresponding to a photon energy higher than the energy of the first excitonic transition, which makes it possible to excite QDs of different sizes at a single wavelength and perform multiplexed detection of large series of analytes [15—18].

At present, colloidal synthesis that is conducted in liquid phase is the most powerful and versatile method for preparation of QDs. A distinctive feature of QDs obtained by colloidal methods is the presence of organic molecules (the surface ligands) on the surface of inorganic nanocrystals. The primary role of the surface ligands is stabilization of small inorganic clusters in a colloidal solution. In addition to this primary role, the ligands affect the nucleation and growth of QDs [14,19,20] by tuning the reactivities of nanocrystals [21,22] or their molecular building blocks [23], or even control the phase composition of nanocrystals [24,25]. Typically, the ligands are formed by conversion of precursors or are themselves components of the reaction medium. When the QD is formed in a colloidal solution, it represents a complex system consisting of inorganic core covered with a capping layer of organic surface ligands, often comprising multiple types of molecules. Modern techniques used for characterization of these complex ligand capping layers are reviewed in detail in Ref. [26].

Surface ligands can modify the optical properties of QDs, either causing shifts of the absorbance or photoluminescence spectra [27], quenching PL [28,29], or considerably enhancing it [30]. Because of their small size, QDs have a large surface-to-volume ratio; therefore, they actively interact with environment. The surface atoms of a QD may be undercoordinated due to the steric repulsion between ligand molecules located at the nanocrystal surface. The level of undercoordination can be reduced by passivation of the core surface using an inorganic shell [31]; however, the remaining unpassivated atoms have unbound orbitals that stick out from the QD surface and are thought to be the origin of charge-trapping states. Through these unpassivated sites, organic or inorganic molecules, semiconductor layers, or oxygen molecules can interact with QDs and affect their optical properties.

Excitation of a QD with the light whose photon energy is above the QD band gap results in the formation of an electrostatically bound electron—hole pair (exciton). Afterwards, the exciton may recombine and emit a photon with an energy beyond the band gap of the QD, recombine without emission of light, or dissociate into a pair of unbound charge carriers. Basically, these three processes determine the parameters of the QD photoluminescence, which, in turn, determines most QD applications. Exciton recombination parameters can be tuned by engineering of the QD inorganic structure: it is widely known that growing a shell of a high-band-gap material atop the photoluminescent core of the QD can dramatically increase the PL quantum yield [32], sometimes even to 100% [33—36]. However, a number of recent studies show that organic ligands, which are always present on the surface of colloidal QDs and are responsible for stabilization of colloidal solutions, can control the charge-carrier separation and transfer processes [37—40].

According to the Marcus theory [41], the driving force of the charge carrier transfer is the difference between the energy levels of the charge donor and acceptor (Fig. 1). Therefore, there are two ways to tune the driving force of charge transfer. The first way is to modify the positions of the QD band edges by changing the size of the QD [42]; the second one is to change the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital

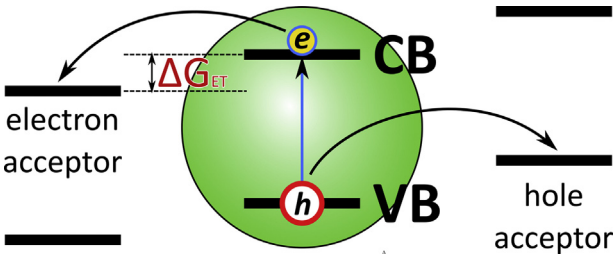

Figure 1 Schematic representation of photoinduced charge transfer between a quantum dot and charge acceptors. CB, conduction band; VB, valence band.

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