Coordination Chemistry Reviews 263–264 (2014) 197–216

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Nanoscale engineering facilitated by controlled synthesis: From structure to function

Jennifer A. Hollingsworth*

Materials Physics & Applications Division, Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545, United States

Contents

ARTICLE INFO

Article history:
Received 13 June 2013
Received in revised form 30 August 2013
Accepted 1 September 2013
Available online 17 September 2013

Keywords:
Nanocrystal quantum dots
Heterostructuring
Partial cation exchange
Blinking
Giant core/shell
Type II

ABSTRACT

It is now well known that the optical properties of semiconductor nanocrystal quantum dots (NQDs) – absorption onset and position of the photoluminescence maximum – can be precisely controlled by simple tuning of particle size within the quantum-confinement regime. More recently, however, the field has evolved beyond straightforward particle-size control to embrace more complex NQD heterostructures. As a result of the inclusion of internal, nanoscale compositional interfaces, heterostructured NQDs afford opportunities for enhanced, emergent and even multi-functional behavior and properties. A common structural motif for achieving such 'engineered' NQDs is to envelop the NQD core within a shell of a different composition. Herein, a summary of our recent research in the development, synthesis, characterization and application of 'core/shell' NQDs is provided. In the first part, enhancement of properties is demonstrated through our work in lead chalcogenide core/shell NQDs. In a subsequent section, emergence of novel properties resulting from specific combinations of core and shell physical and electronic structures is described in the context of non-blinking behavior and suppressed Auger recombination realized for our "giant" NQDs. Examples in this case entail both CdSe and InP cores. Application of these ultra-stable NQDs in the area of light-emission technologies is also demonstrated and discussed. Finally, multi-functionality is shown for the case of a coupled magnetic-semiconductor Co/CdSe core/shell nanocrystal system.

1. Introduction

The study of nanoscale semiconductors and their size-dependent properties has depended upon key advances in their controlled synthesis. Without the ability to reliably synthesize nanocrystals of finely tuned size and shape, our resultant capacity for characterizing, interpreting and benefiting from various size-specific properties afforded by this class of nanomaterial would have been significantly diminished. Furthermore, our ability to access the unique optical and electronic properties of these materials has also benefitted from improved synthetic control over nanoparticle crystallinity and surface chemistry. In this way, the seminal papers in the field that first demonstrated that pyrolysis of organometallic precursors [1] and, subsequently, metal-organic,

* Corresponding author.Tel.: 1 505 665 0399
E-mail address: jenn@lanl.gov

0010-8545/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ccr.2013.09.005

metal oxide and metal salt precursors [2,3], in a hot coordinating solvent could be used to controllably synthesize semiconductor nanocrystals or 'nanocrystal quantum dots' (NQDs) have supported breakthroughs in our understanding of fundamental photophysical properties [4,5]. Other primary early advances included the development of core/shell syntheses for improved NQD photophysical properties [6–9], as well as extension of such refined colloidal synthesis methods to the fabrication of anisotropic semiconductor nanocrystals [10,11], including metal-nanoparticle catalyzed growth of nanowires [12].

More recently, emphasis has evolved from developing synthetic approaches for semiconductor nanocrystals consisting of only a single composition to identifying methods for *heterostructured nanocrystal synthesis*. In this case, two or more compositions make up a single nanostructure. By introducing compositional interfaces at the nanoscale it is possible to enhance intrinsic properties as well as to bring about emergent properties or multi-functional behavior. The earliest demonstrations of core/shell NQDs afforded enhanced properties, including increased quantum yields in emission and improved photostability. These core/shell NQDs were characterized by a 'type I' alignment of electronic states (Fig. 1b), such that the excited-state electron and hole are localized in the NQD core. The shell comprises a higher bandgap semiconductor and surrounds the core, providing a structural and energetic barrier to surface-trap-state and environmental quenching processes. As a result of this 'exciton' (e–h pair) confinement, the protective shell is able to afford enhanced NQD-core emission and photostability [6–9].

Subsequently, however, it was shown that the core/shell motif (Fig. 1a) could be used for 'bandgap engineering' to realize new optical transitions not characteristic of either of the constituent compositions. In this case, core/shell NQDs are synthesized from core and shell materials that afford a 'type II' bandgap alignment, where excited-state carriers are spatially separated between the core and the shell [13]. In the example shown (Fig. 1d), the hole is confined to the core while the electron occupies the shell. The opposite is also possible by changing core and shell composition to alter the relative position of the core and shell conduction and valence bands. Both kinds of type-II band alignments can result in emission energies that are red-shifted (lower in energy) compared to that achievable from the core or the shell materials alone, as emission occurs by electron–hole recombination across the core/shell interface. The new type-II 'effective bandgap' is then the energetic transition between the shell conduction band and the core valence band, or the opposite. For this reason, type-II NQDs fabricated from compositions possessing visible or even ultraviolet bandgap energies can emit in the infrared. Thus, beyond particle-size engineering that takes advantage of semiconductor quantum-confinement (size) effects [14], nanoscale 'bandgap engineering' affords an important additional opportunity for spectral properties tuning.

Type-II heterostructuring is also a convenient way to manage electron–hole wavefunction overlap and, thereby, carrier coupling strength. For many applications emissive electron–hole (exciton) recombination is not the desired outcome following NQD photoexcitation. In photovoltaics or detection schemes relying on photoconduction, efficient carrier *separation rather than recombination* is required, followed by charge transport and collection. The initial step in charge separation can be facilitated by an NQD heterostructure that promotes carrier separation at an atomic-level internal interface, i.e., a type-II core/shell band structure [13].

Furthermore, bandgap engineering can be used to modify 'fundamental' NQD properties. Namely, the strong electron–hole overlap characteristic of single-composition NQDs and of highly confined type-I core/shell NQDs contributes to an efficient and detrimental non-radiative recombination process known as Auger recombination [5,15–17]. Auger recombination controls the fate of excitations involving charged excitons ('trions') as well as multiexcitons (e.g., biexcitons, triexcitons, or higher order excitations). Instead of recombining radiatively and generating an optical photon, due to efficient Auger processes, the energy of recombination for these types of excitations is transferred to the extra charge (trion example) or to a second exciton (biexciton/multiexciton examples) that decays nonradiatively. Core/shell structures that promote partial (so-called 'quasi' type-II: Fig. 1c; see below) or complete (type-II) spatial separation of the electron and hole afford a reduced e–h overlap integral and can also result in 'repulsive' exciton–exciton Coulomb interactions [18]. Both effects diminish the efficiency of Auger recombination and, thereby, enhance opportunities to utilize higher order (multiexciton) states [19].

Type-I and/or type-II core/shell structures are also now known for anisotropic nanocrystals, including nanorods [20] and nanowires [21,22]. Anisotropic elongated structures afford an additional opportunity to create 'non-radial' interfaces, such as nanorods or tetrapods that are tipped on each end with another material ('nanodumbells' [23] and extended or branched rods and tetrapods [24]) or axially heterostructured nanowires whose composition alternates along the nanowire length [25,26]. Furthermore, in addition to combining two (or more) different semiconductors in a single nanostructure, significant effort has been dedicated to coupling semiconductors with other types of functional materials, including noble metals [23,27], magnetic compounds [28,29], and atomic emitters [30]. Such hybrid structures afford the possibility to realize distinct 'multifunctional' behavior and/or properties that emerge as a result of the interactions of the two components.

Here, examples from our laboratory of novel heterostructures or unique synthetic strategies for the 'engineering' of otherwise hard-to-access hetero-nanocrystals are reviewed. Although not a comprehensive review of the field, the examples provided encompass almost the full breadth of hetero-structural motifs and reveal the range of enhanced to emergent to multifunctional properties accessible by creating nanoscale interfaces within single nanoconstructs. Where proof-of-concept applications have been realized in our laboratory, these are described as well.

2. Enhanced properties through nanoscale heterostructuring: lead chalcogenide core/shell nanocrystal quantum dots (NQDs)

Efficient and robust infrared emitters are required for a range of applications from optical communication to advanced bioimaging, while infrared absorbing nanocrystals are valuable for energy harvesting (e.g., solar photovoltaics and thermoelectrics) and photodetection schemes for imaging and sensor technologies [31]. Although CdTe NQDs can access emission wavelengths approaching its bulk bandgap of 860 nm (1.44 eV) and InP can in principal access emission wavelengths out to ~920 nm (1.34 eV), neither of these common NQD materials can provide emission or absorption above 1 micron (1.24 eV), unless they are incorporated into a type-II core/shell structure as introduced above. Instead, to reach, for example, the telecommunication wavelengths of 1300–1550 nm narrower bandgap semiconductors are required, such as InAs, InSb, HgTe, and PbSe. Lead chalcogenides (PbE; E = S, Se or Te) as a compositional class have shown significant potential for this purpose, with bulk bandgaps of 3.35 μm (0.37 eV), 4.59 μm (0.27 eV) and 4.28 μm (0.29 eV), respectively. For example, facile syntheses of PbSe NQDs with photoluminescence (PL) in the near-IR [32–34] were initially reported and subsequently extended to NQDs emitting into the mid-IR (~4 μm), affording the first NQDs to access this spectral range [35]. Significantly, PbSe NQDs offer near-unity quantum yields (QYs) in the telecommunications range.