Coordination Chemistry Reviews 263–264 (2014) 151–160

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Review

Hybrids of semiconductor quantum dot and molecular species for photoinduced functions

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ARTICLE INFO

Article history:
Received 8 May 2013
Received in revised form 11 July 2013
Accepted 11 July 2013
Available online 1 August 2013

Keywords:
Nanoparticle
Photochemistry
Luminescence
Energy transfer
Electron transfer

ABSTRACT

Semiconductor quantum dots are inorganic nanocrystals which, because of their unique size-dependent electronic properties, are of high potential interest for the development of light-responsive nanodevices. Their surface can be chemically modified, by either covalent or non-covalent approaches, in order to interface them with molecular units endowed with specific physico-chemical properties. Photoinduced electron- and energy-transfer processes between quantum dots and attached molecular species offer versatile strategies to implement functionalities such as photosensitized processes, and luminescence sensing and switching. In this review we will discuss the strategies underlying the rational construction of this kind of multicomponent species, and we will illustrate a few examples taken from our own research.

1. Introduction

Semiconductor nanocrystals known as quantum dots (QDs) are spherical particles with diameters typically ranging between 1 and 15 nm. Owing to a strong quantum confinement of the charge carriers, they exhibit peculiar size-dependent optical and electronic properties; in particular, they are strongly luminescent [1–3]. Since their discovery [4,5] in the early 1980s and the development of solution-based preparation methods affording an accurate size control [6], it became clear that these particles could represent a valid alternative to molecular species for luminescence applications [7,8]. The interest on QDs as alternatives to organic dyes has increased dramatically, as witnessed by the number of papers, reviews [9–19] and books [20–23] dealing with such nanomaterials.

Quantum dots were initially prepared for basic studies on quantum confinement, and were rapidly transferred to biological applications [9,10,16,17,19] as soon as convenient synthetic methods became available. The development of nanocrystal-molecule hybrids and a detailed physico-chemical understanding

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http://dx.doi.org/10.1016/j.ccr.2013.07.014

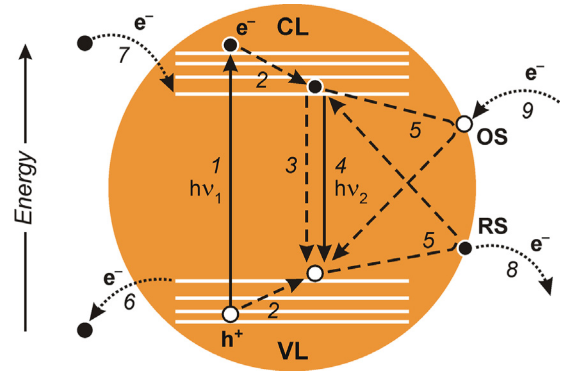

Fig. 1. Schematic representation of important optical and electronic processes in a semiconductor nanocrystal. Full, dashed, and dotted lines represent radiative, non radiative, and redox processes, respectively. Legend of processes: 1, optical excitation; 2, thermal relaxation of the excited electron and hole; 3, nonradiative exciton recombination; 4, radiative exciton recombination (luminescence); 5, non radiative recombination mediated by surface states; 6, oxidation involving valence electrons; 7, reduction into conduction levels; 8, oxidation involving a surface trap; 9, reduction involving a surface trap. VL, valence levels; CL, conduction levels; OS, oxidizing trap site; RS, reducing trap site.

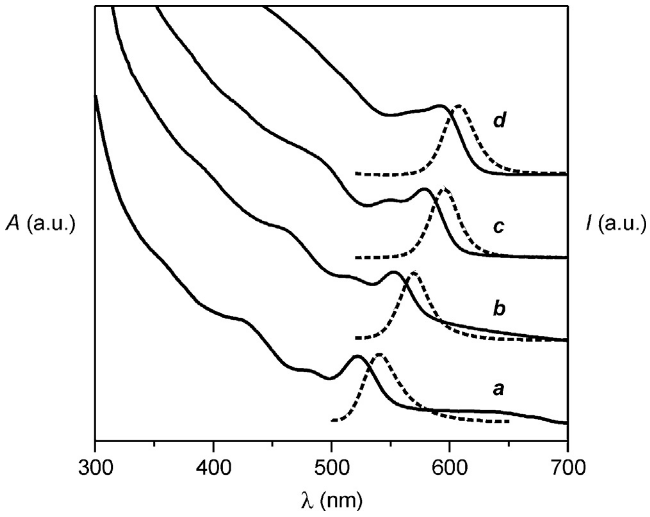

Fig. 2. Normalized absorption (—) and photoluminescence (- - -) spectra of CdSe QDs with a diameter of (a) 2.6 nm, (b) 3.1 nm, (c) 3.8 nm, and (d) and 4.3 nm, capped with tris-*n*-octylphosphineoxide (TOPO) and *n*-hexadecylamine (HDA) ligands ($CHCl_3$, room temperature, $\lambda_{ex} = 480$ nm). The spectra are vertically offset for clarity.

of nanocrystal-molecule interactions are crucial for extending the basic knowledge on these fascinating systems and foster the design of QDs tailored for specific technological applications.

This review will describe luminescent nanocrystals whose surfaces are decorated with molecular units exhibiting photochemical or redox properties. In these nanohybrids the combination of the QD and molecular components is exploited to bring about light-triggered functionalities such as switching and sensitization of photoluminescence, and chemical sensing. The first part of the paper will deal with the basic physico-chemical properties of quantum dots, present the methodologies for the chemical modification of their surface, and discuss the general approaches that can be followed to impart light-induced properties to chemically derivatized nanocrystals. Such concepts will be illustrated in the second part by describing some examples taken from our own work. These examples are subdivided according to the type of interaction (surface chemisorption or non-covalent forces) holding together the nanocrystal and molecular components. Perspectives and limitations of this kind of systems will also be discussed.

2. Basic electronic and optical properties of semiconductor QDs

Several physical properties of bulk materials change substantially when they are in the form of particles with a size on the order of nanometers. Specifically, for semiconductor nanoparticles the band gap – that is, the energy difference between the valence and conduction band edges – can be changed upon varying the particle size. In a semiconductor, absorption of a photon with energy equal or greater than the band gap results in excitation of an electron from valence to conduction levels, leaving a hole in the valence band. Such an electron–hole pair is bound by the electrostatic attraction between the opposite charges and is called an exciton. The exciton Bohr radius measures the average distance between the photogenerated electron and hole. When the size of the particle approaches that of the exciton (for example, the exciton Bohr radius for CdSe is about 6 nm), the optical and electrical properties of the material become dependent on its physical dimension, owing to quantum confinement effects [3,24,25]. In these conditions, the band structure of the semiconductor changes into discrete levels (Fig. 1), and the energy difference between the highest occupied level and the lowest unoccupied level widens as the particle size decreases (Fig. 2), following in many cases the behavior expected for an electron inside a three-dimensional box. In some cases a description in terms of molecular orbitals is more appropriate than that of band theory, reflecting the nature of QDs as systems lying between bulk materials and molecular species.

As discussed above, QDs can absorb photons with energies equal or greater than the band gap energy (process 1 in Fig. 1). The corresponding absorption spectrum is characterized by a sharp band on the low energy side, corresponding to population of the first exciton state exhibiting strong oscillator strength. Its position and intensity depend on the particle size, while its width and shape reflect the size distribution of the QDs. In general, quantum dots are characterized by large molar absorption coefficients in the UV–vis, hence they can be effectively excited in a wide spectral region and with low intensity light. They also exhibit a remarkable cross section for two-photon absorption. Indeed, the superior performance of QDs as light harvesters makes them promising nanoscale components for photovoltaic cells [26,27] and artificial photosynthetic devices [28].

In direct band gap semiconductors (i.e., in which the lowest energy conduction level and the highest energy valence level have the same momentum), such as CdS, CdO, CdSe, CdTe, ZnS, ZnSe, GaAs and InP, the recombination of the exciton leads to emission of a photon (process 4 in Fig. 1). The luminescence shown by QDs of these materials is very intense and, in contrast with organic fluorophores, it occurs with a remarkably narrow spectral profile: the full width at half maximum (fwhm) is typically on the order of 30 nm. The emission energy can be adjusted to fall in a spectral region ranging from the UV to the IR, by selecting the chemical composition (i.e., the band gap of the bulk material) and the size of the particles (to take advantage of quantum confinement). CdSe is the most frequently used semiconductor to make QDs for optical applications because size modulation of its band gap enables an accurate tuning of the emission maximum across the visible region (Fig. 2). It should be noted that, in order to have an efficient emission, the surface of the nanocrystals must be appropriately passivated; otherwise, the charge carriers would be most likely trapped in surface states and undergo non radiative recombination (processes 5 in Fig. 1). As a matter of fact, the presence of surface states, originating from the dangling bonds of the surface atoms, crystal defects and/or impurities, have a profound influence on the spectroscopic and redox properties of QDs [22,29]. The luminescence quantum yield can be improved by coating the nanocrystal with a layer of