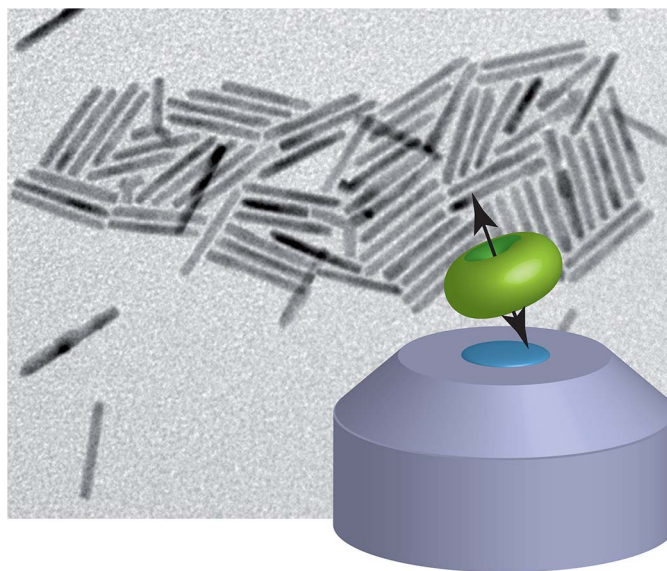# Breakthroughs in Photonics 2014: Semiconductor Luminescent Colloidal Core–Shell Nanorods and Dot-in-Rods

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Breakthroughs in Photonics 2014: Semiconductor Luminescent Colloidal Core–Shell Nanorods and Dot-in-Rods

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(Invited Paper)

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Abstract: One-dimensional semiconductor colloidal nanostructures such as nanorods and core–shell dot-in-rods can now be synthesized with excellent chemical stability and photostability, large absorption cross section, reduced blinking, and high quantum efficiency. These structures have generated great interest because, compared to spherical nanocrystals, their morphology is attributed to their specific electronic and optical properties, such as increased charge transfer and large polarization anisotropy. They are very good candidates for application in photovoltaics, lighting, and visualization and even for biomedical applications.

Index Terms: Dot-in-rods, nanocrystals, quantum dots and colloidal systems, semiconductor confined system, spectroscopy, photoluminescence, photovoltaics, optoelectronic sources, polarization, self-assembly, charge transfer.

1. Introduction

The synthesis of colloidal spherical semiconductor nanocrystals (also called quantum dots) has been greatly improved since the first reports in 1984, with applications for bio-imaging, light-emitting diodes, displays, and single-photon emission. The luminescence wavelength of nanocrystals depends on their size, which can be finely tuned by chemical synthesis duration and conditions. By addition of a shell of a different semiconductor [see Fig. 1(a)], the spherical core can be protected from the fluctuations of the environment, thus improving the optical properties. By introducing appropriate ligands and controlling the synthesis kinetics, the nanocrystal shape can be tuned, and elongated "nanorods" can be obtained [see Fig. 1(b)]. "Dot-in-rods," which are constituted of a spherical core and a rod-shaped shell [see Fig. 1(c)], have drawn attention over the past ten years for their strongly polarized emission and charge transfer properties; CdSe/CdS is the most studied core/shell materials combination. We summarize below the progress reported in the last year on the preparation, optical properties, characterization, and applications of these structures.
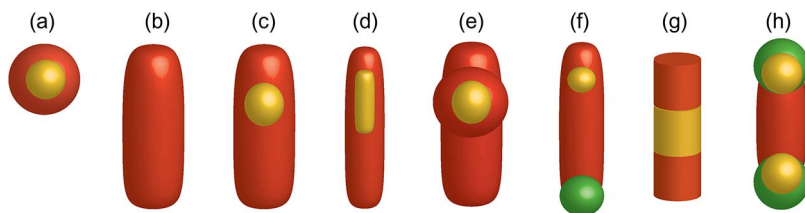
Fig. 1. Schematics of various colloidal structures. (a) Spherical core/shell nanocrystal, (b) nanorod, (c) core/shell dot-in-rod, (d) core/shell rod-in-rod, (e) bulb-shaped dot-in-rod, (f) CdSe/CdS–Pt dot-in-rod, (g) segmented nanorod heterostructure, and (h) double heterojunction nanorod.

2. Nanorods and Dot-in-Rods Morphology

A good control of the dot-in-rod geometry (core diameter, shell length and thickness) is now possible, which provides ways for tuning the dot-in-rod emission wavelength and fine structure [1], [2], polarization [3]–[6], single-photon emission or blinking properties [7]. Slightly different structures can also be fabricated, such as rod-in-rods [see Fig. 1(d)], dot-in-rods with bulb-shaped shell around the core [see Fig. 1(e)] [8], CdSe/CdS–Pt dot-in-rods [see Fig. 1(f)] [9], CdS/CdSe/CdS heterostructure segmented nanorods [see Fig. 1(g)] [10], or double-heterojunction nanorods [11] [see Fig. 1(h)]. Di Stasio et al. [12] have studied the solubility of dot-in-rods in water, a crucial issue for bio-labeling as well as fabrication processes designed for orthogonal solvents, e.g., lasers, multi-layered light-emitting diodes, etc. The photoluminescence quantum yield was measured as $50 \pm 5\%$ for both the original dot-in-rods (in organic solvent) and ligand exchanged dot-in-rods (in water solvent).

Control of the dot-in-rod orientation is essential for many applications related to charge transfer or emission polarization. Therefore, some groups have developed self-assembly methods to orient a collection of nanorods. The morphology of 2-D sheets of self-assembled parallel horizontal nanorods at the solvent–air interface has been studied as a function of the initial solution concentration and nanorod morphology [13], while a vertical deposition of the dot-in-rods was used in [2], following a previously reported method. Pelliser et al. studied the photoluminescence of individual dot-in-rods aligned in the stripes of a liquid crystal matrix and showed that for each individual nanocrystal, the emission polarization was oriented along the same direction which was controlled by the liquid crystal deposition protocol [14].

3. Photoluminescence Properties

Nanocrystal shell engineering is an established strategy for decreasing the photoluminescence blinking (random switching between bright and dark states) and improving the emission quantum efficiency. Single-emitter microscopy of CdSe/CdS dot-in-rods showed single-photon emission, suppression of dark states and a quantum efficiency of ∼78% [7]. With a different method involving a metallic surface at a tunable distance, an ensemble quantum efficiency of 87% has been measured [15]. Manceau et al. [16] analyzed the random switching between the bright state and a less intense gray state attributed to a charged state of the dot-in-rod; the gray state showed degraded single-photon emission properties, which were related to a higher ratio between the biexciton and exciton quantum yields for the gray state.

A much debated question is whether the dot-in-rod band alignment belongs to the type-I or type-II category; the type-I leading to both electron and hole confinement in the core, while the type-II would lead to one charge being confined in the core and the other in the shell. For CdSe/CdS dot-in-rods, both types have been previously reported, as the charge localization can be tuned from type-I to quasi-type-II by varying the core, rod and shell size, and rod interfacial strain [10]. In [17], electronic structure simulations find a transition, with decreasing core size, from a type-I behavior to a quasi-type-II behavior, where the fundamental hole state is confined inside the dot-core, while the electron is delocalized in both the core and the rod-shell, because of the small offset between the CdSe and CdS conduction bands. The electron wave function

for the lowest conduction band state, however, does not extend over the whole rod, but only near the core. The observations of dot-in-rod fine structure [1], [2], blinking [18], and transient absorption [8], [19] are in agreement with this prediction. In [1], Bayer *et al.* used the luminescence decay curves and their temperature dependence as information about the separation between the allowed and forbidden transition sublevels, following classical equivalent work on spherical nanocrystals. The fine-structure splitting was found to depend not on the rod length but on the rod width, independent of the core diameter, which confirms the type-II nature of the dot-in-rods. Christianen *et al.* [2], on the other hand, excite at a frequency very close to fluorescence transition (Fluorescence Line Narrowing) to reduce the emission linewidths (down to 0.7 meV) and access the various fine structure sublevels, as well as the phonon contributions, and study the Zeeman splitting of the spin-1 and spin-2 states.

4. Polarization Anisotropy

Semiconductor nanorods and dot-in-rods are well known to present both excitation and polarization anisotropy, which are to a certain extent dependent on the shape of the core and shell, and on the conditions of excitation and detection. For example, for excitation in the UV, far from the band edge, the density of possibly excited states becomes high, such that the excitation transition anisotropy is reduced or even suppressed. On the contrary, close to resonance, the excitation can be reduced to a single transition inducing a maximum in the excitation polarization anisotropy [3].

For nanorods, the growth of the rod along the c-axis of the wurtzite structure favours linearly polarized transitions [20] and induces a predominance of the linear dipole compared to the 2D dipoles (incoherent sum of two orthogonal linear dipoles orthogonal to the c-axis), which are characteristic of spherical nanocrystals [4]. For neutral dot-in-rods, the exciton is localized inside or close to the core for any shell length [17] and the spherical shape of the core induces a competition between 2-D and 1-D dipolar transitions. Moreover, it has been proved that the excitation and emission polarization anisotropies are both due to a combination of the electronic transition polarizations and a dielectric effect caused by the elongated shape of these nanostructures [3]. These competitive effects lead to a polarization anisotropy which, depending on the characteristics of the nanostructure, may be oriented along the rod axis or tilted [3], [6], [21].

For determination of the polarization anisotropy, excitation and emission anisotropies have to be analysed in different ways. For a field $\vec{E}_{exc}$ exciting a dipole $\vec{d}_{exc}$, the excitation efficiency, and therefore the emitted amplitude (below saturated excitation), is proportional to $\|\vec{E}_{exc} \cdot \vec{d}_{exc}\|^2$. On the contrary, the field radiated by an emitting dipole has its own orientation in every direction. The degree of polarization of the detected light and its direction is highly dependent not only on the dielectric environment of the dipole but also on the direction and solid angle of detection [22]. For ensemble measurement in solution, the analysis relies on a selective excitation of dipoles of specific orientation, and detection of the polarized emission. The result therefore reflects both the excitation and the emission anisotropy. Single-nanocrystal analysis makes it possible to independently measure the excitation and the emission anisotropies [22] which can be coupled with AFM topographic measurements [5]. As the emission in such semiconductor core–shell nanostructures is mainly due to the core, the emission anisotropy appears to be larger in the case of rod-in-rods than in dot-in-rods [5]. As 2-D transition, 1-D linear transition and dielectric effect are competing and are highly dependent on the synthesis protocol and on the nanostructure morphology, polarization anisotropy reports can be quite different in different papers. In dot-in-rods, 1-D-like linear dipoles have been reported, which are either aligned with the rod axis [4] or tilted with respect to it [6]. The quantitative influence of dot size, and rod diameter and length is still being debated. Several papers in 2014 analyze the origin of polarization anisotropy in detail. The roles of the dielectric effect and the polarization of electronic transition [8] have been emphasized, but attention has also been pointed to the influence of band alignment, charges and Coulomb interactions [18], non-uniform rod shape [23], and anisotropic pressure on the CdSe core originating from the lattice mismatch with the CdS shell [4].
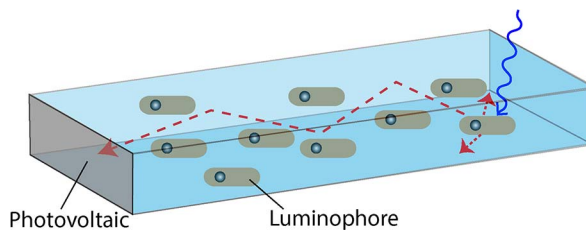
Fig. 2. Principle of a luminescent solar concentrator. Sunlight (blue arrow) is absorbed by the lumino-phore, and it emits luminescence light (red dashed arrows), which is guided to the photovoltaic cell.

5. Charge Transfer

Charge transfer in semiconductor nanoparticles is of great importance for solar cells applications. Because of their elongated morphology, one-dimensional semiconductor emitters are good candidates for solar energy conversion applications. Their elongated shape facilitates fast charge separation, which can be reinforced by band alignment. Functionalizing the nanorod tip with a metallic nanoparticle can even permit excitons dissociation and charge transfer to the environment. For nanorods, size, shape and morphology heterogeneities have major influence on exciton transport dynamics [23]. Transient absorption spectroscopy was used by Xu *et al.* [24] and Lian *et al.* [8], [19] to characterize charge transfer dynamics. Hot carriers relaxation, which is in competition with charge transfer, can be slowed down in nanocrystals and nanorods due to their discrete charge and phonon energy levels (phonon bottleneck); however, the quasi-continuum nature of the hole levels and the Auger transfer between electrons and holes may assist carrier relaxation. In [24], it is shown that the intraband relaxation is slower for CdSe nanorods than for spherical dots of the same volume, and that it becomes slower with increasing rod volume. In [8], various electron-hole recombination channels, involving states either in the core, trapped in the shell near the core or further in the shell, are described the latter has the slowest rate in photovoltaic applications.

In the case of segmented CdS/CdSe/CdS heterostructures, Subha *et al.* [10] showed that for a large number of excitons, the rate of charge transfer from CdS to CdSe is assisted by Auger recombination, which is predominant at high intensity. This charge transfer results in a large two-photon absorption cross-section.

6. Applications

The possibility of controlling the size, shape, and composition of dot-in-rod structures—leading to new properties—opened many areas of applications for them. The year 2014 saw a continuation of this trend with novel synthesis techniques and application methods that have improved these structures and increased their applicability.

To increase the absorption of sunlight in solar cells, the use of luminescent solar concentrators has been suggested (see Fig. 2). They consist of luminophores that absorb a broad spectrum of sunlight, especially in the blue region, and emit photons which are detected by the solar cell [25]. Direct exposure to blue light that can damage the solar cell is thus avoided. Due to the overlapping of the absorption and emission spectra of the luminophores, emitted light can be reabsorbed, which limits the performance of luminescent solar concentrators. Using CdSe/CdS dot-in-rod luminophores, Bronstein *et al.* [25] have shown that by increasing the size of the CdS rod shell with respect to the CdSe core, the Stokes shift is better controlled and the reabsorption losses are reduced resulting in more light absorption by the photovoltaic. Similar effects of size are noted in CdSe/CdS spherical core/shell nanocrystals but the elongated geometry of the dot-in-rod structures allows the growth of much larger volumes of CdS than in the former, and therefore less reabsorption. Larger Stokes shift permits longer photon propagation distances in the solar concentrator, which can allow larger areas of luminophores, thereby improving the quality of solar cells. Bradshaw *et al.* [26] have compared CdSe/CdS spherical core/shell, CdSe/CdS dot-in-rod core/shell, $Zn_{1-x-y}Cd_xMn_ySe/ZnS$ and $Cd_{1-x}Cu_xSe$ nanocrystals as potential

luminophores for solar cells. Unlike Bronstein *et al.*, they have reported CdSe/CdS dot-in-rods as the worst performers due to their reabsorption losses. They found $Cd_{1-x}Cu_xSe$ nanocrystals as the best.

Fuel cells efficiently produce clean electricity by oxidizing the fuel (H_2), and releasing only water as a waste product. The results of Wu *et al.* [9] show CdSe/CdS–Pt dot-in-rod-metal heterostructures as promising candidates for solar-to-fuel conversion. The paper attributes higher H_2 generation to faster hole transfer rates in these structures, which was made possible by the suitable choice of electron donor.

Various lighting and display applications have been discussed. Nam *et al.* [11] have explored the effects of structural shape and optical anisotropy of CdS/CdSe/ZnSe double-heterojunction nanorods [see Fig. 1(h)] in light-emitting diodes. With a brightness of 76 000 cd/m^2 and a power efficiency of 34.6 lm/W, these dot-in-rod diodes have been noted to significantly surpass the performance of CdSe/ZnS and CdSe/CdS/ZnS spherical core/shell nanocrystal, and CdSe/CdZnS nanoplatelet diodes. For light-emitting diode backlighting in liquid crystal displays, nanocrystals offer several advantages such as better colours (high saturation and wider gamut), more contrast, higher optical efficiency, and reduced requirements from other components such as colour filters and polarizers. Due to their high photoluminescence quantum yield and polarized emission, dot-in-rod structures have been suggested as propitious candidates for liquid crystal display backlighting [27]. The main unresolved issue is the toxicity of Cd in CdSe/CdS nanostructures. Lasing applications may also benefit from dot-in-rods. Using water soluble CdSe/CdS dot-in-rods, and choosing the appropriate dot and rod dimensions, the authors of [12] fabricated a single-mode ring micro-laser using droplet deposition, which under 15 μJ/cm^2 of fs-excitation, emitted at 632 nm with a bandwidth of 0.79 nm.

Dot-in-rods may also find their use in biomedical devices [28], [29]. Bareket *et al.* [28] have attached CdSe/CdS dot-in-rods to carbon nanotubes, achieving efficient charge transfer between the nanorod and the carbon nanotube. Due to its shape, size and composition, the dot-in-rod efficiently absorbs light, allowing better charge separation at the nanorod-nanotube interface, which generates a neural response that can be used to stimulate blind retinas. For retina stimulation, conducting polymers are an alternative but they are unstable under continuous stimulation and degrade after UV light or heat exposure; this is not the case with dot-in-rods. Because of higher photocurrent generation, CdSe/CdS dot-in-rods were found to be more appropriate than CdSe/CdS spherical core/shell and CdSe nanocrystals.

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