Quantum Dots for Electro-Optic Devices

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Semiconductor quantum dots (QDs) have been studied for more than 25 years; however, there was an immense increase in interest in these materials after the 1993 publication[1] of a synthesis method that resulted in high-quality QDs (to date, this article has been cited almost 4000 times, and the keyword "quantum dot" returns nearly 25 000 publications with a steadily increasing rate over the years). This enthusiasm was mainly driven by the fascinating mesoscopic properties that can be observed in these materials and two potential areas of application: the rapidly emerging field of bioanalysis and diagnostics,[2] and electro-optic devices. It is surprising that, despite the intense research activity during the past two decades, there are very few QD-based products on the market yet. In this Perspective article, we will analyze the difficulties in using QDs for electro-optic devices and speculate on the future direction in the field as related to the article by Geyer et al. that appears in this issue of ACS Nano.[3]

Quantum dots are attractive materials for electro-optic devices because their electronic and optical properties can be tuned by changing the size, morphology, and composition of the nanoparticles.[4] Compared with molecular substances, their optical and chemical stability is much improved. Furthermore, they can be produced by wet-chemical synthesis, which has several advantages compared with standard cleanroom technologies (e.g., it is much cheaper). The major difficulty in exploiting QDs for electro-optic devices lies in the colloidal nature of the particles. Typical QDs have a diameter of about 5 nm and are colloidally stabilized by a surface-ligand coating. Since QDs may have surface atom percentages of 50% or more, surface imperfections may dominate the electronic and optical properties. The ligand coating determines the ability of the QDs to be dispersed in the surrounding

ABSTRACT We discuss the use of quantum dots (QDs) in electro-optic devices. The focus of the article is on key problems in this area: the electronic and optical properties of QDs, dispersing QDs in polymers and the requirements for both, and QDs and polymer composites in devices such as solar cells, light-emitting devices, and detectors. The accompanying article by Geyer et al. in this issue of ACS Nano demonstrates an excellent example of a detector device, which also points to future directions for research in this field.

KEYWORDS: quantum dots · polymer composite · nanoparticles · detector · light-emitting device · photovoltaic cell

medium. Thus, the surface of the QDs influences both the electronic and optical properties as well as their ability to be incorporated successfully in devices.

> Quantum dots are attractive materials for electro-optic devices because their electronic and optical properties can be tuned by changing the size, morphology, and composition of the nanoparticles.

Electronic and Optical Properties of QDs: Importance of Surface States. The nonlinear optical properties of QDs are chiefly determined by quantum confinement effects that come into play at the nanometer scale in particle size. The subsequent high surface-to-volume ratios mean that the electronic structure, and hence optical behavior, can be strongly influenced by surface states that often derive from the QD synthesis process itself. Nanocrystal growth defects and oxidation at the surface may introduce accepting or donating levels in the density of states (DOS) that act as trap states for photogenerated charge

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carriers and provide alternate relaxation pathways or loss mechanisms. These result in lowered photoluminescence (PL) efficiency, quantum yield (QY), and/or blue or red shifts in absorbance/fluorescence.

Quantum mechanical modeling is one route to examining the impact of defects[5] on the DOS and, therefore, electro-optical properties of QDs; however, surface-sensitive techniques such as X-ray photoemission spectroscopy (XPS) offer a direct means of measuring surface compositional and electronic environments and correlation with performance. X-ray photoemission spectroscopy, by its very nature, probes the electronic environments of occupied core states of QD component atoms and ligands, as well as the valence band portion of the DOS. The character of defects induced by off-equilibrium nanocrystal growth kinetics[6] may be monitored by XPS, enabling close control of synthesis parameters for defect minimization.[7] Surface oxidation, either during or post-synthesis, may be followed by XPS, and the efficacy of stabilizing/passivating organic ligands can be subsequently assessed. With core—shell QDs, the overall system electronic structure, core—shell interface, and shell quality and thickness can be studied.[8] Synchrotron-based XPS offers significant enhancements as the energy of the exciting X-ray source may be "tuned" to maximize depth sensitivity[7] and/or photoionization cross section for the element of interest. Innovations in laboratory-based electron spectroscopies such as metastable-induced electron spectroscopy (MIES) allow the valence bands of the surface monolayers and subsurface to be separated.[9]

Until recently, there has been little exploitation of electron spectroscopies; however, the prospects for the future include, in combination with fluorimetry, gaining a comprehensive picture of QD electronic structure, from bulk to surface to ligand and ligand—matrix interface.

Quantum Dots and Polymers. For many electro-optic devices, dispersion of QDs in a polymer matrix is of critical importance. For example, in QD-based solar cells, the active material is a bulk heterojunction nanocomposite consisting of QDs and a conducting polymer. Other applications, such as down-shifting detectors in the accompanying article[3] or color-corrected light-emitting diodes,[10] require perfectly dispersed QDs in a polymer matrix. The physicochemical principles that govern the dispersion of nanoparticles in polymers are depletion interactions and steric stabilization: if a non-adsorbing polymer is added to a sterically stabilized QD dispersion, attractive forces are induced that may lead to complete flocculation. Very high polymer concentrations may stabilize the colloid again—this effect is called depletion stabilization.[11] We will discuss two different examples of QD stabilization in polymers to demonstrate the different requirements and approaches.

In QD-based solar cells, there have to be pathways for charge carriers to migrate to the anode and cathode (usually, the QDs are in contact with the cathode). This means that, for bulk heterojunction composites, the QDs must not be isolated but allow for the transfer of charges between particles. The active layer of QD-based solar cells is usually spun onto a substrate, where QDs and conducting polymers are codissolved (dispersed) in a common solvent. In order to be dispersible in the solvent, the QDs have to bear stabilizing surface ligands, which also prevent the adsorption of the conducting polymer. This is a typical depletion flocculation situation, and if the conditions are chosen well, the QDs form larger aggregates in the solvent that remain intact once spun onto the substrate.[12] Quantum dot aggregates ensure contact between QDs and thus enable charge transfer between individual particles. However, the stabilizing ligands on the QDs' surfaces may prevent both charge transfer and the adsorption of the conducting polymer, which is a prerequisite in order to form a heterojunction. This problem is usually solved by employing volatile surface ligands (for example, pyridine or butylamine) that can be removed by heating in vacuo (e.g., Han et al.[13]). This is an example where depletion flocculation and surface ligands (stabilization) are carefully balanced to obtain the desirable QD/polymer composite.

The requirements of the down-shifting detector device in the accompanying article are very different from those of a QD-based solar cell: as discussed by the authors, the distance between individual QDs has to be large enough to prevent energy transfer and has to be balanced in such a way as to optimize transmission, absorption, and emission of light. This can only be achieved when the QDs are perfectly dispersed in the polymer matrix. The most straightforward approach for this is to dissolve the nanoparticles in the monomer and then start the polymerization. Unfortunately, depletion flocculation is frequently triggered under these circumstances, as the polymer chains grow in their monomer. It has been shown that depletion flocculation during polymerization can be kinetically hindered by very rapid polymerization.[14] However, this method is not practical for many applications. A better way to prevent flocculation during polymerization is to render the particle surface highly compatible with the polymer matrix. This can be done either by functionalizing the QDs with compatible ligands or by using a strongly adsorbing polymer. In the article by Geyer et al.,[3] poly(methyl methacrylate) (PMMA) was codissolved with the QDs in chlorobenzene and cast onto the substrates. The fact that no aggregation of the QDs was observed leads to the conclusion that PMMA has a high affinity for either the oleic acid ligands and/or the QD surface.
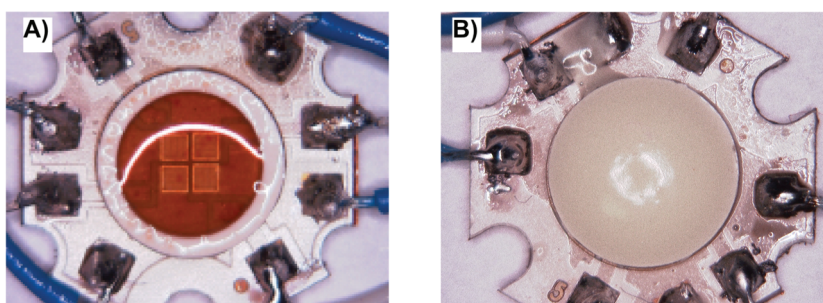
Figure 1. (A) Quantum dots perfectly dispersed in a silicone-based polymer. (B) Aggregates of particles in the same polymer. Reprinted with permission from ref 10. Copyright 2008 Wiley.

TABLE 1. Quantum Dot Properties in Relation to the Requirements of Different Devices

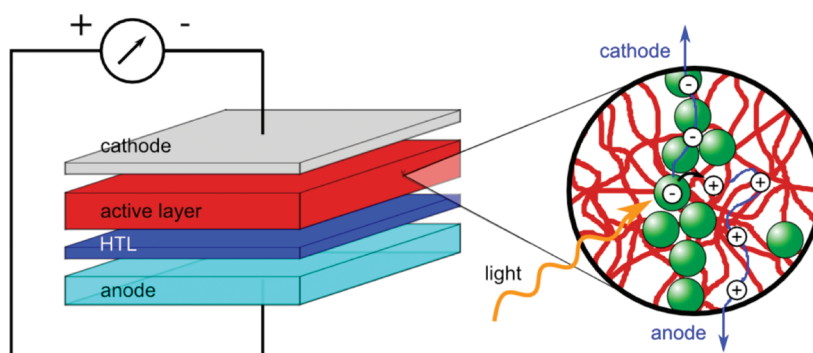|	charge-transfer devices	down-converting devices
surface	must enable charge transfer steers aggregation behavior	prevents aggregation
optical properties	must be balanced with electronic properties	highly important
electronic properties	highly important	not relevant
doping	n/p-doping might be necessary	not relevant

Figure 2. Schematic of a bulk heterojunction nanocomposite solar cell and its principle of operation (inset, right).

Unfortunately, many polymers used in electronics (*e.g.*, silicones) do not have this intrinsic affinity for typical QD ligands or surfaces. In these cases, the QDs have to be modified accordingly. Figure 1A shows an example where QDs were perfectly dispersed in a silicone—the underlying electronic structure is visible, as opposed to the aggregated structure in Figure 1B. In order to achieve this perfect dispersion, the QDs had to be coated with a thin layer of silica and thus rendered compatible to silicone.[10] Depletion flocculation was prevented by modifying the QD surface so that silicone becomes an adsorbing polymer.

Quantum-Dot-Based Electro-Optic Devices. In principle, there are two types of QD-based electro-optic devices: applications where the QDs are involved in charge-transfer reactions (*e.g.*, bulk heterojunction photovoltaic or light-emitting devices) and techniques where the QDs serve solely an optical function (*e.g.*, downshifting detectors). As mentioned above, the requirements for the QDs are very different in these two types of applications as summarized in Table 1.

By far, the most studied electrooptic devices that use QDs so far are photovoltaic cells[15] and lightemitting devices (LEDs).[16] A typical scheme of a QD-based photovoltaic cell is depicted in Figure 2: a transparent electrode (anode) is coated with a hole transport layer (HTL) that allows, exclusively, for the conduction of holes. On top of this, there is the active bulk heterojunction composite consisting of QDs and a conducting polymer. Finally, the active layer is coated with the cathode. On illumination, excitons are created in the active layer and separated at the QD/polymer interface. Then, the respective charges migrate to the electrodes, as depicted in the inset of Figure 2.

To date, the best certified efficiency of a QD/polymer solar cell has been 3.13%[17] (an all-inorganic device has achieved an efficiency on the same order of magnitude[18]). However, efficiencies of these devices are typically below 1%.[15]

Quantum-dot-based LEDs and displays follow the same basic

concept as photovoltaic devices, with the difference being that charges are injected into the active layer and recombine in the QDs by emission of photons (an LED is basically an "inverse" solar cell). Very attractive features of QD-based LEDs and displays are the good color range and purity, as well as their potential for simple processing, even on flexible substrates. Several companies including Philips, QD Vision, and others are trying to commercialize QD-based displays and LEDs.

Although bulk heterojunction nanocomposites of the type used as active layers for solar cells and LEDs have been discussed as materials for printable electronics, we are not aware of any realization of this idea.

The article by Geyer et al. in this issue represents a nice example of the second class of electro-optic devices, where QDs are used as luminescense down-converters.[3] A major initiative in this direction was the quest for the white LED (e.g., Jang et al.[19]). A large number of groups have tried to "correct" the emission spectra of down-conversion phosphors in so-called luminescence conversion LEDs (LUCOLEDs) to realize LEDs with an acceptable color rendering index (CRI) for domestic illumination. Unlike the QDs used by Geyer et al., the requirements for the dispersion of QDs in the polymer matrix were very low as they were simply "mixed" with crystalline phosphors.

Devices that require a perfect dispersion of the QDs in the matrix, such as solar concentrators[20,21] or detectors, are much more challenging and, to the best of our knowledge, no commercial product of this type is currently on the market.

CONCLUSIONS AND OUTLOOK

The above brief overview of the state-of-the-art in QD-based electro-optic devices leads to the conclusion that two main factors influence the overall performance of electro-optic devices: the electronic and

optical properties of the QDs and the dispersion of the QDs in the respective polymer matrix (if we ignore the exception of devices where no polymer matrix is being used). The first factor—the electronic and optical properties of the QDs—is mainly affected by the synthesis of the QDs. Synthesis methods for the production of high-quality group II_B and IV chalcogenides have been developed in abundance; however, the majority of these QDs contain heavy metal elements (e.g., lead or cadmium) and are thus intrinsically toxic. The future research direction in this area points to the synthesis of high-quality, nontoxic QDs. Some articles on InP[22,23] and $CuInX_2$ (X = chalcogenide)[24,25] QDs have been published; nevertheless, there is still no competitive alternative to toxic QDs. Major difficulties in synthesizing nontoxic QDs are typically caused by the lack of appropriate reagents (e.g., for phosphides

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and nitrides) and/or competing side reactions in multicomponent systems. It can be expected that the availability of high-quality, nontoxic QDs that can be produced inexpensively will boost the commercialization of QD-based electro-optic devices.

A second aspect of the electronic and optical quality of QDs comprises advanced electronic spectroscopies such as XPS (including synchrotron XPS) or MIES. These techniques offer enormous potential for understanding

the electronic structure of QDs and its relation to the synthesis. As mentioned above, few researchers have made use of these capabilities to date. Systematic exploitation of these surface-sensitive techniques should help to build deeper insights in both synthesis and the electronic structure of QDs.

The second major factor—the dispersion of QDs in polymer matrices—is much more complex than it appears at first glance: some applications require perfect dispersion of the QDs; others need a QD network. Depletion flocculation depends on both the nature of the polymer and the surface ligands of the QDs. Some applications require electronic contact between QDs, polymers, and electrodes, whereas others do not. Even though many researchers have found solutions to disperse QDs in polymers according to their requirements, there has been no systematic, fundamental work on depletion flocculation of QDs. It would be highly desirable to build a comprehensive fundamental understanding of the interactions between QDs, ligands, and polymers that would enable researchers to tailor their system according to their requirements.

An issue of critical importance that has been neglected in almost all of the past literature is the optical interaction of the QDs with both other components of the system and each other. In this issue of ACS Nano, Geyer et al. have demonstrated exceptionally well how modeling can be used to understand and optimize these devices.[3] More systematic work in this direction will help us to understand the limitations and possibilities of QD-based electro-optic devices.

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