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Set 1

Sintesi di nanocristalli colloidali mediante approcci in soluzione

Fabbricazione e caratterizzazione di nanocompositi ibrido organici-inorganici

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SET 1

Size Dependence of the Spontaneous Emission Rate and Absorption Cross Section of CdSe and CdTe Quantum Dots

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In this paper, the size dependence of the band gap, of the spontaneous emission rate, and of the absorption cross section of quantum dots is systematically investigated over a wide size range, using colloidal CdSe and CdTe QDs as model systems (diameters ranging from 1.2 to 8 nm and from 2 to 9.5 nm, respectively). The size dependence of the band gap is well-described by theoretical models, and is dominated by the quantum confinement contribution ($1/d^2$ scaling). The spontaneous emission rate increases linearly with the emission frequency for both CdSe and CdTe QDs, in good agreement with theoretical predictions. By extrapolating the frequency dependence of the emission rates to the bulk band gap values, the exciton radiative lifetime in bulk CdSe and CdTe could be estimated for the first time (viz., 18 and 20 ns, respectively). Comparison between the empirical trends and theoretical predictions provides new fundamental insights into the size dependence of the $IS_{(e)}IS_{3/2(h)}$ oscillator strengths of QDs, both for emission and absorption. The results highlight the importance of the balance between quantum confinement and coulomb interaction contributions to the size dependence of the exciton properties in QDs and offer an explanation to the long-standing discrepancies observed between the empirical size-dependent trends and the theoretical predictions. The difference between the size dependence of the radiative decay rates and of the absorption cross sections is shown to be due to the fundamental differences between the emission and absorption transitions (viz., spontaneous versus stimulated). The results are also relevant from a practical viewpoint, since they show that the molar extinction coefficients at energies far above the band gap are better suited for analytical purposes. Moreover, more extended and accurate sizing curves are provided for CdSe and CdTe QDs.

1. Introduction

The remarkable size-dependent properties and chemical versatility of colloidal semiconductor nanocrystals, also known as quantum dots (QDs),^{1–3} have turned them into promising materials for many applications, such as light-emitting diodes,^{4,5} lasers,^{6,7} nonlinear optics,^{8–11} photovoltaics,^{12,13} and biomedical imaging.^{14,15} The knowledge of the concentration of QDs is of crucial importance for these applications and also for the chemical preparation of heteronanocrystals,^{16,17} silica-encapsulated QDs,¹⁸ nanocrystal superlattices,^{19,20} and QD–polymer composites.²¹ Optical absorption spectroscopy is probably the most convenient way to determine the concentration of chromophores in general, provided the molar extinction coefficient of the absorbing species is accurately known. This has motivated several groups to investigate the size dependence of the extinction coefficient of colloidal QDs for a number of materials, such as CdS,^{22,23} CdSe,^{23–27} CdTe,^{23,28} InAs,²⁹ PbS,³⁰ and PbSe.³¹

Understanding the size dependence of the absorption cross section of colloidal QDs is also important from a fundamental viewpoint. Theoretical models^{32–34} predict that the oscillator strength per unit (i.e., per single ion pair) of the lowest energy exciton transition for QDs in the strong confinement regime scales as $1/r^3$ (r is the QD radius), which implies a size-independent oscillator strength per QD. However, most of the experimental results^{23–26,30,31} are in contradiction with these theoretical predictions. Further, large discrepancies are also observed between the empirical size-dependent trends reported

by different groups, even for the same material. The size dependence of the molar extinction coefficient (ϵ) per QD of the lowest energy exciton transition is usually expressed in the form of a power law ($\epsilon = cr^n$, where c is a constant), with exponents varying from zero (i.e., size-independent, as theoretically predicted) to ~ 3 for different materials or groups (e.g., $n = 0$ for CdTe,²⁸ CdS,²² and InAs;²⁹ $n = 1$ for CdSe²⁶ and PbSe;³¹ and $2 < n < 3$ for CdS,²³ CdTe,²³ CdSe,^{23–25} and PbS³⁰). The discrepancies between the results reported by different groups are widely recognized in the literature^{23,27,29–31} and have been attributed to the inherent experimental difficulties associated with the accurate determination of sizes and concentrations of QDs. The variety of techniques and methodologies employed further complicates the issue, since it is often difficult to precisely evaluate the combined uncertainties of all the measurements involved in the determination of molar extinction coefficients and absorption cross sections of QDs (viz., sizing by TEM or XRD techniques, sample digestion and measurement of elemental concentrations, etc.).^{23,27,29,30} Further, the reported values are not always fully comparable, since some authors have used peak intensities,^{23,24} but others employed the integrated intensities either in wavelength²⁶ or energy.^{25,29}

The size dependence of the exciton radiative lifetime of QDs is also of great scientific interest from both fundamental and applied viewpoints but has been much less investigated^{35–38} than the absorption properties, probably due to the difficulty of synthesizing QDs yielding purely radiative exciton decay. The recent availability of high-quality QDs showing single-exponential photoluminescence (P^{exc} decay has made the

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Consiglio Nazionale delle Ricerche

Set 2

Approcci chimici per la sintesi di nanocristalli di perovskite in soluzione

Proprietà elettroniche di nanocristalli di semiconduttori

Strategie di funzionalizzazione superficiale di nanocristalli inorganici



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Correlation between Single-Photon Emission and Size of Cesium Lead Bromide Perovskite Nanocrystals

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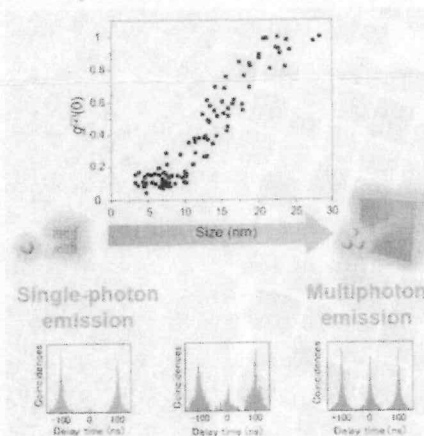


Article Recommendations



Supporting Information

ABSTRACT: Emission photon statistics of semiconductor nanocrystal quantum dots (QDs), including lead halide perovskite nanocrystals (PNCs), are important fundamental and practical optical properties. Single QDs exhibit high-probability single-photon emission owing to the efficient Auger recombination between generated excitons. Because the recombination rate depends on QD size, single-photon emission probability should be size-dependent. Previous studies have researched QDs smaller than their exciton Bohr diameters (twice the Bohr radius of excitons). Here, we investigated the relationship between the single-photon emission behavior and size of CsPbBr₃ PNCs to elucidate their size threshold. Simultaneous single-nanocrystal spectroscopy and atomic force microscopy observations on single PNCs with approximately 5–25 nm edge length showed that those smaller than approximately 10 nm, which had size-dependent photoluminescence (PL) spectral shifts, exhibited high-probability single-photon emissions, which decreased linearly with PNC volume. Novel single-photon emission, size, and PL peak correlations of PNCs are important for understanding the relationship between single-photon emission and quantum confinement.



Lead halide perovskite nanocrystals (PNCs) are gaining attention owing to their outstanding optical properties such as narrow photoluminescence (PL) spectra, high PL quantum yield (PLQY), high defect tolerance, and tunable PL spectra via size and composition.^{1–10} Thus, PNCs have been used in optoelectronic devices including light-emitting diodes,^{11–16} lasers,^{17,18} and photodetectors.^{19,20} As with typical II–VI, III–V, and IV–VI semiconductor nanocrystals known as quantum dots (QDs), single-photon emission from an isolated single PNC is an interesting optical property.^{21–31} The observation of single-photon emission is essential for determining whether the object is a single emitter. Additionally, single-photon emission is important for practical quantum information technologies. Single quantum systems such as single atoms and ions,^{32–34} molecules,^{35–39} and color centers in diamond^{40–42} are representative single-photon emitters because only one excited state is generated in a single system simultaneously upon photoexcitation.

For QDs, including PNCs, multiple excitons can be simultaneously generated in single QDs. Nevertheless, single QDs can behave as single-photon emitters because multiple excitons decay nonradiatively to a single exciton by Auger recombination (AR) faster than the radiative rate of multiple excitons.^{28,43–50} Thus, nonradiative AR is a key process in determining whether single QDs behave as single or multiphoton emitters. Traditional QDs usually exhibit a nearly linear scaling of the AR rate with QD volume.^{43–46} For PNCs, both the same linear scaling and deviation from the linear

scaling depending on their size have been reported.^{47–50} Thus, almost all typical QDs, except giant core/shell QDs,⁵¹ behave as single-photon emitters because AR efficiently occurs in QDs with strong quantum confinement regimes, that is, smaller than their exciton Bohr diameter (BD).

Although PNCs show a quantum confinement effect depending on their size, PNCs larger than their BD exhibit “quantum-dot-like” emission behavior with a sharp PL band and PL blinking behavior.^{52–55} Thus, the emission photon statistics of such PNCs is an interesting research topic. It is known that sub-micrometer-sized perovskites (no quantum confined regime), much larger than PNCs, exhibit no single-photon emission.^{55,56} However, the single-photon emission size threshold is not known because the single-photon emission behavior and AR rate of PNCs between weak-quantum-confined (slightly larger than their BD) and no-quantum-confined regimes have not been systematically investigated. Recently, Zhu et al. reported the size-dependent single-photon emission behavior of PNCs using CsPbI₃ PNCs of two different sizes (6 and 10 nm) and CsPbBr₃ PNCs (10

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SET 3

Particle–Particle Interactions in Semiconductor Nanocrystal Assemblies

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ABSTRACT

To study possible interactions between semiconductor nanocrystals, crystalline superstructures of $\text{Cd}_{17}\text{S}_4(\text{SCH}_2\text{CH}_2\text{OH})_{26}$ have been studied spectroscopically. Interactions between the particles have been detected which are discussed with simple models including electronic and dipole–dipole interactions.

Over the past two decades, research on structures in the size regime of a few nanometers has proven to be one of the most rapidly growing fields in modern science. This sector is being investigated by solid state physicists, inorganic chemists, physical chemists, colloid chemists, material scientists, and recently even biological scientists, medics, and engineers. Phase transition pressures, melting points, optical and optoelectronic, catalytic, magnetic, and electric properties of nanomaterials differ from those of the solid as well as from those of the molecular species of which they consist.^{1–7}

The monodisperse particles become useful as building blocks of big supramolecular units.^{4–6} Reports on the self-organization into quantum dot solids built from semiconductor^{8–10} and metal particles^{11–14} already exist.

Up to now only very little is known about the properties of these solids made from nanoparticles. Some work has been published by Heath et al. on collective properties of interacting metal nanoparticles.^{15–17} Depending on the interparticle distance, those solids reflect dipole–dipole interaction followed by pure electronic coupling when the particles come into closest contact. Recently, Remacle and Levine studied theoretically electron-transfer processes in arrays of quantum dots.¹⁸ A shift of the first electronic absorption of small cadmium sulfide clusters to lower energies compared to their solutions was first published by Vossmeier et al.¹⁹ for closely packed layers of cadmium sulfide nanocrystals. The layers were built up from solutions of the clusters by a spin-coating technique and were examined by absorption spectroscopy. Further investigations have been performed on such kind of closely packed layers and will be presented in a forthcoming paper.²⁰ Besides some further studies on Förster energy transfer in semiconductor quantum solids consisting of particles of different sizes,^{21,22} little is known about the interaction between identical

semiconductor nanoparticles. For this purpose cluster crystals are ideal candidates.

For our preliminary studies presented in this letter, we choose the cluster crystal compound $\text{Cd}_{17}\text{S}_4(\text{SCH}_2\text{CH}_2\text{OH})_{26}$, which has been prepared according to the literature.²³ The structure of this thiol-stabilized molecule-like cadmium sulfide nanocrystal is known from single-crystal X-ray diffraction. In Figure 1 the internal structure of the cluster is shown. It represents a tetrahedral cutout from the bulk cubic structure consisting of four adamantane-like cages capped with barrelane-like cages at the four tips of the tetrahedron. This tetrahedron has an edge length of 1.4 nm. It is also seen from Figure 1 that neighboring clusters are bound covalently via a bridging sulfur atom from the ligand at each tip of the tetrahedra. A 3D network is formed in this manner in a cubic diamond-like superstructure. Single crystals with sizes in the millimeter range are obtained via this preparation route. Because of absorption coefficients of the clusters as high as 84 000 L/mol·cm, it is impossible to perform absorption spectroscopy on this kind of solid. To study the optical properties of this material reflection spectroscopy has been performed. For this, we milled the crystals down to grain sizes of about two μm and measured the diffuse reflection in an integrating sphere. In Figure 2 the UV–vis absorption spectrum of this compound in solution is shown together with the reflection spectrum of the crystalline material. It is clearly seen that in the spectra of the crystalline material the first electronic transition is shifted to lower energies by about 150 meV. Additionally, the transition is broadened from a full width at half-maximum of about 390 meV to about 520 meV.

For explaining the observed energetic shifting of the first electronic transition, surface and solvation effects of a surrounding polar environment were considered. Recently, Brus and co-workers presented theoretical studies on cad-



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ALL. 2

Set 3

Strategie per la progettazione e realizzazione di nanocristalli inorganici con controllo della dimensione

Tecniche di funzionalizzazione superficiale post-sintesi di nanocristalli e nanoparticelle inorganiche

Caratterizzazione morfologica di nanomateriali a base di nanostrutture inorganiche



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Set 4

Strategie sintetiche per la progettazione di nanocristalli colloidali con il controllo della forma

Caratteristiche elettroniche di semiconduttori nanostrutturati e loro potenziale utilizzo in campo energetico

Caratterizzazione morfologica e spettroscopica di film a base di nanocristalli di semiconduttore



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SET 4

SOLAR CELLS

Conformal quantum dot-SnO₂ layers as electron transporters for efficient perovskite solar cells

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Improvements to perovskite solar cells (PSCs) have focused on increasing their power conversion efficiency (PCE) and operational stability and maintaining high performance upon scale-up to module sizes. We report that replacing the commonly used mesoporous-titanium dioxide electron transport layer (ETL) with a thin layer of polyacrylic acid-stabilized tin(IV) oxide quantum dots (paa-QD-SnO₂) on the compact-titanium dioxide enhanced light capture and largely suppressed nonradiative recombination at the ETL-perovskite interface. The use of paa-QD-SnO₂ as electron-selective contact enabled PSCs (0.08 square centimeters) with a PCE of 25.7% (certified 25.4%) and high operational stability and facilitated the scale-up of the PSCs to larger areas. PCEs of 23.3, 21.7, and 20.6% were achieved for PSCs with active areas of 1, 20, and 64 square centimeters, respectively.

Efforts to realize metal halide perovskite solar cells (PSCs) with power conversion efficiencies (PCEs) of >23% have focused on formamidinium-rich lead iodide (FAPbI₃) formulations (1–7) because their narrower bandgap is closer to the Shockley-Queisser optimum than for methylammonium-based or mixed-halide perovskites (8). By fully using the broad absorption spectrum of FAPbI₃, a certified PCE of 25.21% with a short-circuit current density (J_{sc}) of >26 mA/cm² was obtained for the mesoporous-structure PSCs (7). However, the mesoporous-TiO₂ (m-TiO₂) electron transport layer (ETL) may show unwanted photocatalytic effects under ultraviolet (UV) light illumination, and the low electron mobility of m-TiO₂ limits the charge transport (9–11).

Among alternative metal oxide ETLs (10–17) for PSCs, SnO₂-based PSCs could potentially be more efficient and stable given that SnO₂ is UV resistant and has a higher carrier mobility

than TiO₂, which facilitates electron extraction and transport (10–12). Several techniques, such as spin coating (11, 16), atomic layer deposition (1), and chemical bath deposition (CBD) (12, 17), have been used to deposit the SnO₂ ETLs. Spin-coated SnO₂ ETL from a SnO₂ colloidal quantum dot (QD-SnO₂) solution onto the indium-doped tin oxide (ITO) substrate enabled a certified PCE of >23% for the corresponding planar-structure PSCs (2, 16). Recently, a thin SnO₂ ETL on fluorine-doped tin oxide (FTO) deposited with a well-controlled CBD method enabled PSCs with a certified PCE of 25.19%, because of the improved carrier properties of SnO₂ ETL (17). However, compared with the m-TiO₂-based PSCs, the SnO₂-based PSCs still suffered from a relatively low J_{sc} of <26 mA/cm², which is attributed to the optical losses arising from reflection and destructive interference of the incident light waves at the interfaces.

One approach to reduce these optical losses is to use the textured surface of FTO as the front contact that scatters the incoming radiation, destroying the coherence of the incoming light and affording light trapping by increasing the optical path length (18). The enhanced light absorption by the perovskite benefits the photocurrent delivered by the photovoltaic (PV) cell. Similar strategies have been used for textured crystalline silicon-based PSCs (19). However, early efforts to deposit a thin, uniform, and high-quality SnO₂ ETL using a solution process were incompatible with the underlying textured FTO surface (1, 12, 20–22), causing optical losses. The highest reported J_{sc} of SnO₂-based PSCs of ~25.2 mA/cm² (17, 20) still limits the overall PV performance.

Here we introduce an architecture for the ETL of PSCs that consists of a compact-TiO₂ (c-TiO₂) blocking layer covered by a thin layer of polyacrylic acid (PAA)-stabilized QD-SnO₂ (paa-QD-SnO₂) deposited in a contiguous and

conformal manner on the textured FTO. The uniform bilayer of paa-QD-SnO₂@c-TiO₂ largely improved the perovskite's absorption of sunlight and formed an outstanding electron-selective contact with the perovskite film. The quantum size effect increased the bandgap of the QD-SnO₂ from 3.6 eV for bulk SnO₂ to ~4 eV (21, 23) and produced a corresponding upward shift of its conduction band edge energy. This shift aligned it well with the conduction band edge of the perovskite so that electron capture by the SnO₂-based ETL proceeded with minimal energy losses (5, 11, 16, 21).

PAA, a polymer binder, was added to the SnO₂ QD solution to attach the colloidal QD-SnO₂ firmly to the c-TiO₂ surface, providing a contiguous, thin, and conformal SnO₂ layer that fully covered the c-TiO₂ layer underneath. The carboxyl groups of PAA undergo strong hydrogen and coordinative bonding with the metal oxide surface, facilitating the lamination process, especially for production on a large scale (24–26). By choosing FTO substrates with suitable diffuse transmittance and reflectance, the textured paa-QD-SnO₂@c-TiO₂ bilayer enabled a PCE of 25.7% (certified 25.4%) with a J_{sc} of 26.4 mA/cm² and high stability for the corresponding PSCs. We further demonstrate that the paa-QD-SnO₂@c-TiO₂ bilayer could be applied to realize large PSC modules with an active area up to 64 cm² while maintaining a PCE of >20%.

We investigated the microstructures of the spin-coated QD-SnO₂ layer on the c-TiO₂ using commercially available SnO₂ colloidal QDs with and without PAA. Unless otherwise noted, the QD-SnO₂ solution was diluted by deionized water (1:20) in this study. Figure S1, A to C, shows the top-view scanning electron microscope (SEM) images of the c-TiO₂, QD-SnO₂@c-TiO₂, and paa-QD-SnO₂@c-TiO₂, respectively. Because of the textured surface, the c-TiO₂ layer was not fully covered by the spin-coated QD-SnO₂ (fig. S1B). In contrast, a uniform, conformal paa-QD-SnO₂ layer was formed (fig. S1C). Atomic force microscopy images (fig. S1, D to F) further confirmed the uniform morphology of the paa-QD-SnO₂@c-TiO₂ (fig. S1F), which is different from that of the QD-SnO₂@c-TiO₂ (fig. S1E).

Figure 1, A and B, shows the cross-sectional transmission electron microscopy (TEM) images of the QD-SnO₂@c-TiO₂ and paa-QD-SnO₂@c-TiO₂ bilayers on FTO substrates, respectively. The QD-SnO₂@c-TiO₂ bilayer presented an ununiform distribution over the FTO surface with a thickness that varied from ~30 (vertex region) to ~70 nm (valley region), while the paa-QD-SnO₂@c-TiO₂ bilayer had a uniform and conformal distribution over the FTO surface with a uniform thickness of ~30 nm. The different distribution between QD-SnO₂ and paa-QD-SnO₂ layers can also be seen clearly from the cross-sectional SEM images (fig. S2, A and B),

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