ChemPhys Perspective

On the kinetics and thermodynamics of excitons at the surface of semiconductor nanocrystals: Are there surface excitons?

Patanjali Kambhampati

Department of Chemistry, McGill University, Montreal, QC H3A 0B8, Canada

A B S T R A C T

The surface of semiconductor nanocrystals is one of their defining features by virtue of their nanometer size. Yet the surface is presently among the most poorly understood aspects of nanocrystal science. This perspective provides an overview of spectroscopic work that has revealed the first insights into the nature of the surface, focusing upon CdSe nanocrystals. We focus on two aspects of surface processes in nanocrystals: the kinetics of surface trapping and the thermodynamics of core/surface equilibria. We describe femtosecond pump/probe spectroscopic experiments which reveal the signatures of carrier trapping at the surface. We also describe temperature dependent steady-state photoluminescence experiments which reveal new aspects of the surface. This work suggest that the surface emission is largely driven by homogeneous broadening via phonon progressions. The implications are that the surface electronic state bears similarity to the quantized excitonic core of the nanocrystal.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the decades since their discovery, semiconductor nanocrystals have been under intense investigation as a materials platform upon which to explore quantum confinement effects [1–7], as well as path for development of materials based solutions to applications ranging from photovoltaics [8–12], displays and lighting [13–16], lasers [17,18], detectors [19,20], optical switching [21], and biological imaging [22].

These nanocrystals (NC) are formed via solution phase growth [23], and can result in the now well-known quantum confined excitons in colloidal quantum dots (QD). These colloidal quantum dots are somewhat distinct from their self-organized QD counterparts that are epitaxially grown via gas phase methods [24]. The key distinction lies at the surface of the dot itself. Self-organized QD which are grown by molecular beam epitaxy, consist of the dot physically embedded in a host semiconductor with lattice matching [24]. While there is an interface, there is no surface of which to speak. In contrast, the colloidal quantum dot is defined by their very surface itself. The physical surface of a spherical nanocrystal yields a colloidal quantum dot. Moreover, the nanocrystal form of the QD can be grown in a variety of geometries spanning spheres [23], rods [25–27], tetrapods [28,29], radially graded alloys [30–34], etc. Hence the surface of semiconductor nanocrystals is an essential part of their nature.

Whereas semiconductor nanocrystals are defined by their surface, very little is known about this defining characteristic. The initial understanding of the surface of the nanocrystal was largely based upon steady state photoluminescence (PL) measurements. The PL from semiconductor nanocrystals arises from a thermalized distribution of excitons confined by the core of the nanocrystal [35–37]. The nature of the excitonic PL from the core is now reasonably well understood [2], although new insights are still emerging via single dot spectroscopy [38–40]. Chemical modification of the surface of the NC has revealed that the broad, red emission seen in early NC arose from the surface of the nanocrystal. It was considered that the surface presented localized lattice defects [41]. These defects created both unwanted trap PL as well as provided a constraint to producing bright and photostable PL from the excitonic core of the NC. Hence the primary goal of surface studies of nanocrystals has been to eliminate the unwanted trap PL [42–44].

In contrast to this historic view of the surface as a problem to be mitigated, our recent work has suggested that the surface is fundamental part of the nanocrystal system [45–48]. Moreover we propose that the surface may actually be profitably exploited for applications ranging from lighting, to sensing, to optoelectronic devices. In order to achieve these goals, one key element is missing: a microscopic understanding of the nature of the surface of semiconductor nanocrystals and the manner in which the core excitonic states couple to the surface. Here, we review our recent work on the kinetics and thermodynamics of surface trapping in

E-mail address: pat.kambhampati@mcgill.ca

CdSe semiconductor nanocrystals which has produced the first such picture of the factors which govern surface trapping the core excitonic states.

2. Background

### 2.1. Simple observations of the surface of semiconductor nanocrystals

The physical and electronic structure of the core of nanocrystals in terms of excitons has been well described elsewhere [2,4,5,49,50], and will only be briefly described here so as to set the stage to understand their surface electronic structure. Fig. 1 shows a transmission electron microscope (TEM) image of CdSe NC, along with schematic energy level diagrams in two representations. TEM work has revealed that NC are not necessarily spherical. Moreover, with inclusion of atomistic detail, the NC have surfaces with specific periodicities and terminations that are distinct from their bulk phase. With the large surface/volume ratio of NC, it is essential to understanding the electronic structure of these surfaces.

In contrast to the surface electronic structure of NC, the quantized core electronic states are now well understood at various levels of theory [2,4,5,49–51]. The reader is referred to the many excellent reviews which cover this topic in detail. The main result is that a Fourier superposition of bulk Bloch states results in the well-known quantized states of the electron and the hole. Fig. 1 shows this manifold in the electron/hole representation as well as the exciton representation.

These excitonic states can readily be observed in the linear absorption spectra, Fig. 2a. Shown is a representative absorption spectrum of CdSe NC. Also shown are laser spectra tuned into resonance with specific excitonic states so as to perform state-resolved femtosecond pump/probe spectroscopy [5,6,52]. This approach enables specificity in the initial excitonic state thereby enabling direct measurement of the influence of the initial state, as well as direct observation of hot exciton (or hot carrier) processes.

Steady-state photoluminescence (PL) spectroscopy enables simple characterization of their radiative and non-radiative processes. Fig. 1b shows a PL spectrum of CdSe NC with strong PL from the band edge exciton at 2.5 eV and some trap PL spanning 1.6–2.3 eV. This trap PL has been known to exist for decades and has been assigned to defect emission from various sources. The defects are considered to arise at the surface of the NC based upon chemical passivation experiments. This hypothesis was further supported by the early work which demonstrated that growth of inorganic shells (e.g. ZnS) would increase the PL quantum yield, and strongly attenuate the trap PL at 300 K. Hence the idea of shell growth has been to remove the unwanted defects, a process that was validated by the disappearance of the broadened and redshifted trap PL.

The broadening and redshifting characteristic of trap PL was historically rationalized by a broad distribution of trap states, Fig. 1c. Since hot exciton relaxation [5,6,53,54] on the 0.1–1 ps timescale is much faster than exciton radiative recombination on the 1–10 ns timescale in CdSe NC, PL takes place from fully relaxed or cold exciton states. Within the multiband effective mass approach (EMA) [4,55], the lowest coarse excitonic state, X_1 is denoted as $1S_e$-$1S_{3/2}$. This coarse exciton state is further split into fine structure states which will not be further discussed here. The narrow linewidth (~50–100 meV) of the core excitonic PL arises from fine structure effects, weak exciton–phonon coupling, dephasing, and inhomogeneous broadening from the size dispersion (5%). As the trap PL is often redshifted by 0.3–0.5 eV from the band edge PL, and is also ~0.5 eV in width, the simple picture of defects in solids suggest that the observed broadening and redshifting arises from a distribution of trap states. The larger
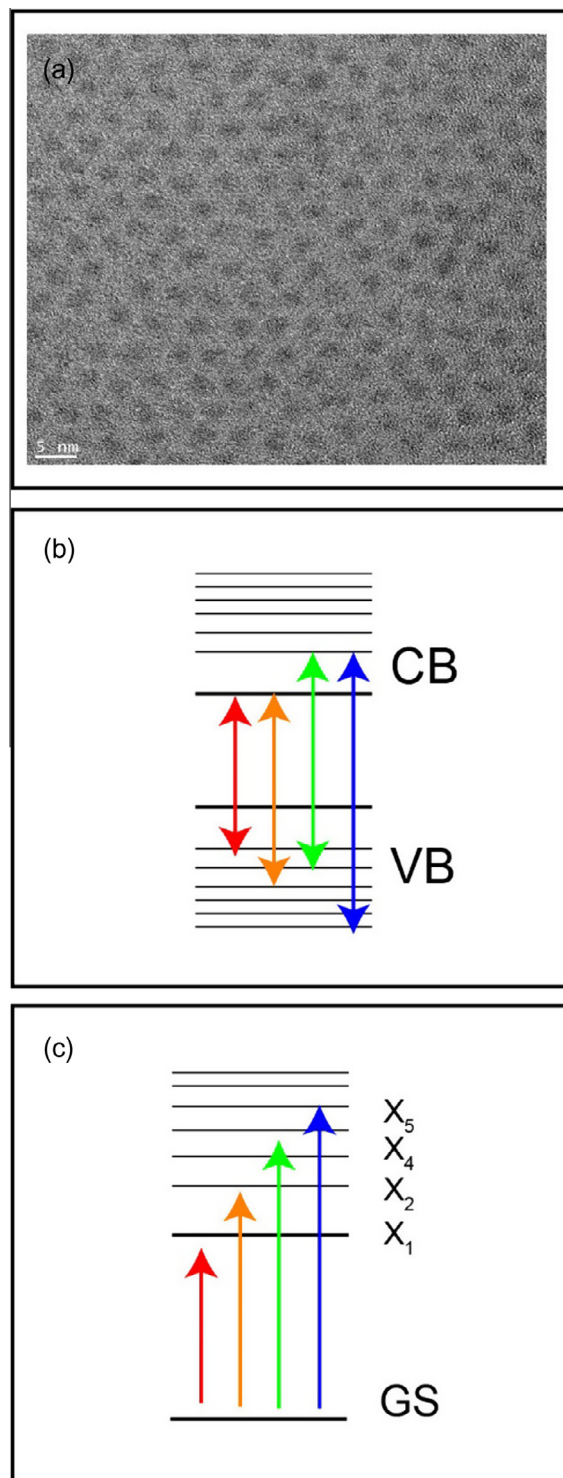
Fig. 1. Transmission electron microscope (TEM) image of CdSe nanocrystals. Real nanocrystals are not necessarily spherical, have atomistic detail, and have a surface which must be considered, (a). The confinement of charge carriers yields quantized states in the electron/hole representation, (b). The exciton representation is convenient for correspondence to spectroscopic transitions, (c).

the linewidth the larger the distribution. And the larger the redshifting, the deeper the traps are within the bandgap. These traps could be either electron or hole traps based upon the NC/ligand system. But in the case of CdSe NC with the standard amine or phosphine oxide ligands, it is expected to primarily be hole traps due to Se atoms being ill-passivated [42–44]. Based