



## Designer polymer–quantum dot architectures

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### ABSTRACT

Quantum dots (QDs) are nanocrystals made of semiconductors, which exhibit intriguing electronic transitions that resemble single atom behavior. Due to their unique, size-tunable optical and electronic properties, QDs are increasingly applied in biology, bioanalytics and optoelectronics. Many of these applications require a combination of the QDs with polymers. The development of methods to obtain well-defined polymer–QD hybrid materials with tunable optical properties is an active field of research. In this review we first describe progress in the synthesis and fabrication of polymer–QD hybrid materials of various architectures. In particular, embedding methods of semiconductor nanocrystals into bulk polymers, polymer thin films, micro- and nanospheres are presented. Direct surface modification of the nanocrystals with polymers using a number of strategies ranging from multivalent surface passivation to functionalized chain-end attachment, as well as layer-by-layer assembly are also reviewed. Finally, we provide examples for applications of QD/polymer materials in the fields of biodiagnostics, bioanalytics, photonics and optoelectronics.

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## 1. Introduction

Semiconductor nanocrystals (also known as Quantum Dots, QDs) due to their small size (1–20 nm), display modified optical and electronic properties, which can be placed between those of bulk semiconductor materials and those of isolated molecules or atoms. During the last 20 years, extensive scientific research has been performed on QDs, and tremendous progress in their synthesis as well as in our understanding of their optical and electronic properties has been achieved [1–3]. Indeed, the quantum dots have come of age, and many applications of QDs in biodiagnostics, bioimaging, photonics, optoelectronics, and sensors have emerged [4]. The swift progress of this field of research can be followed through numerous books and review articles dealing with the synthesis, physical and optical properties of QDs, as well as their applications [5–12].

For many applications, either the surface of the QDs must be chemically engineered or the QDs must be embedded in a solid matrix. Since most synthetic polymeric materials are transparent in the visible part of the electromagnetic spectrum, they are often employed as matrices for nanocomposite materials for optical applications [13,14]. Besides playing the role of the matrix, polymers provide mechanical and chemical stability to the nanocomposite material. Additionally, polymers may prevent nanocrystal agglomeration, and offer processability into technologically relevant structures like thin films, or micro- and nano-spheres. Despite many advantages that a combination of QDs with polymeric materials has to offer, the development in this field of research has been relatively slow. The main difficulties encountered include poor compatibility of the QDs with the polymers and deterioration of the electronic or optical properties of the QDs once they are combined with the polymers. To avoid these drawbacks, research efforts have become concentrated on the chemi-

cal engineering of the QD surface with polymers or on the development of methods for the encapsulation of QDs in polymer matrices.

The present review summarizes recent research in the development of polymer-embedded QD materials, their synthesis and fabrication methods, as well as resulting optical properties and applications. Since the review inadvertently deals with colloidal QDs, the synthesis and main properties of these nanomaterials are briefly described. The following sections display how desired architectures of QD/polymer assemblies are obtained. This is followed by a discussion on the direct modification of nanoparticle surfaces with polymers via a number of strategies including hydrophobic interactions with QD surface ligands, multivalent passivation of the nanoparticle surface, and the “grafting to” and “grafting from” approaches for the attachment of polymer chains directly to the QD surface. Subsequently, the preparation of polymer micro- and nanospheres with encapsulated QDs is presented. Layer-by layer fabrication of polymer–nanoparticle assemblies on planar and curved substrates, as well as directly on the nanoparticle surface is detailed, and methods to obtain bulk materials and thin film architectures of QD/polymer hybrids are reviewed. Finally, the applications of the hybrid nanocomposite materials in the fields of biology, photonics, and optoelectronics are described.

## 2. Colloidal semiconductor nanocrystals, quantum dots

### 2.1. Structure and general properties of QDs

Colloidal quantum dots are nanocrystals made of semiconductor materials. The most common colloidal QDs comprise a combination of elements from the II and VI

**Table 1**

Chemical formula, bandgap energy and crystal structure of the most common semiconducting materials.

Semiconductor	Bandgap, $E_g$ [eV]	Crystal structure	Semiconductor	Bandgap, $E_g$ [eV]	Crystal structure
CdS	2.53 <sup>a</sup>	Zinc blend	PbSe	0.26 <sup>a</sup>	Sodium chloride
CdSe	1.74 <sup>a</sup>	Wurtzite	PbTe	0.29 <sup>a</sup>	Sodium chloride
CdTe	1.50 <sup>a</sup>	Zinc blend	HgS	0.50 <sup>a</sup>	Zinc blend
ZnS	3.8 <sup>a</sup>	Wurtzite	HgSe	0.30 <sup>b</sup>	Zinc blend
ZnSe	2.58 <sup>a</sup>	Zinc blend	HgTe	0.14 <sup>b</sup>	Zinc blend
ZnTe	2.28 <sup>a</sup>	Zinc blend	GaAs	1.43 <sup>a</sup>	Zinc blend
PbS	0.37 <sup>a</sup>	Sodium chloride	ZnO	3.35 <sup>b</sup>	Hexagonal

<sup>a</sup> Data taken from ref. [20].<sup>b</sup> Data taken from ref. [19].

groups (e.g. CdSe, CdS, ZnO), as well as, although less commonly, from the III and V groups (e.g. InAs, InSb, GaAs) of the periodic table of elements. Table 1 lists the most studied II–VI semiconductors together with their respective crystal structure and electronic properties, such as the bulk energy bandgap, i.e. the energy difference between the valence and conduction bands of the semiconductor.

Excitation of the nanocrystals with energies above the bandgap leads to the promotion of an electron to the conduction band, leaving behind a hole in the valence band of the semiconductor. The electron and the hole can form a bound state called an exciton, and the characteristic size of this electron–hole bound state is often referred to as the Bohr radius. The Bohr radius  $a_B$  depends on the materials properties and it is given by:

$$a_B = \frac{\hbar^2 \epsilon}{e^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right), \quad (1)$$

where  $e$  is the elementary charge,  $\epsilon$  is the bulk dielectric constant, and  $m_e^*$  and  $m_h^*$  are the effective masses of the electrons and holes, respectively. When decreasing the size of the nanocrystals below the Bohr radius, a three-dimensional confinement of the electrons and holes in the nanocrystals arises [15,16]. In consequence, the nanocrystals display modified optical and electronic properties, as compared to bulk materials. Most notably, the energy levels in the conduction and valence bands become discreet. These properties vary as functions of the degree of confine-

ment, and therefore as functions of the nanocrystals' size [3]. As the confinement increases, so does the energy difference between the valence and conduction bands. According to Brus [17], the change in the bandgap width with respect to its bulk values as a function of the size of the nanocrystals can be expressed as:

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R}, \quad (2)$$

where  $R$  is the nanoparticle radius. By examining Table 1 and Eq. (2), one can notice that, depending on the material type, the same nanocrystal size will result in different degrees of confinement. The electronic properties of the nanocrystals can therefore be tuned by properly choosing the material and size of the nanocrystals.

Upon excitation with energies above the bandgap and promotion of an electron to the conduction band, the electron can recombine with the hole left in the valence band giving rise to an emission of light. The direct recombination of the electrons and holes from the conduction and valence bands is referred to as the “band edge” recombination process. When defects are present in the crystal structure, or at the crystal surface, the electrons and holes may recombine from “traps” formed in these defects, and the emission may be shifted to other wavelengths. The smaller the nanocrystal, the higher is the percentage of atoms that will be located at the surface. For instance, 30% of the atoms of a CdSe nanocrystal with a ~6 nm radius will form the QD sur-



**Fig. 1.** Luminescence emission from CdSe/ZnS QD solutions. The size of the QDs increases from ~2 nm to ~6 nm (left to right). The emission spans across the visible part of the electromagnetic spectrum from the blue (2 nm nanocrystals) to the red (6 nm nanocrystals). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

face. In the case of a  $\sim 2$  nm CdSe QD, 90% of atoms will be located at the surface [2]. The surface structure and presence of defects may therefore play substantial roles in determining the luminescence properties of the nanocrystals. A proper handling of the surface is essential to obtain highly luminescent QDs. The efficiency with which the QDs luminesce is expressed in terms of luminescence quantum yield (QY), which is the ratio between the number of emitted photons and the number of photons absorbed. For a majority of the QDs, the QY values usually lie between 10% and 30%, and higher values indicate high-quality materials.

Given that the bandgap is size-dependent, so is the wavelength of the emitted light. It is therefore possible to obtain tunable light emitters by varying the size of the nanocrystals without changing their chemistry. Fig. 1 shows UV-illuminated solutions of CdSe/ZnS QDs with sizes ranging from 2 nm to 6 nm. For this particular type of QD, the emission spans the whole visible part of the electromagnetic spectrum, from the blue (2 nm QDs) to the red (6 nm QDs). Had the nanocrystals all been of equal size and structure, the emission, even from an ensemble of QDs, would have been very narrow. This is due to the discreet nature of the energy levels in the valence and conduction bands. However, the application of QDs in, e.g. biology has been slowed down by the difficulties in synthesizing large quantities of monodisperse QDs. Nowadays, QDs with an emission spectrum with full widths at half maximum (fwhm) values of 20–50 nm can be routinely synthesized, and fwhm values below 20 nm are also being reported in the literature [18]. High QY and narrow emission lines are therefore the main figures of merit when assessing the quality of the nanocrystals, and are the determinants for many applications of the QDs.

Apart from the tunable, narrow, and size-dependent emission, QDs are also inherent of other attractive properties, which can be fully appreciated when contrasted with those of organic chromophores. Compared with organic chromophores, QDs display a much higher stability under illumination, lower photobleaching (i.e. the decrease in luminescence due to the chemical changes in the material) rates, and the ability to luminesce orders of magnitude longer in time. Unlike for organic chromophores, the absorption profiles are broad. Such broad absorption spectra allow for the excitation of many different QDs at a single excitation wavelength, while each of the nanocrystals will emit light with a characteristic wavelength depending on the QD structure and size. Strong, narrow and tunable emissions in combination with broad absorption spectra, such features are of interest for numerous applications, particularly in bioimaging and biolabelling.

## 2.2. Synthesis of semiconductor nanocrystals

The synthesis of the most investigated group of colloidal semiconductor nanocrystals (groups II–VI in the table of elements) has been touched upon in recent reviews [20–22]. Since the emission wavelength depends on the nanocrystals' size, it is important

to obtain nanocrystals with a narrow size distribution. This has proven to be a challenging task and extensive research in the synthesis of II–VI semiconductor nanocrystals has taken place during the last two decades. Colloidal routes based on controlled precipitation and syntheses in restricted geometries have been widely explored as ways to obtain high-quality nanocrystals.

Although some advances have been made using these methods, the real breakthrough came with the synthesis of high-quality QDs based on organometallic routes. Murray, Norris and Bawendi synthesized CdE (E = S, Se, Te) QDs by pyrolysis of organometallic reagents in a hot coordinating solvent. Such a procedure provided a discrete homogeneous nucleation followed by slow growth and annealing [23]. The QY of the resulting QDs was relatively high and the size distribution was quite narrow. The luminescence properties of the QDs could be further improved by passivating the semiconductor nanoparticles with suitable organic ligands [23], or by coating the QDs with an additional layer of another semiconductor material. Core-shell structures, fabricated by coating the nanocrystals with wider bandgap semiconductors, were found to display enhanced photochemical stabilities and their luminescence quantum yields were improved by 50–100% [24–26]. The synthesis of high-quality QDs has matured, and part of the research effort has been redirected toward improving the functionality and luminescence properties of the QDs by surface chemical engineering. Due to the high surface area of the nanocrystals, colloidal solutions of QDs are unstable and proper surface functionalization with suitable ligands is necessary. Since the ligand interacts with the nanocrystal surface, it also influences the luminescence properties of the QDs. The choice of the ligand is therefore crucial. The control over the amount of ligand on the QD surface and the stability of the resulting coating were in many cases found to be somewhat limited [27]. The hydrophobic nature of the surface ligands was identified as another problem for many applications. For instance, the preparation of high-quality quantum dots has in numerous cases been performed at elevated temperatures in the presence of trioctylphosphine oxide (TOPO) as the stabilizing ligand [23–25]. As a result, the nanoparticles were coated with a monolayer of TOPO, a hydrophobic molecule, and the QDs were soluble in nonpolar solvents but did not disperse in aqueous buffers. However, water-soluble QDs that are stable in a specific pH range constitute a prerequisite for applications in, e.g. biology. The QDs can be transferred to water by exchanging the TOPO molecules for other ligands consisting of one part that is able to bind to the nanocrystal surface (e.g. thiols, phosphines, carboxylic acids), and of another part, i.e. a polar headgroup (e.g. hydroxyl), directed toward the water. However, exchanging the TOPO molecules at the QD surface usually has a great effect on the QDs' luminescent properties, in many cases decreasing the luminescence quantum yields. The proper choice of ligand is therefore crucial in order to achieve functionality and retain the optical properties of the QDs, and very often limits the final application range of the QDs. In this context, polymers may be used as substitutes for the small organic ligand molecules or as surface modifiers to avoid the ligand exchange step.

**Table 2**

Polymers for coating QDs via hydrophobic–hydrophobic interactions.

Coating	Quantum dots	Width of the polymeric shell	Comments	Reference
Poly(maleic anhydride <i>alt</i> -1-tetradecene)	CdSe/ZnS	6–7 nm	Mixing, cross-linking	[44]
Poly(maleic anhydride <i>alt</i> -1-tetradecene)	CdSe/ZnS	9–20 nm; 11–18 nm	Additional grafting of PEG chains	[29]
Amphiphilic triblock copolymer	CdSe/ZnS	2 nm	Additional grafting of PEG chains	[43]
Alkyl-modified poly(acrylic acid)	CdSe/ZnS	8–10 nm	Mixing; solubilization; the polymer coating is further cross-linked by coupling to lysine or polyethylene glycol-lysine	[38–42]
Polymer-modified phospholipids	CdSe/ZnS	3–6 nm	Mixing, micelle formation	[36]
Gallate amphiphile with PEG as the polar head group	CdSe/ZnS	7–15 nm	Mixing, solubilization	[45]

### 3. Direct surface modification of QDs with various polymers

The introduction of polymers directly onto the nanocrystal surface is explored in the context of applications of such assemblies in biology and optoelectronics. The stability of the nanocrystals in solution is limited by the stability of the ligand at the QD surface. Polymer-coated QDs were thought to be more stable as compared to QDs coated with small organic ligands. Additionally, by using polymers, multiple and diverse chemical functionalities can be introduced at the QD surface. The success of approaches based on the direct functionalization of the QD surface lies in the ability of the QDs to retain the luminescence properties after functionalization. The polymers at the QD surface may also play an interfacing role between the QDs and the surrounding matrix. For example, electron transfer processes between the QDs and the surrounding matrix are essential in a range of optoelectronic devices such as solar cells. Functionalization of the QD surface with electroactive polymers is therefore explored with the aim of facilitating the charge transfer across the QD/polymer interface.

A number of strategies were developed to obtain polymer-coated QDs. Hydrophobic interactions between the nanocrystals' surface ligands and polymers are for instance used to create a thin polymeric coating on the QD surface. This approach does not involve ligand exchange reactions and is therefore expected not to interfere with the optical properties of the QDs. Other methods of QD-functionalization include the attachment of macromolecules directly onto the QD surface via multiple or single bonds, or polymerization of polymeric chains directly from the QD surface. All the latter methods require an intermediate ligand exchange step and usually lead to changes in the photophysical properties of the QDs.

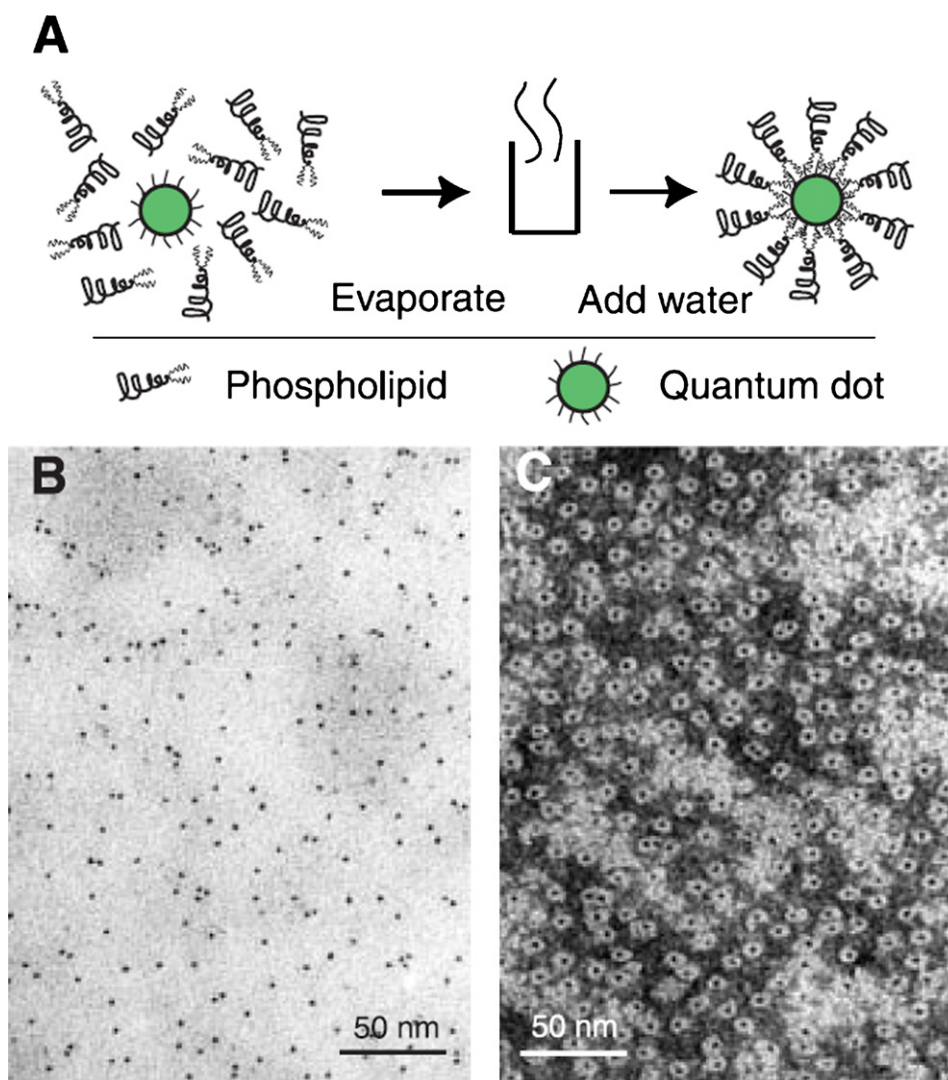
#### 3.1. Surface coating of QDs with amphiphilic polymers

The most common methods used to synthesize QDs result in materials that are insoluble in polar solvents, e.g. water. This low solubility is primarily due to the choice of surface stabilizing ligands, which often contain alkyl chains in their structure. However, many applications, especially

in biology, require the QDs to be soluble in aqueous solutions. To avoid unnecessary ligand exchange reaction steps, alternative methodologies have been explored to obtain water-soluble, functionalized QDs. One such method involves the exploitation of the interactions between the hydrophobic parts of the ligands at the QD surface (like the octyl chains of TOPO) and the hydrophobic parts of the polymers, to form a uniform polymeric coating around the QDs. Water-soluble, polymer-coated QDs can be obtained by using polymeric amphiphiles, i.e. polymers with both hydrophobic and hydrophilic parts. The hydrophobic part of the amphiphile (very often octyl side chains) is designed to interact with the hydrophobic chains of the surface ligands, and the hydrophilic part (most commonly in the form of carboxylic groups or polyethylene glycol chains) provides water solubility and chemical functionality [28,29]. However, coating QDs with polymers increases the overall size of the assemblies by as much as 5–10 nm depending on the coating (see Table 2). Nevertheless, the major advantage of the hydrophobic interaction method is that one is not required to perform ligand exchange reactions. Despite this attractive feature, relatively few reports on such strategies are described in the literature. It may be noted that such an approach has already been explored with some success using small organic molecules instead of polymers. The QDs were in that case coated with amphiphilic phospholipids [30], calixarenes [31–34], or cyclodextrines [35] to be rendered water soluble.

In the first report on the modification of QDs with polymers using hydrophobic interactions, Dubertret et al. [36] described how the QDs can be encapsulated in the hydrophobic core of a micelle composed of a mixture of 40% 1,2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine-*N*-[methoxy(polyethylene glycol)] and 60% of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (Fig. 2). A mixture of these two compounds exhibits a complex phase behavior depending on the fraction of the polymer lipids in the lipid mixture. At a concentration of 40% of the polymer lipid, a polymer-grafted micelle with a hydrophobic central core and hydrophilic polymer chains in the outer shell can be obtained [37]. Stable micelles form when both the surfactant with two alkyl chains and the PEG are combined together. The micelles provide a hydropho-





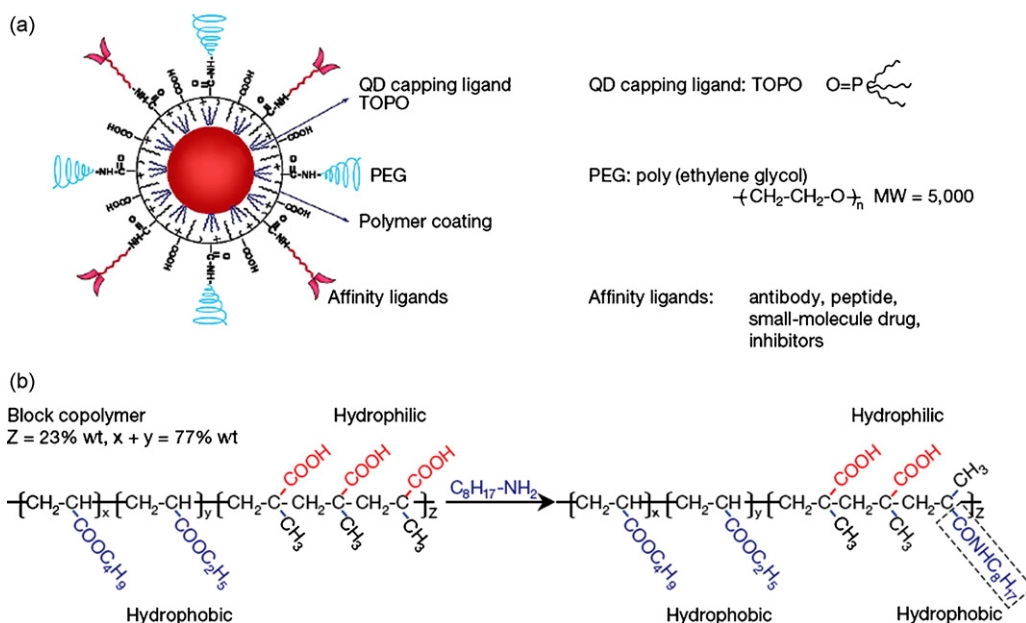
**Fig. 2.** (A) Phospholipid block-copolymers are used to prepare a polymeric coating around the TOPO-coated QD. The QD is present in the hydrophobic core of the phospholipid micelle and the PEG chains help to maintain a colloidal stability of the assembly in water. TEM images of (B) an unstained and (C) a stained material reveal the presence of an organic shell around the QD as well as the formation of QD-micelles. From [36] reprinted with permission from AAAS.

bic interface for the nanoparticles and the presence of PEG helps in maintaining a high colloidal stability.

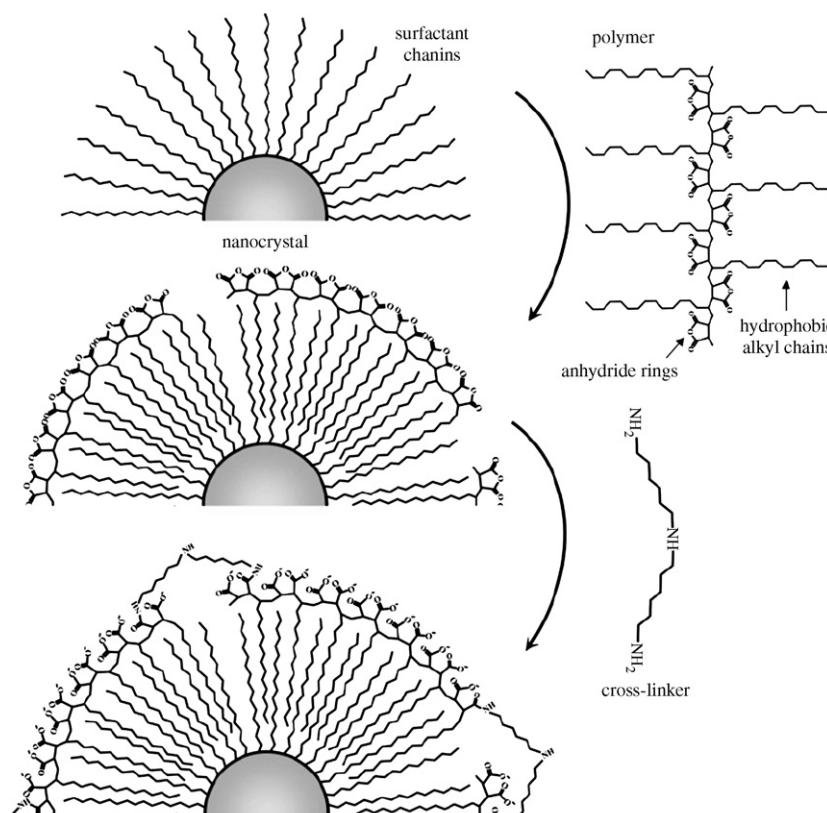
Different approaches, relying not on a polymer micelle formation but rather on a direct coating of the QDs with amphiphilic polymers, were developed. Amphiphilic, alkyl-modified (with octylamine or isopropylamine) low molecular weight polyacrylic acids were shown to coat TOPO-protected nanocrystals and solubilize the QDs in water [38–41]. To further stabilize the surface coating, it was often cross-linked with lysine or polyethylene glycol-lysine [38,39,42]. In similar efforts, Gao et al. [43] used a high molecular mass amphiphilic tri-block copolymer consisting of a poly(butylacrylate) part (hydrophobic), a poly(ethylacrylate) part (hydrophobic), and a poly(methacrylic acid) part (hydrophilic) to directly encapsulate the QDs (Fig. 3). Subsequently, PEG chains could be grafted onto the polymeric shell to improve

water solubility and introduce biocompatibility. The hydrodynamic radius of the resulting assembly was equal to 10–15 nm as determined by dynamic light scattering, and it was estimated that the shell consisted of 4–5 copolymer chains onto which 5–6 PEG chains were grafted. The remainder of the 400–500 carboxylic groups could be used for further derivatization, e.g. to attach diagnostic and therapeutic agents for medical applications. Single quantum dot emission and TEM imaging confirmed that the particles did not aggregate. The coating also prevented signal loss caused by surface ligand degradation leading to surface defects and luminescence quenching.

A more general approach than the block copolymer route is to coat the QDs with poly(maleic anhydride *alt*-1-tetradecene) [29,44]. Here, the structure of the polymer is far less complicated than for the block copolymers, and after coating of the QDs, the anhydride functionality allows



**Fig. 3.** (a) A schematic illustration of a QD coated with a triblock copolymer shown in (b). Each of the blocks of the copolymer is designed to perform a specific function, e.g. protection in vivo, ligand targeting and improvement of biocompatibility and circulation. The polymer spontaneously encapsulates the TOPO-coated nanoparticles through strong hydrophobic interactions. Subsequently, PEG chains or biologically active molecules are grafted onto the polymeric shell [43]. Reprinted by permission from Macmillan Publishers Ltd.: Nature Biotechnology, copyright (2004).



**Fig. 4.** The coating of QDs with poly(maleic anhydride *alt*-1-tetradecene) via hydrophobic interactions. An amino functionalized cross-linker is added to stabilize the shell. The opened rings of the anhydride give rise to charged carboxylic groups on the surface of the QDs, thus stabilizing them in aqueous solutions. Reprinted with permission from [44]. Copyright (2004) American Chemical Society.

for facile cross-linking of the resulting shell with, e.g. bis(6-aminoethyl)amine (Fig. 4). Although not always necessary, the cross-linking reactions are thought to increase the stability of the polymeric shell on the QDs. Hydrolyzation of the remaining anhydride groups transfers the polymer-coated QDs to the water phase. It also provides a large number of carboxylic units, which can be used for further derivatization.

Agarose gel electrophoresis experiments have showed that the resulting polymer-coated nanoparticles had narrow distributions of their diameters and of the number of surface charges. However, the overall size of the particles was increased due to the presence of the polymer shell. Amphiphilic polymers for nanoparticle solubilization based on multiple anhydride units are reactive toward primary amines without the addition of coupling agents and may therefore be used for further derivatization of the QDs with, e.g. poly(ethylene glycol) (PEG). Functionalization of nanoparticles with PEG not only improves the stability of the QDs in solution, but is also of relevance in bioapplications since it minimizes the nonspecific interactions of a QD/polymer assembly with, e.g. cell membranes. Finally, a lyotropic, gallate amphiphile with poly(ethylene glycol) chains has also been utilized [45] (Fig. 5). An aromatic core was grafted with three dodecyl chains in order to induce strong hydrophobic interactions, and PEG was used as the polar head group. At high dilutions, isolated micelles (with diameters around 25 nm) were formed and the PEG chains were shown to prevent nonspecific adsorption of the QDs onto cellular membranes.

Although there are relatively few examples in literature of QDs coated with amphiphilic polymers, the methods based on hydrophobic interactions between the QD ligands and polymer functionalities have already enabled many problems related to ligand exchange reactions to be avoided. Such methods have also offered a robust platform for functionalization of the QDs with, e.g. biomacromolecules. The synthetic polymers mentioned in this section are commercially available, and the procedures related to the QD coating with the polymers are relatively easy to perform.

### 3.2. Coating QDs with multidentate polymeric ligands

Semiconductor nanocrystals coated with small organic phosphines (like TOPO), amines or thiols can be readily obtained, however the stability of such a system in complex environments is limited. This is due to the fact that the ligands covering the QD surface remain in equilibrium with free species in the surrounding medium. Desorption of the ligand from the QD surface results in simple functionality losses and could lead to nanocrystal aggregation. A reduced stability significantly limits the application range of the QDs, and a solution to this problem would be to coat the nanocrystals with molecules that provide numerous anchoring points on the QD surface. Such multidentate ligand molecules [46,47] bind to the nanocrystals cooperatively, and desorption of the whole molecule from the nanocrystals surface is substantially slower. In this multivalent passivation approach, the main challenge lies in the control of the photophysical properties of the QDs (in

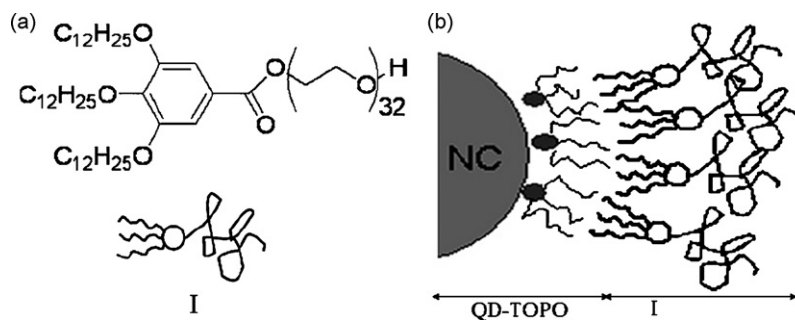
most cases the ability to retain the luminescence quantum yields) and to simultaneously provide the necessary colloidal stability with chemical functionality. Synthetic linear or hyperbranched polymers, as well as biomacromolecules [48], or bioengineered macromolecules [49] inherent of high densities of functional groups have been explored as multidentate coatings. Surface passivation is usually performed by single- or multistep ligand exchange reactions, however direct mixing of the nanocrystallites with functionalized polymers can also be carried out. Suitable functionalities, which can be introduced into the polymer main chain or side groups, include thiols, sulfides [50], amines [51], and carboxylic acid groups [52,53]. Carbodithioate groups, for instance, have been shown to form strong chelate-type bonds with cadmium or lead [54,55], and were also found to exchange the TOPO ligands at the QD surface already under mild conditions. The introduction of such functional groups to the polymer side chains has allowed for the coating of the QDs with poly(thiophenes) [55], an important polymer in optoelectronic applications.

Amine-containing polymeric compounds are also effective multidentate ligands. Polymers containing tertiary amines, e.g. poly(dimethylaminoethyl methacrylate) (PDMAEM), replace the TOPO units from the CdSe/ZnS and CdSe surfaces [56,57]. The resulting polymer-passivated QDs are stable in hydrophobic solvents such as toluene, but also in more polar, protic, solvents such as ethanol. The radius of the nanocrystals upon surface passivation changed from 3 nm to 6 nm, and no aggregation was observed. Moreover, the modified nanocrystals retained 70% of their original luminescence. A quantitative analysis of the polymer coating could be obtained by labeling the PDMAEM multidentate ligand with the fluorescent tracer pyrene and using size exclusion chromatography (Fig. 6) [57]. On average, an estimated 12 polymer chains were bound to each 4 nm CdSe and around 5 chains to each 3.4 nm QD. Moreover, the thickness of the polymer corona was directly proportional to the length of the polymer chains [58]. This is important when the aim was to control the size of the polymer-coated QDs as well as the number of functional units on the QD surface. Since not all amine groups took part in the surface passivation, certain of the remaining amino groups could be used for further functionalization, e.g. to render the QDs water soluble.

Higher densities of functional units able to bind to the QD surface are provided by hyperbranched structures. Amine-containing dendrimers, for instance, can act as effective multidentate ligands. Second generation poly(amido amine) (G2-PAMAM) dendrimer ligands carrying a number of hydrophobic aliphatic chains attached to the dendrimer periphery have been used by Zhang et al. [59] to passivate CdSe nanocrystals. The presence of the aliphatic chains attached to G2-PAMAM dendrimers rendered the dendrimers amphiphilic. The internal amine groups of the dendrimer reacted with the QD surface and the aliphatic chains protruded into the solvent preventing aggregation of the nanocrystals after surface passivation. In contrast, using only amine-terminated PAMAMs often caused aggregation of the nanoparticles.

The amphiphilic nature of some dendritic structures, such as hyperbranched poly(ethyleneimine) (PEI), has been





**Fig. 5.** (a) The chemical structure and a schematic representation of a gallate amphiphile with poly(ethylene glycol) chains (I). (b) A scheme of the TOPO-coated nanocrystals functionalized with I. The dodecyl chains interact with the alkyl group of the TOPO ligand, and by using PEG chains as the polar head groups, they increase the solubility of the QDs in aqueous solutions. Reprinted with permission from [45]. Copyright (2006) American Chemical Society.

exploited for phase transfer of the QDs into aqueous buffers (Fig. 7) [60]. The average diameter values of PEI-modified QDs were between 10.7 nm and 17.5 nm for PEI with molar masses of 800 g/mol and  $25 \times 10^3$  g/mol, respectively. However, an adverse effect of the PEI surface coating consisted in PEI enhancing the photooxidation of the QDs in both chloroform and water.

Finally, an example lying in between a multidentate ligand and an end-attached polymer chain is that of a PEG end-functionalized with a bidentate thiol motif [61]. Such a group is able to bind strongly to the surface of CdSe/ZnS core shell nanocrystals, and the PEG chains can generate a hydrophilic polymer shell. In this particular approach, an aqueous solubility over a broad range of pH values has also been achieved. A threshold value for the minimum PEG chain length was found to be 400 g/mol.

Due to the presence of multiple anchoring points on the QD surface, multidentate polymeric ligands generally provide higher stability to the QD/polymer assembly. Another attractive feature of this methodology is that it enables a larger number of functionalities to be introduced to the assembly, as compared to a procedure with simple organic

ligands. The necessary exchange of the TOPO ligand from the surface of the QDs represents a major drawback of using multidentate ligands and more efforts should be concentrated on the preservation of the high brightness of the QDs.

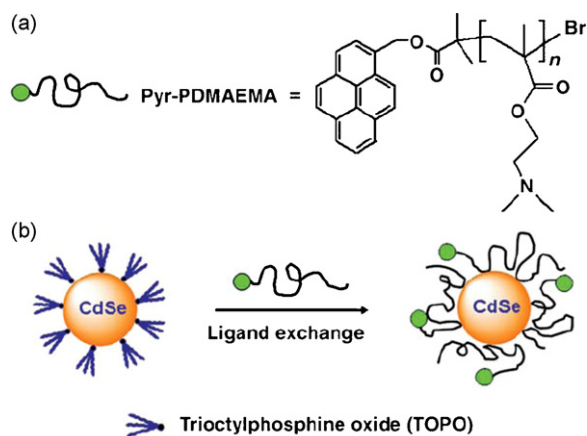
### 3.3. Attachment of end-functionalized polymers to the QD surface

There are two general approaches when attaching a polymer chain to a surface via a single-point attachment: the “grafting to” and the “grafting from” methods. In the “grafting to” method, an appropriately functionalized polymer chain-end reacts directly with the nanoparticle surface. The “grafting from” technique [62–64] is a method where the polymer growth is initiated from a surface functionalized with appropriate polymerization initiators. The initiator-functionalized ligands must be able to survive the polymerization conditions, and the chain length and polydispersity control of the resulting polymers are major issues. Monodisperse, presynthesized, polymers can be used for the “grafting to” method. However, the control of the number of attached molecules to the QD surface is limited.

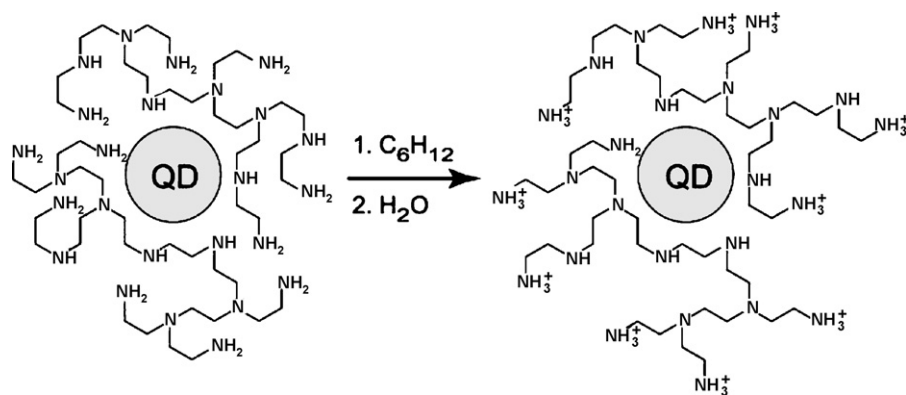
#### 3.3.1. Polymer “grafting to” methods for the functionalization of QDs

The “grafting to” approach involves attaching end-functionalized linear polymers, or hyperbranched polymer architectures with functionalities introduced in the focal points, to the nanocrystal surface. Various end-functionalities, such as pyridine [65], thiols [66] or phosphonic acids [67], have been used. For small organic ligands, these functionalities have already demonstrated that they can bind effectively to the surface of the nanocrystals. By grafting water-soluble polymers to the QD surface, e.g. pyridine-terminated PEG [65], the QD can be rendered soluble in polar solvents [65]. The “grafting to” approach is also a convenient route for introducing macromolecules onto the QD surface, which would be directed outwards toward the environment and would thus be able to interact with the molecules in the solution.

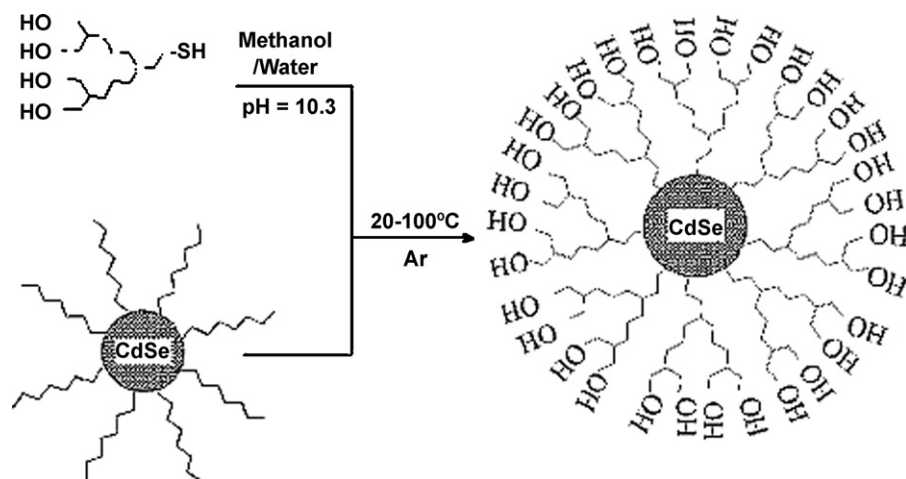
Hyperbranched polymeric architectures may be explored for systems where it is necessary to provide a greater stability or where a larger amount of functional



**Fig. 6.** (a) The structure of pyrene-modified PDMAEM. The tertiary amine in the side chain binds to the nanocrystal surface, and the pyrene functionality allows one to investigate the composition of the polymer-coated QDs in more detail. (b) The exchange of the ligand at the nanocrystal surface with the PDMAEM polymers results in a polymeric shell approximately 3 nm to 6 nm thick [57]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.



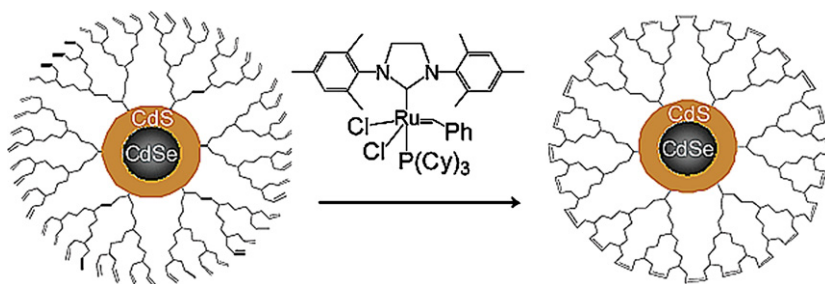
**Fig. 7.** The phase transfer of QDs from nonpolar to polar solvents using amphiphilic hyperbranched poly(ethyleneimine). Nonprotonated primary and secondary amines interact with the QD surface while partially protonated primary amines render the PEI-coated QDs water soluble. From [60], reproduced by permission of The Royal Society of Chemistry.



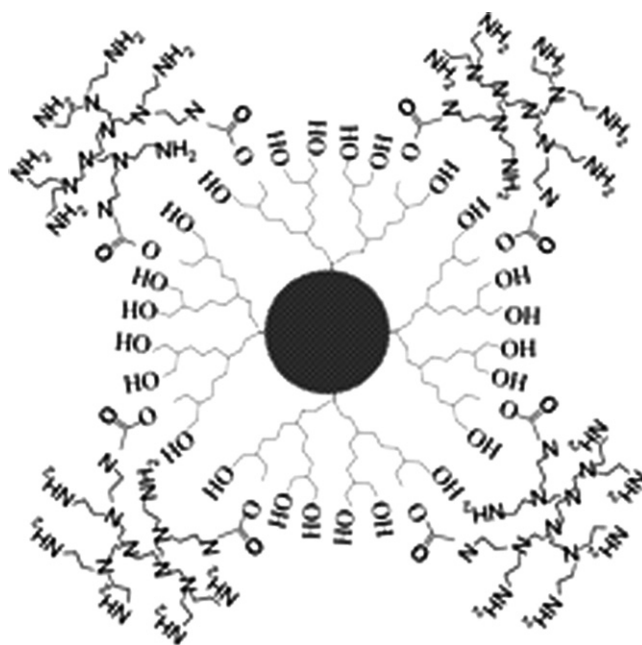
**Fig. 8.** Organic dendrons functionalized with thiols at the focal point, attached to the QD surface via ligand exchange reactions. Hydroxyl-terminated dendrons render the QD water soluble and offer protection against oxidation. Reprinted with permission from [69]. Copyright (2002) American Chemical Society.

units at the QD periphery is required. Using organic dendrons functionalized with thiols at the focal point [68] leads to thin (1–2 nm), closely packed, and dense organic shells around the QDs (Fig. 8) [69]. Such dendron-encapsulated QDs have been found to be more stable against oxidation as compared to thiol-based ligands. The surface-attached dendrons were also stable against

standard purification and bio-separation techniques. The stability of the nanocrystals increased as a function of the dendron generation used. Compared with dendrimers, the cone-shaped structural feature and the single binding site provided a better packing in the ligand shell and a well-defined orientation, with most of the functional end-units pointing outward.



**Fig. 9.** Dendrons attached to the QD surface at the focal point and with vinyl functionalities at the dendrimer periphery are cross-linked via ring-closing metathesis reactions thus forming "box-nanocrystals". The cross-linked ligands improve the thermal and chemical stabilities of the QDs. Reprinted with permission from [70]. Copyright (2003) American Chemical Society.



**Fig. 10.** Cross-linking of OH terminated dendrons with amine-terminated dendrimers renders the polymer–QD assembly water-soluble and enhances the stability of the QDs. Reprinted with permission from [71]. Copyright (2003) American Chemical Society.

Cross-linking of the ligands can be performed to further improve the stability of the dendron shell, for example through ring-closing metathesis (RCM) of vinyl end-functionalized dendrons (Fig. 9) [70]. Such globally cross-linked “box-nanocrystals” have demonstrated improved thermal, chemical and photochemical stability when compared to dendron-coated QDs. However, such materials were not soluble in water and required the use of a catalyst for the reaction. Cross-linking of OH-terminated dendrons with second generation amine-terminated dendrimer bridges circumvented this problem (Fig. 10) [71]. Here, the dendrimer cross-linker simultaneously took part in the formation of the “box-nanocrystals” and functionalized the QD shell. The stability of the “box-QDs” prepared as such was superior to that of QDs with simple thiol-based ligands and comparable or better than that of the “box-nanocrystals” prepared by RCM.

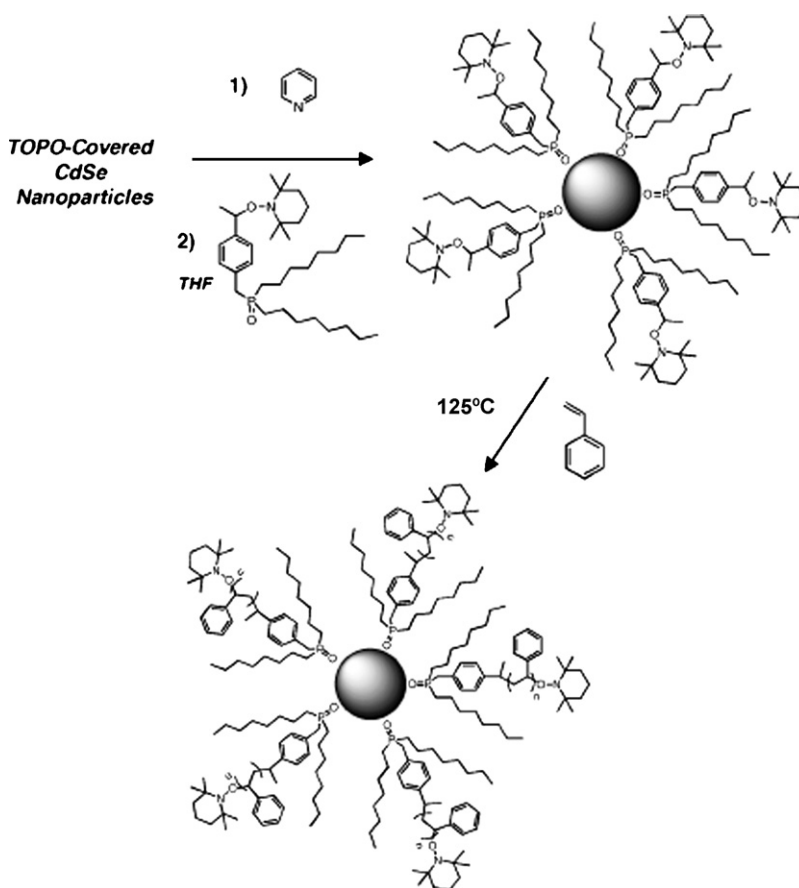
### 3.3.2. Polymer “grafting from” methods for the functionalization of QDs

Many polymerization methods are incompatible with the nanocrystals. Anionic conditions are too harsh, and the radicals generated by conventional radical polymerization may damage the nanocrystals. In order to polymerize directly from the QD surfaces, alternative routes of polymerization have been explored such as controlled radical polymerization schemes and polymerization based on ring-opening reactions.

Atom transfer radical polymerization (ATRP) [72] of methyl methacrylate from the surface of QD/silica core-shell nanoparticles was explored in the context of obtaining polymer-functionalized QDs [73]. The polymerization was however initiated from an initiator attached to silica shell-precoated QDs [74] rather than directly

to the QDs. It would be more desirable to apply a method allowing the polymerization to occur directly from the QD surfaces. Such an approach is of particular importance in applications involving charge or energy transfer to, or from, the nanocrystals. A nitroxide-containing ligand was used to polymerize polystyrene and poly(styrene-co-methacrylate) copolymers directly from the CdSe surface via controlled nitroxide-mediated free-radical polymerization (Fig. 11) [75]. Nitroxide functionalized phosphine ligands were attached to the QD surface through ligand exchange via an intermediate step involving pyridine molecules. The luminescence of the resulting polymer–QD composite increased as compared to initiator-functionalized nanocrystals.

Beside simple vinyl monomers, also cyclic olefins were directly polymerized from the CdSe nanocrystal surface. To polymerize cyclic olefins, a ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) was employed [76]. The QDs were first coated with functional phosphine oxide ligands. The initial optical properties of the QDs could be preserved as a result of the ligand providing the required functionality for initiation of ROMP as well as mimicking a TOPO-like coverage of the QDs. The ROMP method was shown to be quite general, and polymerization of cyclooctene, dicyclopentadiene and oxanorbornene derivatives from the QD surface has been carried out to obtain various types of functional materials. For instance, polymerization of dicyclopentadiene gave rise to a cross-linked network as a result of the bifunctional character of the monomer. Polymerization of oxanorbornene derivatives provided anhydride- or imide-functionalized materials and there thus exists an opportunity to obtain QDs coated with functional polymers that are otherwise difficult to attach directly to the QD surface.



**Fig. 11.** The polymerization of styrene from nitroxide-functionalized CdSe nanoparticles. Initial TOPO ligands are exchanged to nitroxide-functionalized phosphine ligands via an intermediate pyridine step. The nitroxide-functionalized ligands are then used for polymerization of styrene by a way of a nitroxide-mediated polymerization reaction. Reprinted with permission from [75]. Copyright (2004) American Chemical Society.

Although grafting block copolymers onto the QD surface may open up routes to new types of materials, obtaining such systems by using the methods described above might be problematic. Besides the ruthenium-catalyzed polymerization strategy one can also utilize coordination-insertion ring-opening polymerization. This method enabled the polymerization of  $\epsilon$ -caprolactone initiated from hydroxyl-functionalized CdS nanocrystals [77,78]. The polymerization occurred selectively from the surface after activation of the surface OH groups with  $\text{AlEt}_3$ . The “living” character of the polymerization has been exploited for the synthesis of a block copolymer poly( $\epsilon$ -caprolactone-*b*- $\delta$ -valerolactone) on the QD surface.

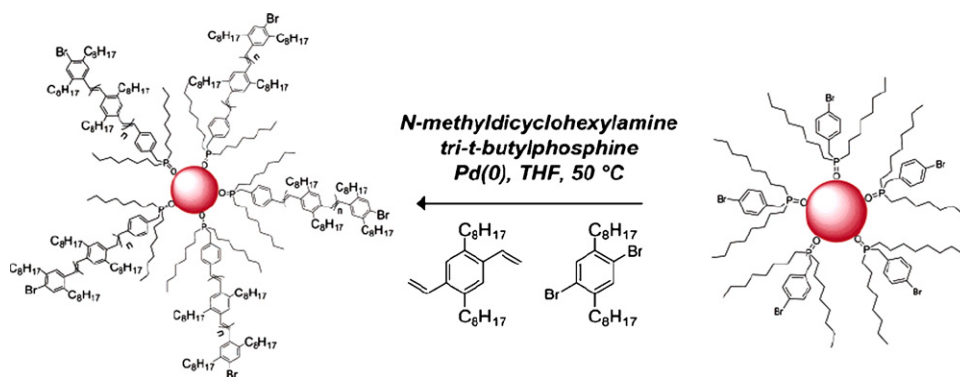
The transition metal catalyst may cause some problems if one wishes to preserve the optical properties of the QDs or to obtain “clean”, metal-free systems for bioapplications. One can then opt for the reversible addition fragmentation chain transfer (RAFT) polymerization since there is no need for transition metal catalysts in this method [79]. Phosphine-containing trithiocarbonate-based RAFT initiators have been attached to QD surface and the polymerization of linear polymers, random and block copolymers of styrene and acrylates has been performed. Polymers with molar masses ranging from 9 kg/mol to

50 kg/mol, and low polydispersity indices ranging from 1.17 to 1.32 were polymerized. Most importantly the nanoparticles retained their luminescence properties after the polymerization and could be well dispersed in polymeric media.

The synthesis of QDs by using functional ligands that are stable at high temperatures eliminates the ligand exchange step. Phenyl bromide-functionalized phosphine oxide was used as the ligand for the synthesis of CdSe QDs [80]. The polymerization of poly(para-phenylene-vinylene) (PPV) was then performed directly from the QD surface by copolymerization of 1,4-divinylbenzene with 1,4-dibromobenzene derivatives by palladium-catalyzed Heck-type coupling reactions (Fig. 12).

“Grafting from” methods used to functionalize QDs with macromolecules have so far been applied only to several polymers. However, this particular method offers specific advantages over the “grafting to” approach. The number of growing polymer chains is directly related to the number of initiators coated on the QD surface. Thus, by controlling the surface concentration of the initiator one would also be able to control the amount of attached macromolecules. Moreover, this method is unique in that it allows the functionalization of the QDs with more complex macromolecules, such as block copolymers. The rich physics of





**Fig. 12.** The synthesis of poly(paraphenylene vinylene) (PPV)-modified QDs by polymerization directly from the nanocrystal surface. By using phosphine-based functional ligands, exchange reactions are avoided. PPV is polymerized by Heck-type coupling reactions. Reprinted with permission from [80]. Copyright (2004) American Chemical Society.

block copolymer systems would certainly lead to many new applications for such advanced materials.

### 3.4. Dendrimer-encapsulated quantum dots

Hyperbranched macromolecules are a particularly interesting class of polymers that has been used for the controlled synthesis of nanocrystals [81]. By taking advantage of the well-defined structure and monodispersity of the dendrimeric materials, one can perform synthesis of relatively monodisperse nanocrystals. Depending on the type and size of the dendrimers, intradendrimer synthesis (where the QDs are synthesized at the dendrimer periphery) [82] or interdendrimer synthesis (where the QDs are synthesized in the dendrimer interior) [83] can be carried out. The dendrimers act as nanoscale reactors by first sequestering for instance the  $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$  ions, and after reaction with  $\text{S}^{2-}$ , stabilizing the growing CdS or PbS clusters [84–86]. The high concentration of chelating amine groups in poly(amido amine) (PAMAM) dendrimers allows for the effective capture of the growing nanocrystals. However, most often, the final materials are large aggregated structures consisting of QDs surrounded by many dendrimers. Photon correlation spectroscopy has revealed that the formation of the semiconductor clusters is very fast, but the dendrimer-stabilized QDs aggregate slowly on longer time scale [87]. The optical properties of the resulting dendrimer-CdS composites were found to depend on the dendrimer type, dendrimer functionality, solvent used, concentration of the reagents, and the pH of the reaction solution. The overall QY of the so-synthesized QDs is usually quite low (0.1–0.2) [85]. By utilizing amphiphilic dendrimers, one can take advantage of the different aggregation states of the amphiphile in various solvents to control the nanocrystal growth as reported by Donners et al. [82].

The synthesis of CdS nanoparticles *within* the dendrimers in order to obtain discrete, luminescent dendrimer-encapsulated quantum dot assemblies was reported by Lemon and Crooks [83]. The CdS nanoparticles were grown inside hydroxyl-terminated PAMAM, and the control of the particle size was achieved by varying the degree of branching of the dendrimer. The diameter

values of the QD/dendrimer hybrids were in the range of 1–3 nm. The CdS nanoparticles within the dendrimers could be coated with ZnS shells, and the QY of the resulting core/shell nanoparticles was 20% higher than that of the initial CdS/dendrimer nanocomposites. Furthermore, the dendrimer periphery could be functionalized with PEG to increase the solubility of the QD/dendrimer materials in various solvents [88]. The dendrimer/QD nanocomposites have also been patterned on a variety of functionalized substrates using a microcontact printing technique [89,90] or have been embedded in other matrices, such as sol–gel glasses [91] to form stable monolithic optical materials. In summary, the *in situ* synthesis of QDs in dendrimers deserves to be studied in more detail. For instance, single QDs synthesized in individual dendrimers may be explored as building blocks of well-defined nanostructured materials.

## 4. Embedding quantum dots in polymer colloids

The efforts to incorporate QDs in polymeric nano- and microspheres are mainly motivated by the promising applications of such materials in bioanalytics and photonics. These applications can take advantage of the luminescence properties of the QDs but can also be based on other photo-physical processes such as energy transfer. In the latter case, the density of the QDs inside the spheres, and hence the distance between the luminophores, is crucial. The spatial separation between the QDs becomes even more important in applications where the energy transfer, and a consequent quenching of the overall luminescence, is undesirable [92].

Due to the size of the nanocrystals, their variable surface chemistry, as well as the related colloidal stability, the major task has been to design reliable synthetic approaches in order to obtain highly loaded QD/polymer assemblies. Although certain progress has been achieved, there are no standard off-the-shelf methods to embed QDs in polymer colloids. In fact, a rather broad range of methodologies has been investigated, and among these methods, those based on polymerization in the presence of QDs are the most promising. However not all polymer–QD assemblies can be prepared by such approaches. Hence, alternative methods for incorporating QDs inside polymer microspheres have

been investigated. For example, in the case where stimulus-responsive polymers, such as hydrogels, are employed, one can take advantage of the volume-changing phase transitions in order to physically entrap the QDs inside the polymer matrices. However, physical entrapment methods usually do not prevent the QDs from leaking out of the polymer colloids. This is a problem in for instance bioimaging applications. In view of the possible cytotoxic effects of the QDs, leaking of QDs should in general be prevented. To overcome this problem covalent linkage of the QDs to the polymer chains by using polymerizable surface ligands or reacting the QDs with functionalized polymers after swelling has been explored.

#### 4.1. Polymerization of polymer colloids in the presence of QDs

Polymerization methods leading to polymer colloids are well known and well developed for numerous polymer systems. In many instances, monodisperse polymer micro- or nanospheres can be obtained, and the diameter of the polymer colloids can be tuned from the micrometer to the sub-100 nanometer lengthscale. Many polymeric systems have already been studied in detail and different types of core-shell structures have even been obtained. Many efforts have therefore been focused on incorporating QDs into well-defined polymeric particles via monomer polymerization in a dispersed media.

##### 4.1.1. Emulsion and dispersion polymerization of monomers in the presence of QDs

Emulsion and dispersion polymerizations have been found to be very promising methods for encapsulating hydrophobic QDs in polymer colloids. An extension of these methods, such as miniemulsion polymerization, results in polymer particles with a narrow size distribution and with well-dispersed QDs in the polymer spheres. This particular method involves the formation of oil droplets, containing the monomer and the nanoparticles, which are dispersed in an aqueous phase. There is no need for ligand exchange reaction since the hydrophobic (most often TOPO-coated) QDs are soluble directly in the monomer (e.g. in styrene or butyl acrylate) droplets. The use of water-soluble initiators limits the contact between the radicals and the QDs at the beginning of the polymerization and consequently also limits the QD degradation. The main issues related to these polymerization methods include the effective dispersion of the QDs inside the polymer particles, and the prevention of nanocrystal phase separation and aggregation during the polymerization reaction. Despite the attractive features of polymerization in the presence of QDs, only certain polymers have so far been explored in detail; especially the polymerization of styrene [93] and acrylates [94] have received much attention. An extensive study of styrene miniemulsion polymerization in the presence of TOPO-coated CdSe/ZnS QDs was presented by Joumaa et al. [95]. The obtained polymer-QD spheres were characterized with respect to conversion, solid content, particle size, particle size distribution, the number of embedded QDs, and the resulting optical properties of the fluorescent spheres. The amount of added QDs had no visible effect on the reaction

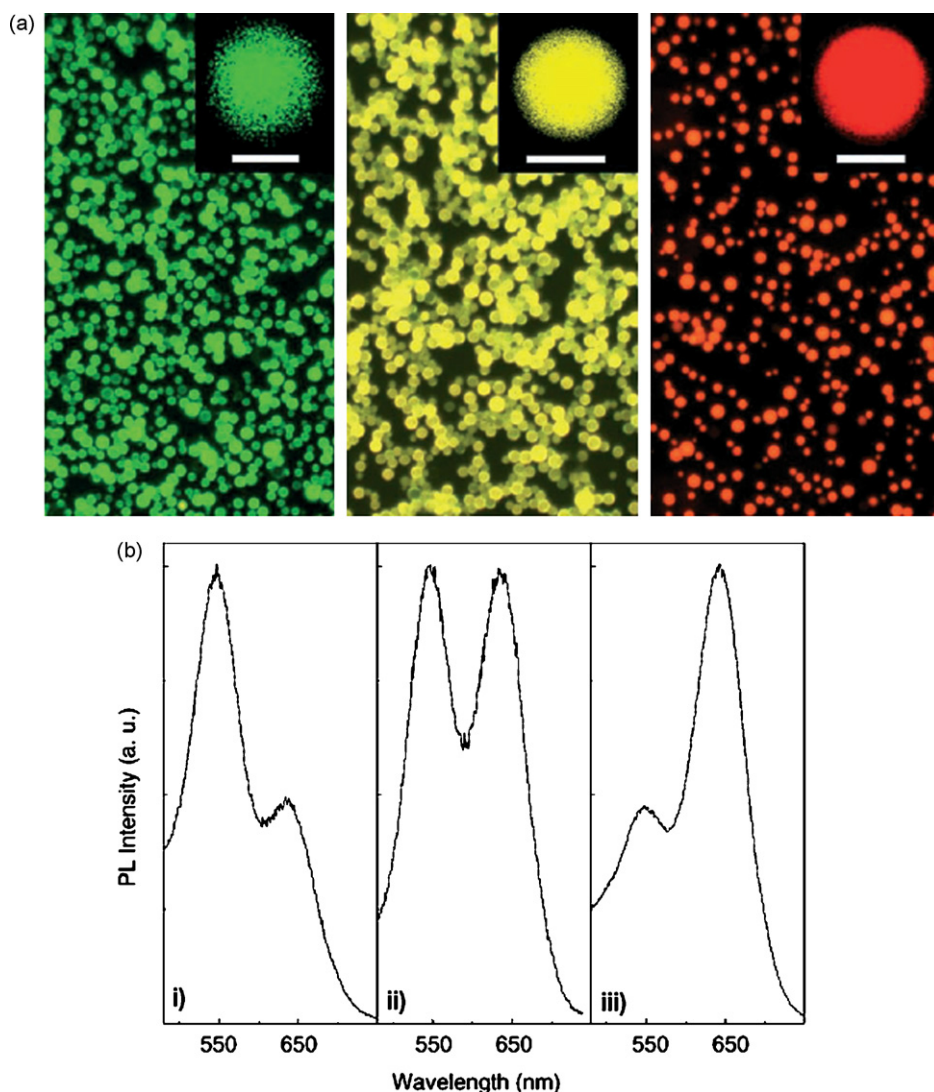
kinetics or on the final particle size (which could be tuned between 100 nm and 300 nm). The number of incorporated nanoparticles was directly proportional to the initial concentration of the QDs in the polymerization solution. However, as evidenced by TEM imaging of ultrathin slices of the polymer particles, the nanoparticles were found to be located in the outer parts of the polymer spheres instead of being homogeneously dispersed in the polymer. Similar surface segregation effects were found by Bradley et al. [96] for suspension-polymerized polystyrene particles in the presence of TOPO-coated CdSe and CdSe/ZnS QDs.

The copolymerization of styrene with other monomers can be used to endow the polymer particles with a particular functionality. Yang et al. [97] have reported on the encapsulation of TOPO-coated CdSe nanoparticles within cross-linked poly(styrene-co-methacrylic acid) microspheres via emulsion polymerization. The size of the spheres could be controlled by tuning the polymerization conditions, e.g. the oil/water ratio, or the amount of surfactant. QD/polymer spheres with diameter values ranging from 300 nm to 20  $\mu\text{m}$  could be obtained with this method. The negatively charged, carboxyl-coated spheres were subsequently coated with a silica shell to form a core-shell structure for further functionalization. Core-shell polymer microparticles obtained by miniemulsion polymerization with QDs embedded in the core were also reported [98]. The polystyrene (PS) core was prepared by polymerization in the presence of CdSe coated with hydrophobic ligands. Subsequently, a poly(methyl methacrylate) (PMMA) shell with a desired thickness was obtained around the PS core by shot growth emulsion polymerization.

To improve the stability of the QDs in the polymer spheres, the nanocrystals can be directly coupled to the polymer matrix [99]. The coupling can be realized by using functionalized polymers able to bind to the nanoparticle surface or by employing functionalized surfactants. Thiol-modified polystyrene microparticles have been used to immobilize CdS or CdS/ZnS nanoparticles [100,101], and hybrid particles with diameter values ranging from 0.5  $\mu\text{m}$  to 1.5  $\mu\text{m}$  [101] and 10  $\mu\text{m}$  to 50  $\mu\text{m}$  [100] have been prepared. The resulting CdS-PS hybrid spheres were, however, not stable against photoirradiation, and fusion of the nanoparticles was found to occur inside the polymer spheres. Such fusion of the nanoparticles leads to a broadening of the size distribution, as well as to the deterioration of the photophysical properties. Coating the QDs with a ZnS shell or encapsulating the CdS-PS particles with an in situ prepared polyurethane shell has been found to suppress the undesirable CdS growth [101].

##### 4.1.2. Coupling QDs to polymer microspheres via polymerizable surface ligands

Nanoparticles coated with ligands able to take part in the polymerization process allow for coupling of the QDs directly to the polymer chains. Such nanoparticles have been successfully used to prepare bulk QD/polymer nanocomposite materials (see Section 6.2). The vinyl functionality on the QD surface ligands takes part in the polymerization or cross-linking processes, effectively pinning the QDs to the growing polymer chains. The use of

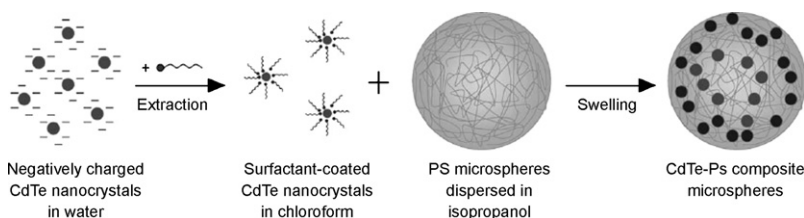


**Fig. 13.** (a) Fluorescence images of PS beads tagged with green, yellow, and red QDs. The insets display the corresponding confocal fluorescence images of the individual 2  $\mu\text{m}$  beads. (b) Fluorescence spectra of PS beads tagged with two different QDs at various QD ratios: (i) 2:1, (ii) 1:1, and (iii) 1:2 [106]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

a polymerizable surfactant also prevents aggregation and phase separation of the QDs inside the beads [95].

However, in most cases ligand exchange reactions have to be performed to introduce polymerizable ligands onto the surface of the QDs. The new ligands must be able to bind to the nanocrystal surface without deteriorating the optical properties of the QDs, and should also have functionalities so as to be able to participate in the polymerization process. The polymerizable ligands reported in the literature usually had one of the common functionalities known to be able to bind well to the QD surface, i.e. phosphine, carboxylic acid or thiol [95,102]. For instance, O'Brien et al. [103] prepared a phosphine-based polymerizable ligand to covalently immobilize the QDs in polystyrene beads during suspension polymerization. The same group also reported on the polymerization of polystyrene micropar-

ticles in the presence of oleic acid coated CdS [104]. The luminescence of the resulting QD/polymer microsphere was found to be stable, and confocal microscopy experiments showed that the QDs were uniformly incorporated into the PS particles. Methyl methacrylate functionalized oligomeric phosphine ligands [46] were used by Sheng et al. [105] to incorporate CdSe/ZnCdS/ZnS core-shell quantum dots into PS microparticles. Such oligomeric phosphine ligands bind more strongly to the nanocrystal surface and prevent the loss of ligands during polymerization. Moreover, the methyl methacrylate groups can be cross-linked to form stable polymer shells around the QDs, thus protecting the QDs from the radicals formed during the polymerization reaction. However, self-polymerization of the QDs through the functional ligand also took place. Additionally, the presence of the QDs and the phosphine ligands per-



**Fig. 14.** In order to incorporate water-soluble QDs inside a hydrophobic PS matrix the negatively charged CdTe QDs are coated with positively charged surfactants and transferred into chloroform. The QDs are then incorporated into the polystyrene microspheres upon swelling of the spheres in chloroform. Reprinted from [109], Copyright (2006), with permission from Elsevier.

turbed the nucleation and growth processes of the polymer beads and resulted in a broadening of the size distribution of the beads.

The least successful class of ligands essayed thus far was based on thiol and vinyl functionalities. Fluorescence loss was observed when the original surface ligands were exchanged to 4-mercaptopvinylbenzene for copolymerization of styrene via miniemulsion polymerization [95]. Furthermore, TEM imaging of ultrathin sections of the particles revealed that the vinyl-terminated QDs were mainly located at the bead edges. Despite the presence of the vinyl function, the polymerization led to phase separation of the QDs inside the polymer spheres indicating that almost no copolymerization occurred. When ligand exchange reactions result in undesired properties, the best solution is to avoid the ligand exchange and modify the existing ligand. If the polymerizable ligands contain charges, they can act as phase transfer agents of water soluble QDs [106]. By using such a scheme, negatively charged CdTe QDs were coated with octadecyl-p-vinyl-benzyltrimethylammonium chloride (OVDAC) surfactant. During subsequent polymerization of styrene, the OVDAC surfactant took part in the polymerization process and the QDs could be efficiently incorporated into PS particles. QDs of various sizes could also be incorporated simultaneously into the same PS beads using this method (Fig. 13).

#### 4.2. Incorporation of QDs into preformed polymer colloids

Although the methods based on polymerization in the presence of QDs result in high-quality QD/polymer spheres, the main drawback of these methods is that ligand exchange reactions have to be performed first. When water-soluble QDs are used, phase transfer via polymerizable surfactants is necessary. In addition, the exact number and the exact location of the QDs in the spheres cannot be fully controlled. Radical formation during the polymerization can also heavily quench the fluorescence of the QDs. It is therefore important to develop other methods where at least some of these issues can be resolved.

##### 4.2.1. Incorporation of QDs by swelling

Incorporation of the QDs into polymer microspheres by swelling is the simplest and least elaborate method for preparing QD/polymer microspheres. The embedding process involves swelling the polymer particles in suitable solvent/nonsolvent mixtures containing QDs [107]. The swelling polymer draws the QDs into the particle inte-

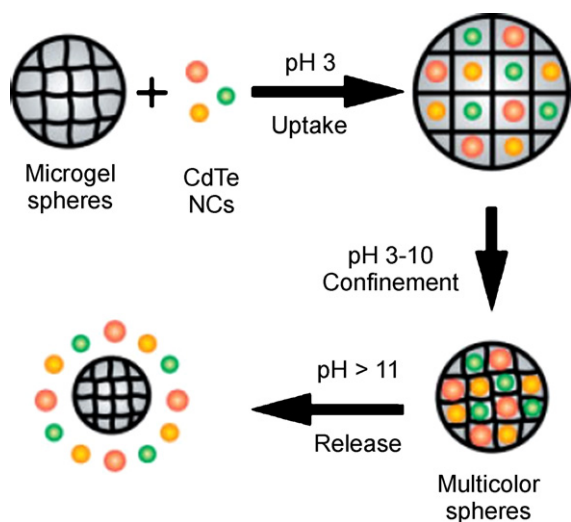
rior and the subsequent washing of the residue with a nonsolvent causes the polymer to shrink thus trapping the QDs inside the microspheres. The main drawback of this method, known also from studies involving organic chromophores, is that the QDs are mainly located in the outer 25% of the bead volume [107].

The swelling method results in polymer microspheres with as many as  $10^3$ – $10^5$  embedded nanoparticles [92,107]. It is remarkable that, even for such a large number of nanocrystals being embedded in the spheres, no energy transfer between the QDs could be observed. In fact, the emission spectra of the nanocrystals became narrower as compared to those in solution. This was attributed to the effect of the polymer network, which spatially separated the QDs. Only QDs within a certain size range were incorporated, thus narrowing the QD size distribution. Since the QD emission is related to the nanocrystals' size, this resulted in narrower emission spectra. Lack of energy transfer between the QDs also indicated that the nanoparticles did not aggregate inside the polymer.

To increase the luminescence intensity of the hybrids Gao and Nie have employed mesoporous polystyrene beads [108]. The bead infiltration proceeded by diffusion, and multivalent hydrophobic interactions between the QDs and the beads played a major role. The resulting mesoporous luminescent beads were three orders of magnitude brighter than their nonporous counterparts, and the porous beads could incorporate as many as  $10^6$  QDs. However, more detailed confocal microscope investigations [96] of the nonporous microparticles impregnated via the swelling methods revealed that the QDs' penetration was highly dependent on the swelling conditions and on the degree of cross-linking. For low degrees of swelling or high cross-linking densities, the QDs only penetrated into the peripheries of the beads, thus limiting the final brightness of the microparticles. Bradley et al. have shown that the same increase in luminescence could be achieved for nonporous beads by properly tuning the extent of the nanoparticle swelling in solution [96].

To incorporate water-soluble nanoparticles into hydrophobic matrices, the surface of the QDs has to be modified. For example, aqueous CdTe nanocrystals were incorporated into PS microspheres by modifying the surface of the negatively charged QDs with positively charged surfactants, such as octadecyl-p-vinyl-benzyltrimethylammonium chloride (Fig. 14) [109]. Up to  $5 \times 10^3$  QDs per a 625 nm diameter sphere were incorporated and multicolor-coded microspheres with no energy transfer between the QDs were reported. The





**Fig. 15.** The pH-dependent phase transition of stimulus-responsive PNIPAM-co-PVP is used to incorporate and release CdTe nanocrystals into and from the hydrogel spheres. At pH 3, the polymer microparticles swell and the QDs infiltrate the microspheres' interiors. Upon increasing the pH, the spheres shrink and the QDs are physically trapped within the spheres. By increasing the pH above 11 the QDs may be released again into the solution [110]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

QDs embedded in the spheres were strongly bound to the polymer matrix, and no leaking of the QDs was observed in either polar or nonpolar solvents.

#### 4.2.2. Entrapment of QDs via volumetric phase transitions of polymer gels

Stimulus-responsive polymers are a class of macromolecules that can undergo changes in their conformation upon external stimulus. Most notable are polymers that respond to changes in temperature or pH. Such polymer systems have found numerous applications, mainly in drug delivery systems. The volumetric phase transitions that such stimulus-responsive polymers undergo have also been exploited for the encapsulation of nanocrystals in polymeric spheres. For instance, the QDs can be confined in the microgel spheres by controlling the stimulus-responsive swelling of the microgels [110]. *N*-isopropylacrylamide and 4-vinylpyridine copolymer (PNIPAM-co-PVP) microspheres display a pH-dependent phase transition because of the reversible protonation of the pyridine units. Consequently, internal charge repulsion leads to the expansion of the polymer spheres. When the pore size becomes large enough, the spheres can absorb QDs from the solution, and after increasing the pH, the sphere size decreases and the QDs are physically entrapped inside the spheres. The resulting hybrid microspheres were stable in a broad range of pH. The total fluorescence intensity of the resulting microgels could be adjusted by simply increasing the initial concentration of the QDs in the solution. An attractive feature of the obtained materials was that the QDs could be released at values of pH higher than 11 (Fig. 15).

The presence of supramolecular interactions between the QDs and the polymer network can provide more stable QD/polymer assemblies by preventing weakly trapped QDs

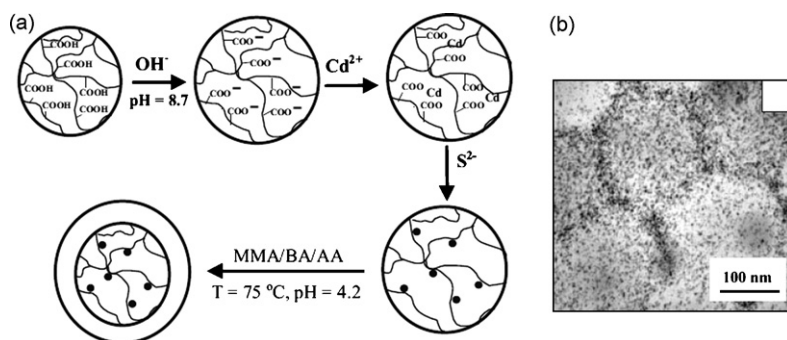
from leaking back into the solution. Electrostatic interactions and hydrogen bond formation between the QD surface ligands and the polymer were the strategies most often used. An important example where such strategies are relevant is the case of PNIPAM. PNIPAM displays a lower critical solution temperature (LCST), above which the hydrophilic polymer particles become hydrophobic and the volume of the hydrogels decreases significantly [111]. It is possible to encapsulate the QDs in the polymer network above the LCST, however, the entrapped QDs are expelled from the microsphere interior when the temperature is lowered back below the critical temperature. To solve this problem, Gong et al. [112] used hydrogen bond formation between the amide groups of PNIPAM and the thioglycerol and thioglycolic acid coated on the CdTe QDs' surfaces. In this case, the QDs acted as physical cross-linkers due to multiple hydrogen bonds between the nanocrystals and the polymer network.

Several research groups have successfully demonstrated entrapment of QDs in hydrogels. A major concern is how the presence of the nanoparticles influences the stimulus-responsive behavior of the microgels. The LCST behavior of PNIPAM has been found to be highly dependent on the loading of QDs in the hydrogels. The phase transitions, upon which many applications are based, were blurred, and at higher QD content, the LCST behavior was virtually missing. In view of this drawback, research efforts should be concentrated on what effects the QDs have on the phase transition behavior of such systems.

#### 4.2.3. Immobilization of charged QDs inside polymer microspheres via electrostatic interactions

Functionalized, charged QDs can be effectively incorporated into polymeric materials by using electrostatic interactions between functional groups on the QD surface and on the polymers. For this approach to be successful, both the QD and the polymer should be derivatized, thereby limiting the range of nanocomposite materials that can be prepared in this way.

Li et al. [113] incorporated positively charged CdTe QDs into poly(*N*-isopropylacrylamide-co-acrylic acid) (poly(NIPAM-co-AAc) microgels by electrostatic interactions. At low pH values, the spheres shrunk and self-assembled into structures showing fractal and dendritic patterns when deposited on surfaces. At high pH values, on the other hand, the microgels swelled and aggregated to form porous films in which phase separation between the QDs and the poly(NIPAM-co-AAc) matrix occurred. Monodisperse hybrid nanoparticles (38 nm) were prepared by mixing the QDs with nanogels of cholesterol-bearing pullulan modified with amino groups [114]. Electrostatic interactions between the negatively charged QDs and the positively charged nanogels, as well as the interaction between the protein-coated QDs and the gel were the two important factors influencing the hybrid nanoparticle formation. The nanoparticles were successfully internalized into various cells and did not form aggregated structures. Chen et al. [115] obtained CdSe/ZnS-loaded glycanospheres formed from negatively charged nanocrystals, negatively charged carboxymethyl dextran and positively charged polylysine. The



**Fig. 16.** (a) Carboxyl-functionalized polymer microspheres are used as templates for the in situ synthesis of semiconductor nanoparticles. As a first step, the pH is set to 8.7 to deprotonate the carboxylic acids. Subsequently,  $\text{Cd}^{2+}$  is introduced into the solution and is complexed by the carboxyl ions. Finally, introduction of  $\text{S}^{2-}$  leads to the formation of CdS inside the polymer beads. The polymer beads can be further coated by a polymeric shell made of various polymers. (b) A TEM micrograph of the resulting CdS doped microgels [125]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

QDs were further cross-linked with the polysaccharide matrix to stabilize the nanospheres. The average sphere diameter value was 190 nm and each nanosphere contained hundreds of QDs. The dextran molecules prevented aggregation between the nanospheres. However, ligand exchange had to be performed to endow the QDs with negative charges and the luminescence quantum yield was reduced. Positively charged amino groups of the chitosan were also shown to bind directly to the negatively charged CdSe/ZnS [116]. Applying higher concentrations of chitosan led to the formation of hybrid nanosphere-like structures with diameters values of 50 nm. The size of the nanospheres could be controlled by adjusting the chitosan concentration and the chitosan/nanoparticle ratio. The QDs encapsulated in the beads were found to retain their optical properties and the beads have been shown to display an enhanced biocompatibility when compared to nonencapsulated nanocrystals. Encapsulation of  $\text{Gd}^{3+}$  in the same beads endowed the beads with fluorescent and paramagnetic properties for simultaneous fluorescence and magnetic resonance imaging [117]. However, the preparation method used did not allow for an accurate control of the amount of each component in the beads and of the size of the beads. Negatively charged CdTe nanocrystals were incorporated into alkylammonium-functionalized polystyrene [118]. The polymer droplets were formed by dispersing the polymer in aqueous solutions of poly(vinyl alcohol). The diameter of the particles could be controlled from several micrometers to several tens of micrometers.

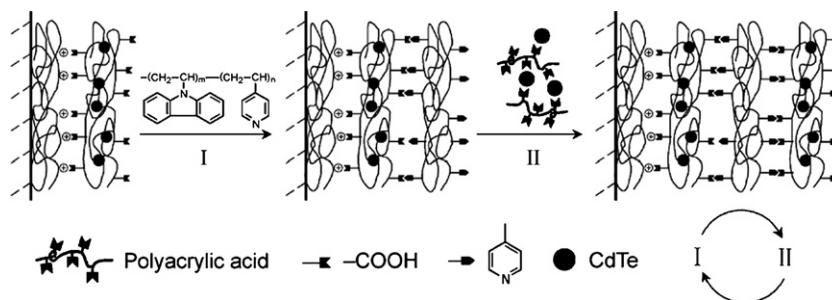
#### 4.3. In situ synthesis of QDs in polymer micro- and nanospheres

Template-based synthesis of semiconductor nanoparticles inside the polymer spheres results in QD/polymer hybrid microparticles [119,120]. The synthesis of the nanoparticles can be carried out either at the microparticle surface [121–123] or in the particle interior. Zhang et al. [124] synthesized CdS nanocrystals on the surfaces of poly(methyl methacrylate)-poly(methacrylic acid) latex particles. Macroscopic nanostructured materials were fabricated by coating the resulting hybrid with an addi-

tional polymeric shell that had a lower glass transition temperature than that of the core [124]. At the right temperature, the shell softened thus filling the interstitial voids between the preassembled particles and subsequently formed a matrix for the CdS-functionalized cores. Poly(*N*-isopropyl acrylamide-*co*-acrylic acid-*co*-2-hydroxyethyl acrylate) (poly(NIPAM-*co*-AA-*co*-HEA)) hydrogels (200–600 nm) have also been used as a template material [125]. As a first step, ion exchange between the solution of precursor cations and the interior ionic groups of the microgels was performed (Fig. 16). In the second step, the cations in the gels reacted with the corresponding counterion giving rise to the nanoparticles. During the microgel synthesis, the concentration of the QDs in the beads was tuned by pH, amount of acrylic acid groups, HEA, and cross-linker. In this second stage, the CdS concentration could be controlled by the  $[\text{Cd}^{2+}]/[\text{COO}^-]$  molar ratio. Heat processing of the nanocrystals narrowed their size distribution but increased their overall size. The microgels could be further coated with a hydrophobic polymeric shell, and such hydrophobic QD-doped microspheres were used as building blocks of photonic crystals [126]. However, their interesting stimulus-responsive behavior in this case was lost [125].

#### 5. QD/polymer layer-by-layer assemblies

Processing quantum dot dispersions into high-quality thin films with controlled film thicknesses from the micrometer to the nanometer length scales is essential in optoelectronic and biosensing applications. Additionally, the vertical and lateral control over the quantum dot location in nanostructures becomes important when various QD types have to be incorporated into the same structure. For instance, to be able to profit from energy transfer processes in photovoltaic or sensor applications, the control over the location and distance between the QDs is essential. This is due to the distance dependence of the energy transfer phenomena. Fabrication techniques, which solve the problems related to the controlled placement of the QDs, are therefore actively explored. A related problem concerns the formation of polymeric shells of controlled



**Fig. 17.** An LbL assembly of QD/polymer multilayers through interaction via hydrogen bonding. Polyacrylic acid is used as a QD surface ligand. The substrate is coated with a layer of a positively charged polyelectrolyte onto which the polyacrylic acid coated QDs are deposited. The subsequent layer is obtained by deposition of poly(*N*-vinyl carbazole-*co*-4-vinyl pyridine). The hydrogen bonds form between the carboxyl groups in polyacrylic acid and pyridine units in the copolymer. From [141], reproduced by permission of The Royal Society of Chemistry.

thicknesses around single QDs. Methods based on polymerization directly from the QD surface, as discussed in Section 3.3.2, were used to form polymeric shells, however the thicknesses of these shells were hard to control.

The layer-by-layer (LbL) assembly technique has been found to solve most of these problems. This method has been employed to obtain molecular level architectures and multilayer organic–inorganic films through noncovalent interactions. The technique, introduced by Decher and Hong [127], is based on the alternating adsorption of charged or non-ionic species onto substrates. LbL assembly has become an enabling technique in bottom-up nanofabrication due to the ease of formation of smooth, uniform, defect-free, high-quality thin films with thicknesses that can be controlled in the nanoscale. The assembly is usually performed from aqueous solutions, and there are virtually no substrate shape constraints. Although the technique has been mainly used for the assembly of polyionic polymers [128], it has been demonstrated that other types of materials could also be used. Metal and semiconductor nanoparticles, organic dyes, polymer nanospheres, electrochemically active materials, and biomacromolecules have been incorporated into the nanostructured films to obtain assemblies with desired mechanical, optical, electro-optical, electrical, magnetic and electromagnetic properties [129–131]. Yet, the LbL technique has one major drawback—it is relatively slow as compared to other fabrication methods. Nevertheless, the ability to control polymer film structures on the nanoscale is so advantageous that this drawback can be neglected in most instances.

The film formation in electrostatic LbL assemblies is based on alternating adsorption steps of charged species onto a pretreated substrate. The QDs are endowed with charges via ionic ligands (e.g. thioglycolic acid (or citric acid) and 2-mercaptoethylamine for negative and positive charges, respectively) or charged polyelectrolytes, such as polyacrylic acid [132]. The key for the formation of the layers is the presence of excess charge after each of the deposition steps. However, too many charges present on the QD surface renders it highly dispersible in water and will cause it to desorb from the layers into the aqueous environment. The surface area per negative or positive charge can be controlled by changing the ratio of charged and non-charged ligands on the nanoparticles surface [133].

### 5.1. Layer-by-layer QD/polymer assembly on planar and nonplanar substrates

The LbL technique has often been used to process QD dispersions into high-quality thin films with controlled nanoscale thicknesses [133–137]. It has been found that, for the majority of cases, the optical absorption follows a linear relationship with the number of deposited layers. The progress of the multilayer formation can therefore be conveniently monitored by absorption measurements, but also ellipsometry and atomic force microscopy can be utilized to determine the multilayer thickness with nanometer accuracy. The thickness of a deposited bilayer (positively and negatively charged species) depends on the type of polyelectrolyte and the counter ions used. Bilayer thicknesses are similar for most polyelectrolytes and in order to achieve thicker bilayers, dendritic macromolecules, such as poly(amido amine) dendrimers [138], can be employed as polyelectrolytes.

Beside electrostatic interactions, LbL structures can be formed by using other supramolecular interactions, such as hydrogen bonding [139,140]. For instance, poly(vinyl pyridine)/CdSe multilayer films have been assembled utilizing the interactions between carboxyl-coated CdSe and the pyridine group of PVP. X-ray diffraction experiments have shown that the hydrogen bond method resulted in homogeneous thin films. In a similar approach, Zhang et al. [141] used polyacrylic acid as an interaction medium between the QDs and a *N*-vinyl carbazole/4-vinyl pyridine copolymer. Controlling the amount of the pyridine units in the copolymers and the PAA concentration in the solutions allowed Zhang et al. to control the amount of the deposited QDs during each adsorption step (Fig. 17).

A problem often observed in many fabrication techniques, e.g. conventional lithography, is the difficulty to obtain nanometer-scale structures on nonplanar substrates. The LbL technique is not exclusively restricted to planar substrates but can also be effectively applied to highly curved surfaces like those of fibers [142] or micro- and nanospheres [143–146]. In this context, two approaches can be identified. The first approach relies on coating a polymer [147], silica [148] or salt template with polyelectrolytes and charged semiconductor nanoparticles. The second approach is based on the direct modification of the nanoparticle surface with polyelectrolytes. For poly-

mer micro-, and nanospheres, the coating process of a single layer is realized by suspending the beads in the QD solutions. Subsequent stepwise immersion in solution of polyelectrolyte and QDs, with intermediate washing steps, leads to the formation of the layer-by-layer assembly. The LbL approach to polymer microsphere functionalization allows one to control the composition of the coating layers. In the work of Gómez et al., the silica spheres were first coated with poly(ethylenimine) (PEI)/poly(styrene sulfonate) (PSS) bilayers, and then the QDs were adsorbed onto the PEI layer [148]. The distance between the QD layers depended on the number of PEI/PSS bilayers coated onto the spheres. Moreover, different types of QDs could be used in subsequent bilayer coating steps [149]. The QD loading in the assembled layers and the total luminescence of the polymer beads could thus be controlled in the assembly process. The radial position of the nanocrystals in the multilayer assembly permitted a fine-tuning of the optical properties of the QD-doped microspheres.

Many QD applications require the control over the location of the QDs on different substrates, not only vertically but also laterally. The key problematic issues in LbL for such applications include the selective deposition of the materials over multiple numbers of bilayers such that non-specific adsorption of the QDs into undesired locations is avoided. Other issues are the preparation of laterally resolved patterned structures with different types of QDs, and the overall temporal and physicochemical stability of the patterns. The first problem has been solved by employing microcontact printing of polyelectrolyte-modified QDs onto prepatterned substrates [150]. However, no demonstration of the stability of the patterns over multiple numbers of layers was provided. To reduce nonspecific interactions of the QDs with the substrates, Zhou et al. [151] modified the surface of the QDs with negatively charged sulfonate groups and used a polymer with a hydrophilic backbone as the assembly partner. In this way selective LbL deposition to up to 20 bilayers was demonstrated. The second obstacle, i.e. the difficulty in obtaining patterned structures using different types of QDs, was solved through patterning by photoactivation as reported by Wang et al. [152] When exposed to ultraviolet radiation, CdSe/CdS nanocrystals were found to exhibit changes in the luminescence quantum yields accompanied by shifts in the emission spectrum. The patterning process was realized by masking the films and varying the exposure time. This technique, in combination with near-field optics, can, in principle, be used to obtain QD patterns with nanometer scale periodicity [152].

## 5.2. Layer-by-layer assembly of polymers directly on quantum dots

Even though the direct modification of the QDs with polymers using the LbL technique leads to well-defined assemblies, the coating of QDs with polyelectrolytes has often been a challenging task primarily due to the small size of the structures and related colloidal stability. Only few successful reports on this subject can be found in the literature [150,153]. A coating consisting of a single polymer layer on top of negatively charged CdSe/ZnS nanocrystals

has been realized by a multifunctional polymer ligand composed of aliphatic and charged side chains [154], and also by using a protein consisting of positively charged leucine zipper attachment domains [155,156]. The charged side chains were attracted by the negatively charged QD and the aliphatic side chains protruded into the nonpolar solvent. The nanocrystals coated with this type of multifunctional polymer have displayed superior stabilities as compared to mercaptoacetic acid coated QDs. A true layer-by-layer assembly has been realized [150] by sequentially coating functionalized CdSe/ZnS nanoparticles with poly(allylamine) (PAA) and poly(vinylsulfonic acid) (PVSA) to obtain QD core-polymer shell nanostructures. Following each coating step, an inversion of the charges present at the QD surface was observed. The LbL technique was therefore used in this case as a convenient QD surface modification method.

## 5.3. Combination of layer-by-layer assembly with other fabrication techniques

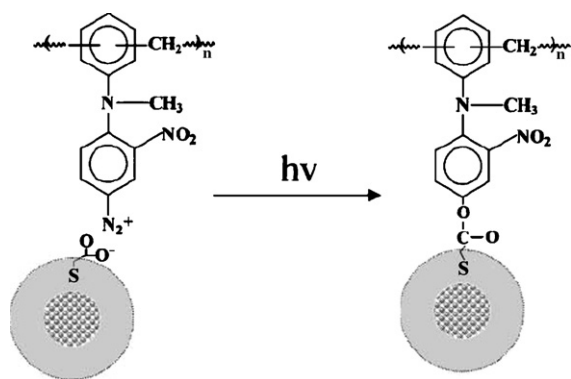
It is very hard to control the amount of materials deposited during each of the LbL coating step, and consequently also the QD packing density in the deposited layers. To by-pass this problem, Lowman et al. combined the LbL technique with Langmuir-Schaefer deposition [157]. Such a combination allowed a controlled deposition of a QD monolayer onto preassembled polyelectrolyte layers. By using this method, ligand exchange reactions that endow the QDs with negative charges can be eliminated, and deposition at various points in the pressure-area isotherm allows one to control the packing density of the QDs in the deposited layer [157].

Selective deposition of the QDs onto substrates will not occur unless the substrate is pretreated [158–160]. Therefore, the LbL assembly has also been explored in combination with other methods to obtain patterned substrates. When a conductive substrate is present, one can use electric field assisted layer-by-layer assembly for the fabrication of CdTe/polymer layers on, e.g., patterned indium tin oxide (ITO).

## 5.4. Enhancing the stability of the QD/polymer layer-by-layer assemblies

The polymer layers formed by LbL are usually tightly packed. The nanoparticles in the LbL films are therefore virtually immobile and one can incorporate different types of QDs and polyelectrolytes into the same multilayer system [133,135,161]. The temporal and physicochemical stability of the structures prepared by LbL can become even more enhanced if the QDs are bonded to the polymers after the formation of the films. In this case, the polyelectrolytes should be polymers with functionalities permitting them to be cross-linked with each other or with an additive. For example, QDs of a nitro-containing diazoresin assembled with thioglycolic acid-stabilized CdTe or CdS can be covalently linked by using ultraviolet irradiation (Fig. 18) [162]. Exposure to UV light through a photomask, with subsequent development and dissolution of the noncross-linked parts





**Fig. 18.** The self-assembly of a nitro-containing diazo-resin with a COO<sup>−</sup> functionalized QD and the subsequent ultraviolet irradiation of the assemblies lead to covalent coupling of the QDs with polymers, thereby enhancing the stability of the fabricated structures. Reprinted from [162], Copyright (2002), with permission from Elsevier.

of the films, has also resulted in patterned substrates [163].

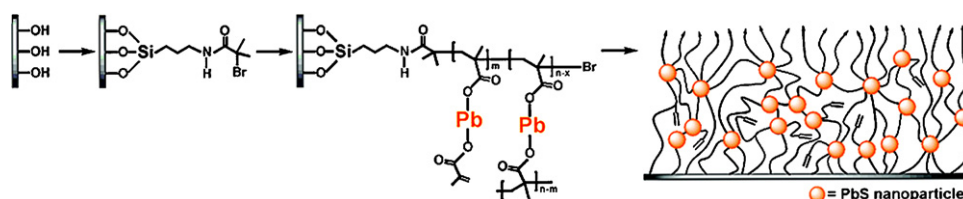
In summary, the LbL assembly technique is a very robust and versatile method, which can be used to obtain hybrid polymer–QD nanocomposite materials. It is possible to assemble different types of nanoparticles within the same thin film structure, and fine-tune the bilayer thicknesses. Furthermore, patterning of the LbL assemblies can be realized. These features are advantageous in many applications. However, before the LbL technique will be widely used in technological processes, problems related to the slow film formation process should be solved.

## 6. Incorporation of QDs into bulk polymeric materials and polymer thin films

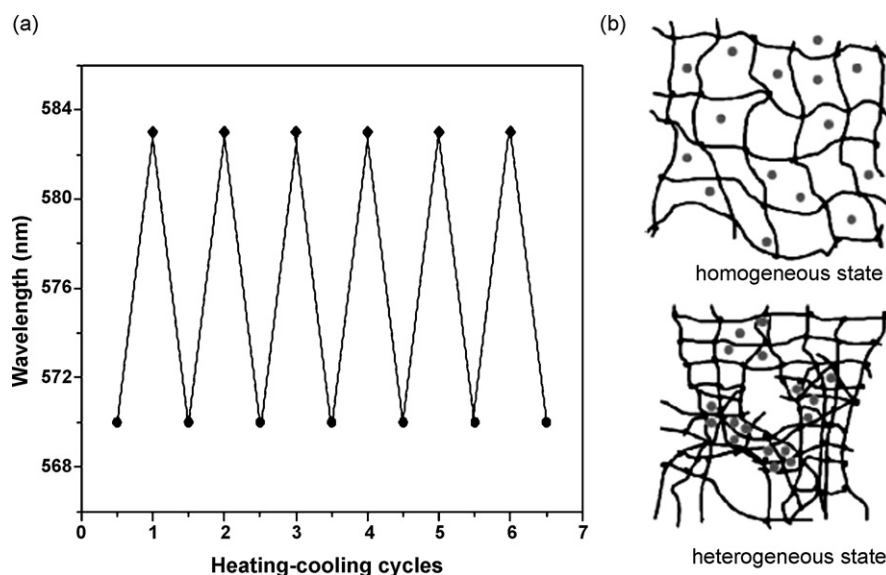
From a technological point of view, the fabrication of bulk QD/polymer nanocomposites, and in particular thin film architectures comprising semiconductor nanoparticles and polymers, is extremely relevant. The development of optoelectronic devices, such as solar cells or light-emitting diodes, has seen its most significant improvement through the control of the quality of such hybrid thin films. However, before such applications can be realized, issues concerning the poor compatibility of QDs with polymeric environments, which generally lead to agglomeration of the QDs inside the polymers, and consequently to the quenching of the luminescence, should be solved.

The main efforts are therefore concentrated on the preparation of fine dispersions of QDs inside polymers such that the photophysical properties of the nanocrystals are not affected. Moreover, transparent QD/polymer hybrid materials are important in many applications. Poor compatibility of the QDs with the polymer leads to aggregation of the nanoparticles inside the films already at relatively low loadings what results in a loss of transparency. One of the goals is therefore to establish methods to obtain transparent materials with high concentration of QDs.

Dispersability and organization of the QDs inside the polymeric matrix can be controlled by modification of the QDs' surface chemistry. The main strategy to improve the miscibility, compatibility and dispersability of the QDs inside the polymer matrix, is to coat the nanocrystals with compatibilizing ligands. For instance, coating CdS QDs with ligands functionalized with phenyl groups improved the solubility of the QDs in pyridine [164], and oleic acid ligands promoted the solubilization of the nanocrystals in PMMA and PS [165]. For certain applications, miscibility is required between the nanocrystals and monomers. Polymerization in the presence of QDs leads to fine dispersions unless phase separation and aggregation takes place during the polymerization. To further increase the stability of the QDs in polymers, covalent linkages between the QD surface ligands and the matrix can be created. Polymerizable surfactants, coated on the nanocrystal surfaces, may also take part in the polymerization process. In this context, functionalized QDs are dissolved in vinyl monomers and the polymerization is performed by, e.g. free radical polymerization methods. The simplest means of incorporating QDs into polymer thin films, however, is to mix presynthesized semiconductor nanocrystals with polymers in solution and employ one of the most common polymer thin film deposition methods such as Langmuir–Blodgett deposition, spin-coating or casting. Depending on the polymer used, other, more “exotic”, techniques including electrodeposition or  $\gamma$ -ray irradiation, were applied [166]. The growth of ZnSe–poly(aniline) films on ITO substrate has, for instance, resulted in enhanced emissions from the nanocrystals [167]. Irradiation with  $\gamma$ -rays has been utilized for the preparation of transparent bulk nanocomposites with high ZnS contents [168]. The advantages of this method include processing under ambient pressure and at room temperature, as well as relatively high polymerization rates. However, due to the need for  $\gamma$ -ray sources, this method is not widely accessible, and is relatively expensive.



**Fig. 19.** The fabrication of cross-linked QD/polymer thin films using lead-containing monomers and cross-linkers. The polymerization initiator is first grafted onto the silica surface, and the polymer film is subsequently exposed to H<sub>2</sub>S vapors, which leads to the formation of PbS nanocrystals inside the films. The growing nanocrystal is stabilized by the polymer and acts as a cross-linker. Reprinted with permission from [173]. Copyright (2002) American Chemical Society.



**Fig. 20.** The emission wavelength of the QD/PNIPAM material as a function of the number of repeated heating-cooling cycles (a), attributed to changes in the network structure below and above the LCST of the polymer (b) [183]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Two interesting methods for preparing QDs in thin films are based on the in situ synthesis of semiconductor nanocrystals. In the first method, metallic ions such as  $\text{Cd}^{2+}$  or  $\text{Zn}^{2+}$  [169] are introduced in the form of metalloorganic monomers or cross-linking agents (Fig. 19) [170–173]. Cadmium (or lead) dimethacrylate and methyl methacrylate were used as monomers for a surface initiated polymerization from a silica surface. Here, CdS nanoparticles were generated in situ in the polymer by exposing the grafted polymer to  $\text{H}_2\text{S}$ . This concept can be applied to thin films [173] as well as to the formation of more complex core-shell microsphere structures [174].

Another method for the simultaneous synthesis and deposition of II–VI semiconductor nanoparticles in polymer films was reported by Salata et al. [175–177]. In this technique, known as gas-aerosol reactive electrostatic deposition (GARED), microdroplets containing polymer and metal ions were first generated electrostatically. These aerosol droplets were then used as restricted reaction volumes and were driven toward the substrate by electrostatic and gravitational forces. The metal ions subsequently reacted with a gas phase compound to form colloidal semiconductor nanoparticles surrounded by polymer. CdS and GaAs nanoparticles in poly(vinyl alcohol) were prepared by this method, but unfortunately, the deposited films were neither uniform nor planar. The technique can nonetheless be applied to a wide range of polymer-semiconductor combinations.

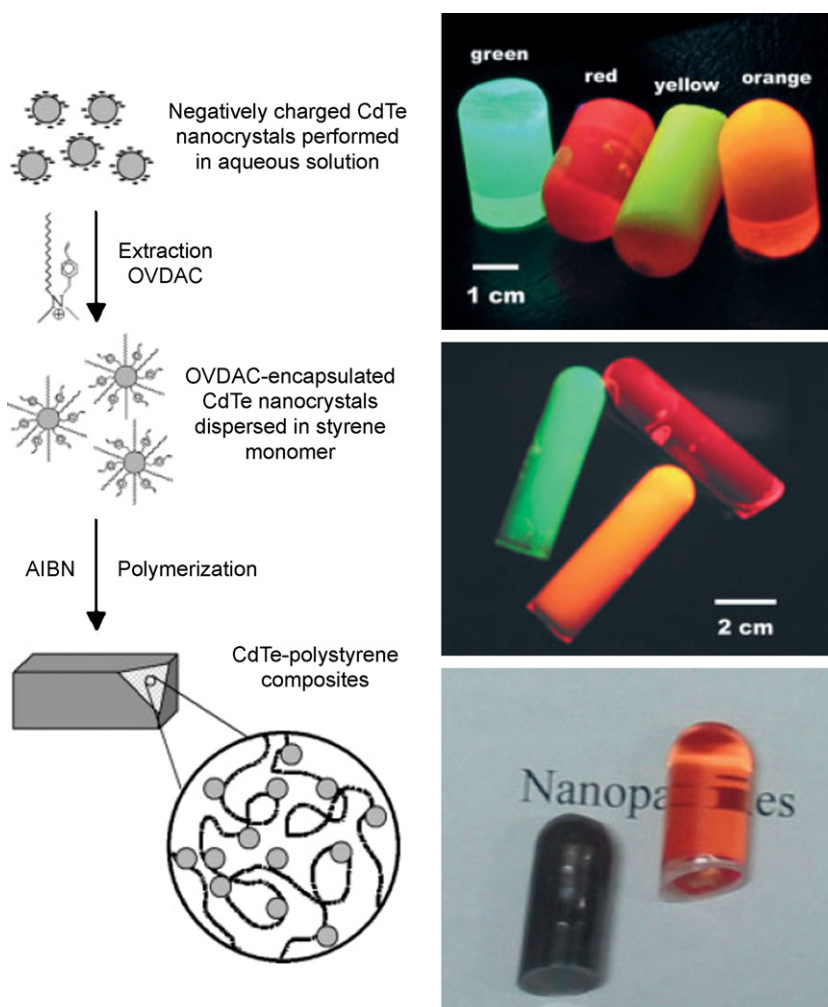
The main drawback of approaches based on the in situ synthesis of the nanocrystals in the polymer matrix is that a relatively broad size-distribution of the nanocrystals is obtained. It was shown that the sizes of semiconductor clusters synthesized this way could cover the entire range from the molecular to the bulk [178]. Due to this broad size distribution, no well-developed absorption edges were present and the interpretation of many optical and electrochemical effects in such synthesized particles was

often very difficult. In numerous cases, thermally induced agglomeration of the semiconductor clusters could also occur upon heating.

#### 6.1. Polymerization of monomers in the presence of QDs

For vinyl monomers, the methods based on polymerization in the presence of nanocrystals primarily require miscibility between the nanocrystals and the monomers. For instance, lipophilic (TOPO coated) QDs can be dissolved in lauryl methacrylate [179]. The alkane side chains of the polymer interact with the TOPO-coated QDs and prevent aggregation. Such a method is relatively inexpensive and since the ligand exchange on the QD surface is avoided, the luminescence properties of the QDs are largely retained. However, the requirement of a specific monomer structure limits the range of polymers that may be used in this approach. The solubility issues and related phase separation during polymerization of the QD/polymer hybrid were partially avoided by using a prepolymerization method, where the QDs were added to a prepolymerized oligomer [180]. The oligomer prevented demixing of the nanocrystals. The polymerization was then continued to obtain polymer-QD composites. With this method, CdSe/ZnS and PbSe QDs were incorporated into electron beam sensitive PMMA [181] and photonic structures with embedded QDs were fabricated by using e-beam and UV light sensitive resists [182].

For water-based synthesis of polymers, water-soluble QDs were used. PNIPAM hydrogels with immobilized CdTe nanocrystals were prepared by polymerization of NIPAM in the presence of the QDs [183]. The luminescence of the QDs in the polymer was found to slightly increase, thus indicating a passivating role of PNIPAM. The presence of the nanocrystals inside the hydrogel matrix did not affect the Lower Critical Solution Temperature (LCST) behavior of the gel. However, shifts in the luminescence spectrum toward



**Fig. 21.** The formation of CdTe/polystyrene composite materials using a polymerizable surfactant. Water-soluble, negatively charged QDs are dispersed in styrene monomer by encapsulating the QD in a positively charged, vinyl-functionalized surfactant. The vinyl-functionalized QDs are then copolymerized with the styrene monomer to yield transparent nanocomposite bulk materials. Materials with a variety of shapes and emission colors can be obtained in this way [195]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

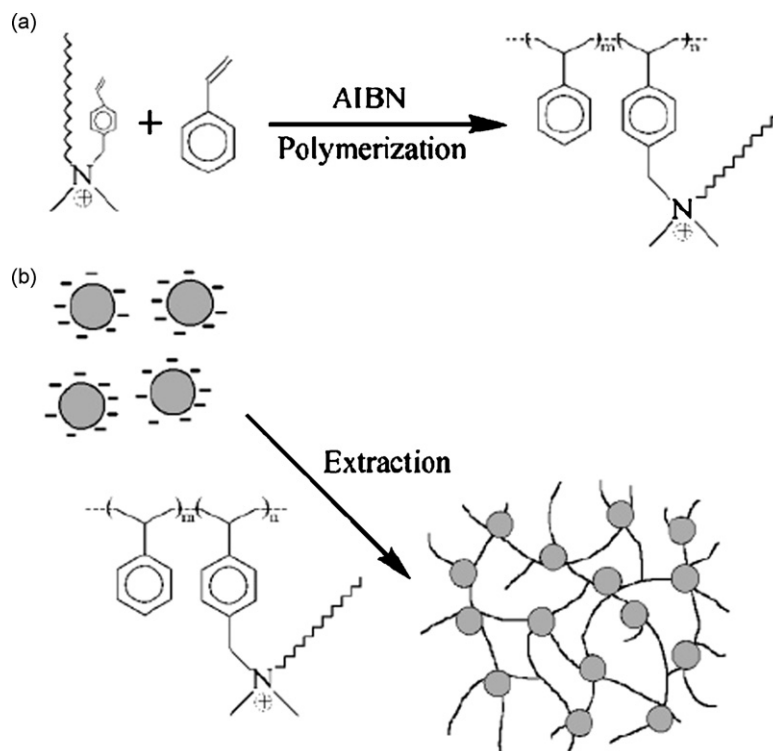
higher wavelengths were observed when increasing the temperature (Fig. 20a). Several explanations for such an effect were proposed, among others a heterogeneous network state above LCST and an enhanced energy transfer rate due to the diminishing interparticle spacing (Fig. 20b).

Water-soluble CdTe nanocrystals passivated with thiocholine bromide may be incorporated into acrylate-functionalized ionic liquids [184,185]. Polymerization of the ionic liquid gives an optically clear and highly luminescent cross-linked polymer hybrid without aggregation or phase separation occurring. Due to the stability of the QD cationic ligand in ionic liquids [186–188], the luminescence emission efficiencies are retained. CdSe/ZnS QDs coated with 2-dimethylaminoethanethiol (DAET) were transferred into an ionic liquid, which was used as a compatible medium for the polymerization and cross-linking of poly(methyl methacrylate). The final composites were flexible, transparent, highly fluorescent, and their flexibility could be tailored by varying the content of the ionic liquid [189].

Polymerization in the presence of QDs is not limited to vinyl monomers. The formation of polyurea is based on the reaction of diisocyanates with water, and polyurethane is obtained when ethylene glycol is reacted with hexamethylene diisocyanate. Hirai et al., have fabricated QDs (including CdS, TiO<sub>2</sub> and CdS/ZnS) encapsulated in polyurea [190,191] and polyurethane [192] by polymerization of the monomers in aqueous micelles, in which the QDs were first synthesized.

## 6.2. Application of polymerizable surfactants and ligands

Methods involving polymerizable ligands rely on the direct modification of the QD ligand periphery with surfactants able to copolymerize with the growing polymer chains. In radical polymerization schemes, vinyl-containing ligands, such as for example 4-vinylpyridine [193,194], have been copolymerized with methacrylic acid. In similar efforts, Zhang et al. have used octadecyl-p-vinyl-benzyltrimethylammonium chloride (OVDAC) as a



**Fig. 22.** (a) The copolymerization of styrene with an alkylammonium-functionalized monomer results in a copolymer with positively charged side-groups. (b) Electrostatic interactions between positively charged side groups of the polymer and the negatively charged ligands on the QD surface cause the formation of a multicross-linked QD/polymer composite material. Reprinted with permission from [196]. Copyright (2005) American Chemical Society.

polymerizable surfactant to transfer the aqueous CdTe QDs into styrene or methyl methacrylate monomer solutions (Fig. 21). Bulk QD/polystyrene nanocomposites were then obtained by radical polymerization of styrene. Importantly, the materials were transparent and showed no signs of phase separation or agglomeration [195,196]. Transparent thin films incorporating QDs were also obtained by directly copolymerizing QDs coated with polymerizable surfactants [197,198].

In polyaddition reaction schemes, the ligand has to be functionalized with a chemical group able to bind to another bifunctional monomer present in the solution. For example, hydroxyl-functionalized nanoparticles were incorporated into polymers by adding the functionalized QDs to polythiourethane oligomers terminated with isocyanate groups [199]. Hydroxyl- or thiol-containing ligands reacted with isocyanate groups forming transparent polyurethane [200] or polythiourethane (PTU) [201] nanocomposites, respectively.

### 6.3. Immobilization of QDs in polymer matrices via electrostatic interactions

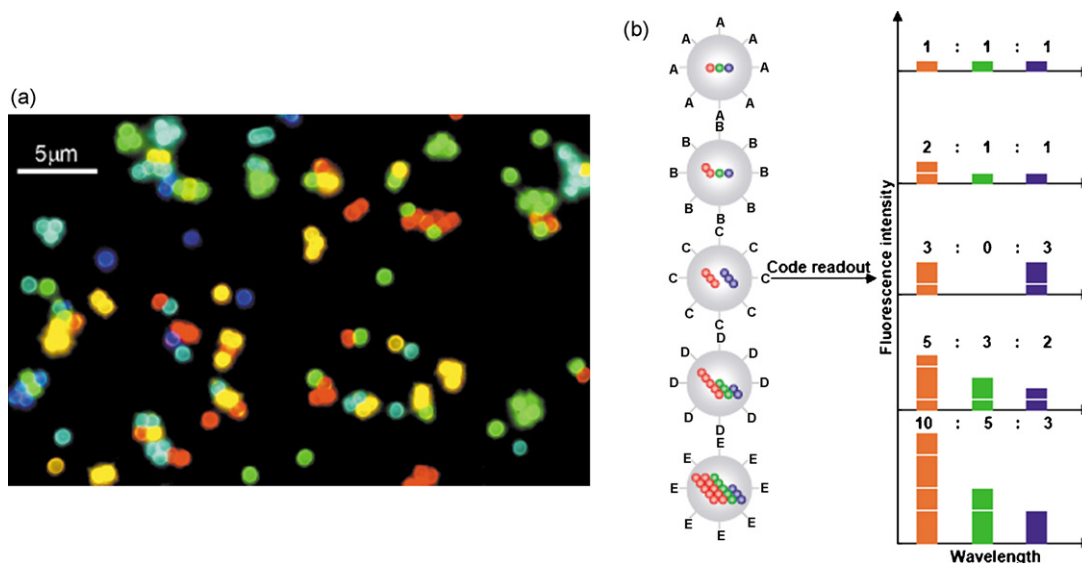
Fine dispersions of nanocrystals in polymer matrices are obtained through noncovalent interactions between the ligand at the QD surface and polymer side groups. Employing electrostatic interactions between charged QDs and the polymer allows one to process water-soluble materials [118,196,202]. The resulting QD/polymer

nanocomposite materials were easily processable into various shapes and the stability of the photoluminescence properties was improved. For example, negatively charged CdTe nanocrystals were incorporated into an alkylammonium-functionalized copolymer [118,196] via electrostatic interactions (Fig. 22). The nanocrystals acted as physical cross-linking centers. Multicolor complexes could be readily prepared by using two types of QDs. In contrast to other methods used to incorporate the nanocrystals into a solid bulk polymer, the luminescence quantum yield of the QDs increased, probably due to a better passivation of the surface by the polymer.

## 7. Applications of QD/polymer hybrids

The progress achieved in the fabrication of polymer–QD assemblies has already made an impact in many applications. For example, by solving problems related to the dispersability of QDs in polymer matrices, and by developing new methods for functionalization of the nanoparticles with polymers, new possibilities have emerged for optoelectronics. Nanocomposite materials made of QDs embedded in micro- and nanospheres have found some applications in photonics and bionanotechnology. Hybrid QD/polymer micro- and nanospheres are for instance of considerable interest in analytical chemistry and bioengineering, as multiplexed assays, medical diagnostics tools, and in drug screening and combinatorial chemical synthesis.





**Fig. 23.** (a) A fluorescence image of a mixture of PS beads tagged with different CdSe/ZnS QDs. (b) A schematic illustration of the optical coding based on wavelength- and intensity-multiplexing. The amount of each type of QD (red, green, blue) can be tuned to obtain a characteristic ratio of the colors for each of the beads. Functionalization of the bead surfaces with receptors (A, B, C, D, E) allows for the identification of numerous bioevents [107]. Reprinted by permission from Macmillan Publishers Ltd.: Nature Biotechnology, copyright (2001). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

### 7.1. Biological applications of QD/polymer assemblies

From the pioneering work of Bruchez et al. [203] and Chan and Nie [204], great progress in the field of biological applications of QDs has been achieved. QD materials have been explored as luminophores for fluorescence microarray technologies [205], labels of biological macromolecules [206], and as sensors [207] in a multitude of biologically relevant systems. An excellent review by Medintz et al. on the molecular and cellular imaging with quantum dots was recently published [208]. However, despite the great promise of QDs for biological applications, issues related to QD cytotoxicity, long-term in vivo stability, and oxidation remain to be solved.

In the context of QD/polymer assemblies for biological applications, QDs functionalized with amphiphilic polymers via hydrophobic–hydrophobic interactions are, along with QDs embedded in polymer microspheres, the most explored systems to date. Functionalization of QDs with an amphiphilic polymer via hydrophobic–hydrophobic interactions is explored for cell labeling and in vivo imaging [40]. The stability of the QDs, their aggregation after internalization, and their biocompatibility were the major roadblocks for the use of QDs in such applications. A complex polymeric shell was therefore designed to solve the problems related to QD storage in physiological buffers. Each of the components of the shell was designed to perform a specific function: protection in vivo, targeting of ligands and improvement of biocompatibility and circulation. The resulting polymer-coated nanoparticle was stable against hydrolysis and enzymatic degradation under in vivo conditions. The polymer-coated particles were also found to be nearly non-toxic and the PEG-coated QDs were able to circulate in the blood for an extended period of time.

Comparative studies on the in vivo stability of QDs conjugated to methoxy- or carboxy-terminated poly(ethylene glycol) revealed that QDs coated with either short-chain methoxy-PEG or long-chain carboxy-PEG had short circulating half-lives, in contrast to the long-chain methoxy-PEG quantum dots [40]. It was concluded that higher PEG densities on the QDs, as well as longer PEG chains, tend to reduce the nanoparticle binding to cells and plasma components. In a recent study, Luccardini et al. [41] reported on the pH dependent interactions of the coated QDs with lipid membranes. They found that the interaction between the polymer-coated QDs and the membrane, in biological buffers, could be controlled by the pH of the buffer.

The fabrication of polymer micro- or nanospheres with encapsulated luminescent semiconductor nanoparticles was largely driven by this material's biological application in high throughput screening and medical diagnostics [209,210]. In such applications, QDs come as a natural extension to common organic chromophores or metallic complexes [211,212]. Microsphere-based fluorescent bioassays [213] have also proved to be good alternatives to slide-based microarray technologies. The main idea is to be able to efficiently tag the latex beads with various combinations of QDs of a variety of colors and at well-defined nanoparticle concentration ratios. This way, massively parallel wavelength- and intensity-multiplexing for coding of biological assays can be achieved (Fig. 23) [214]. For such systems to be successful, the quality, monodispersity, and colloidal stability of the polymer beads, the amount of QDs in the beads as well as the loading capacity of the beads should be controlled. If different QDs are to be embedded in the spheres, then the control over the ratio between the amounts of each of the QDs becomes important. The diffusion of quenchers into the beads is also undesirable.

Finally, the unwanted release of the QDs from the spheres should be suppressed, or controlled, depending on the type of application in mind.

QDs can be also incorporated into hollow polymer capsules [215] providing single- or multicolor-tagged microspheres for multiplexed optical coding [216,217]. Functionalization of the capsule walls and the capsule interior with QDs provides also a versatile and universal carrier system for drug delivery [218] and biodiagnostic applications [217]. Negatively charged CdTe QDs can penetrate the microcapsule walls and be captured by positively charged polyelectrolytes present in the solution and at the inner walls of the microcapsules. This approach has been used to obtain multifunctional materials by incorporating QDs and magnetic nanoparticles into the same capsules [219]. Microcapsules made of biocompatible polymers like alginate acid sodium salt, dextrane sulfate, protamine sulfate, or chitosan, labeled with IR-emitting QDs ( $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  and  $\text{HgTe}$ ; emission wavelength 750–1150 nm) were described by Gaponik et al. [220]. In context of the potential cytotoxicity of the QDs, it was found that the leakage of the nanocrystals from the capsule walls was largely prevented. A greater stability of the polyelectrolyte/QD shell can be achieved by cross-linking the QDs with the polymers. Yang et al. [221] prepared hollow capsules, where the shells were made of adsorbed carboxyl-functionalized CdTe/PAH layers, which were subsequently cross-linked using a coupling agent.

## 7.2. Optoelectronic and photonic applications of QD/functional polymer nanocomposites

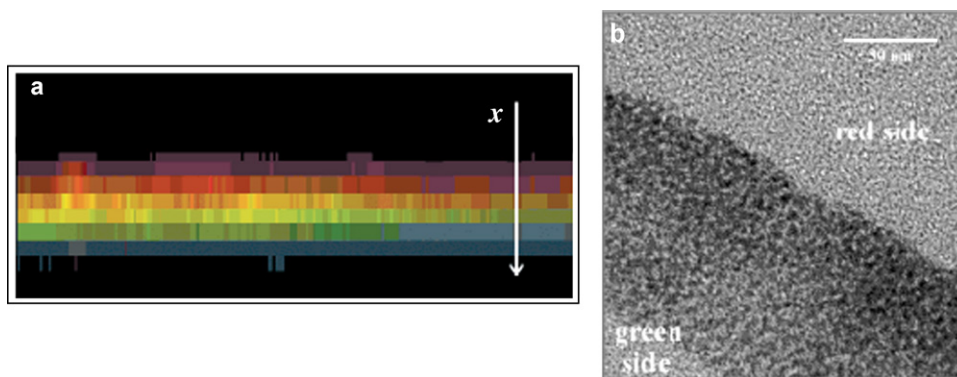
There is an increasing interest to disperse semiconductor nanocrystals into functional polymers for optoelectronic and photonic applications. Conductive and semiconductive polymers have thus been used as dispersive matrices in view of the possible benefits that may arise from the combination of such materials with quantum-confined semiconductor nanoparticles. Incorporating semiconductor nanocrystals in carrier-transporting polymers yields an interesting class of photoconductive nanocomposites [222]. The photoconductivity is a convolution of the photoinduced charge transfer efficiency and charge diffusion in the matrix. The presence of the nanocrystals enhances the photoinduced charge generation efficiency, while the polymer can be responsible for the charge transport to the electrodes. Most importantly, the energy levels of the polymeric host and of the QDs can be tuned and shifted with respect to each other via chemical derivatization of the polymeric backbone, and by changing the size of the nanocrystal, respectively. Careful positioning of donor and acceptor levels in optoelectronic devices translates in turn into improved device performance [223].

Depending on the type of application in mind, one might wish to disperse the nanoparticles in the polymer so as to avoid aggregation with the subsequent loss of optical and electronic properties. High QD content in the polymer is also needed to increase the available interfacial area for charge transfer. The interface between the QD and the polymer plays an important role in the determination of the final properties of the devices since it controls

the carrier transfer efficiency [224,225]. A large variety of methodologies were explored for the fabrication of optoelectronic devices. Spin-coating and casting of codissolved QD/polymer solutions directly onto electrodes, in situ QD synthesis in the polymer host, and layer-by-layer assembly were the techniques the most often used and proved to be both the simplest and most reliable.

QD/polymer nanocomposites attracted much attention as materials for light-emitting diodes (LEDs) [179,226–235], solar cells [222,225,236–243], and photorefractive materials for optical data storage or optical amplification [244–249]. For these types of applications, the polymer matrix offers a high nanoparticle stability, physical flexibility, processability, low cost, and improved lifetime as compared to other matrices.

QDs embedded in polymer microspheres are of interest for applications in photonics for lasing [249], photonic bandgap materials [98], and for studies of light matter interactions [250]. Optical microcavities (MC) have been proposed for applications in threshold-less lasers and quantum information processing. Discrete electronic (QD) and photonic (MC) states can be combined within a single structure to confine electrons and photons in all three dimensions [251]. For instance, CdSe nanocrystals were used as active emitters in planar and 3D optical cavities consisting of micrometer-sized polymeric spheres with diameter values ranging from 1.5  $\mu\text{m}$  to 6  $\mu\text{m}$ . Homogeneously doped or surface-doped microspheres made of PMMA, PS and melamine-formaldehyde were most often used [252,253]. Polymer microspheres allow one to dope the MCs with much higher QD concentrations than, e.g. glass microspheres. The doping is usually performed by partially swelling the spheres in a mixture of solvent and nonsolvent. This technique leads to efficient doping of the subsurface of the polymer spheres where the coupling of the QDs to the cavity modes is at its maximum. Another means of ensuring that the QDs are mainly distributed within the surface region of the cavities is to employ hollow polymeric spheres [249,251]. Such hollow spheres minimize undesirable background luminescence and absorption from the cavity interior. Core-shell structures comprising latex spheres as the core and the semiconductor nanocrystals as the shell can be fabricated by solvent-controlled precipitation [254] or via electrostatic interactions [102]. The former method results in densely packed 15–40 nm QD thick shells, where the amount of QDs precipitated onto the core can be controlled by adjusting the concentration ratio between the QDs and the beads. The latter method can be used to form colloidal stable latexes when the amount of QDs at the latex surface is below 10% or above 100% of the amount needed to form a QD monolayer. Concentrations between 10% and a full monolayer have been seen to cause microsphere aggregation and precipitation. The preparation of functional microparticles is also of interest for applications in photonics [148]. LbL-modified submicron-sized monodisperse polystyrene [255] and melamine-formaldehyde colloids were used as building blocks for colloidal photonic crystals [256,257], as donors in fluorescence energy transfer (FRET)-near-field scanning optical microscopy (NSOM) applications [258], or to prepare “photonic molecules”



**Fig. 24.** (a) A cross-sectional confocal microscopy image of a graded LbL film of CdTe QDs. Small QDs are assembled in the lower part, whereas bigger QDs can be seen in the upper part. (b) A cross-sectional TEM micrograph of the graded LbL film. Reprinted with permission from [264]. Copyright (2001) American Chemical Society.

[259]. The LbL-assembled polymer–QD films have found many interesting applications in memories [260], and non-linear optical materials [261].

By using the LbL approach, one is able to tune the electron and ion transport on a molecular level as well as control the energy transfer [262,263] between the QDs located within each of the layers. Mamedov et al. [264] demonstrated how graded semiconductor films could be obtained using an LbL assembly. Four different CdTe nanoparticles of gradually increasing size (and therefore with emissions ranging from green to red) were used in each subsequent adsorption step, thus creating an effective gradient in the dielectric properties of the assemblies (Fig. 24).

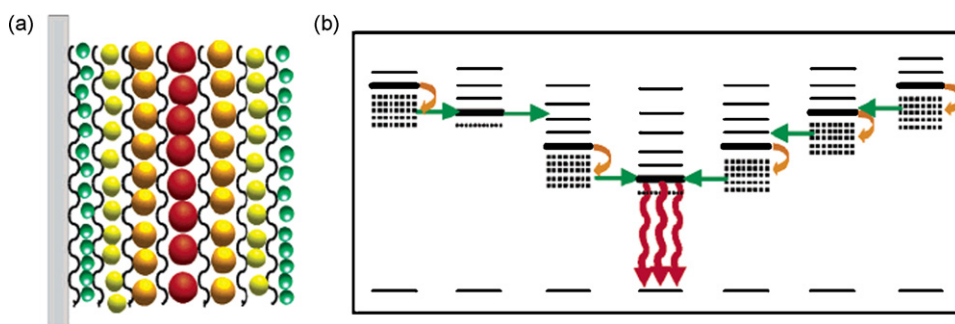
Efficient energy transfer between two CdTe QDs of unequal sizes, positioned in different layers in an LbL assembly was demonstrated [262]. Clever layering of the QDs within the polymer films was used to fabricate QD-based cascade energy transfer devices with high energy transfer rates [265]. In these devices, the exciton energy was transferred from layers comprising smaller nanocrystals (and therefore higher bandgaps) to layers containing bigger crystals (and consequently smaller bandgaps) (Fig. 25). Additional optical processes, such as recycling trapped excitons and avoiding hot excitons, resulted in a very efficient exciton funneling to the parts of the multilayer that contained the biggest nanocrystals [266].

A similar undertaking, but with other nanocrystal types, was reported by Lin et al. [267]. They managed to regu-

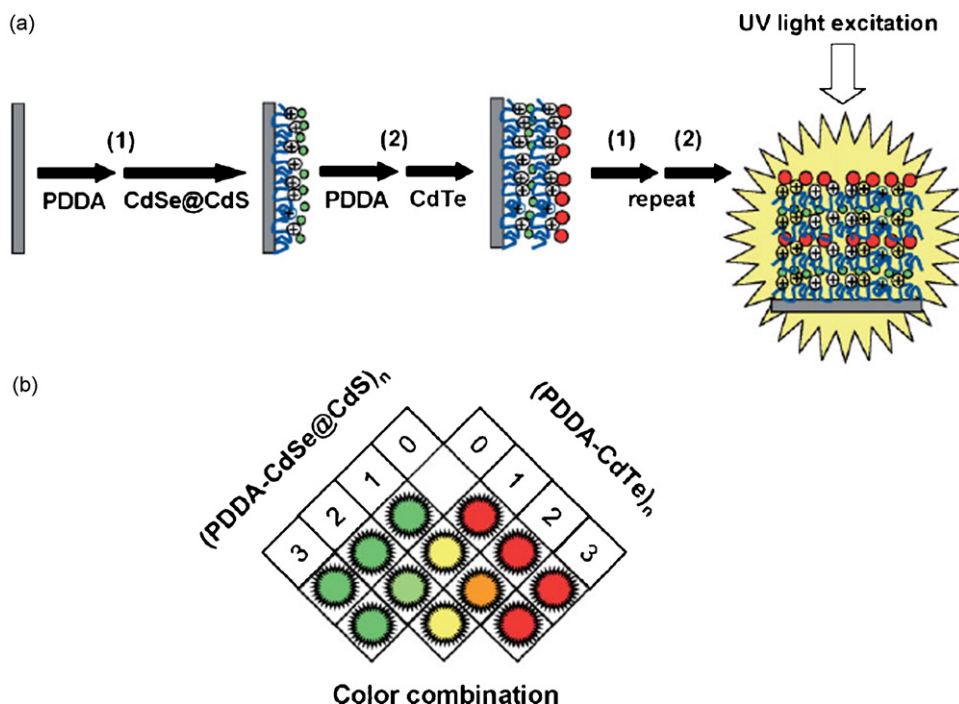
late the degree of fluorescent energy transfer between two types of QDs (CdSe/CdS and CdTe) by controlling the coating sequences of the polyelectrolytes and QDs, as well as the number of the coated bilayers (Fig. 26). This, in turn, allowed them to tune the resulting emission color of the prepared films, from green through yellow to red.

#### 7.2.1. Solar cells

Solar cells are devices that transform solar energy into electric current. An efficient generation of charges must occur in such devices upon absorption of light. The charges then must be transported to the electrodes. In many devices for solar cell applications, the semiconductor nanocrystals mainly serve as photosensitizers for the photogeneration of charges with the charge transfer occurring mainly through the matrix. For instance, the incorporation of QDs (e.g. CdS) in carrier-transporting polymers (e.g. poly(*N*-vinylcarbazole) (PVK) or polyaniline) has proven to enhance the photoinduced charge generation efficiency, while the polymer matrix was responsible for the charge transport [222,268]. Only a small fraction of nanocrystals was typically required (a few weight percent) to sensitize the matrix. PVK is a photostable and efficient hole transport material. It exhibits, however, a low charge generation efficiency in the visible part of the electromagnetic spectrum. Quantum dots embedded in PVK act as photoactive dopants capable of charge injection into the matrix [269]. An attractive feature of PVK is the presence of amine, which



**Fig. 25.** (a) A schematic representation of an LbL-fabricated sample consisting of four differently sized QDs. (b) Cascade band gaps are created and used to facilitate the energy transfer to the biggest nanocrystals. Reprinted with permission from [266]. Copyright (2005) American Chemical Society.



**Fig. 26.** (a) A schematic representation of the LbL fabrication process for a multilayer film comprising two types of QDs. (b) The final colors of the assembled films as a function of the number of each of the assembled bilayers. For example, 2 layers of (PDDA-CdSe@CdS) with 2 layers of (PDDA-CdTe) would result in a yellow emission from the assembled film [267]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

coordinates the CdS surface, leading to an improved charge transfer efficiency. To further improve the device performance, CdS, HgS, or CdSe nanocrystals can be synthesized directly in the PVK matrix [222,224,270,271]. In situ synthesis of nanocrystals resulted in a significant enhancement of the photoconductivity as compared to pure PVK or CdS/PVK blends.

In other types of photovoltaic devices, the nanocrystals may serve as electron acceptors. Such devices take advantage of the good electron acceptor properties and high electron conductivity of the QDs, and the polymer acts as the donor phase with high absorption efficiencies [272]. Semiconductor polymers such as poly(p-phenylene vinylene) (PPV) [238,273], poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene) (MEH-PPV) [225,240,274–276], or poly(3-hexylthiophene) (P3HT) [276] and their derivatives [238] have often been employed in combination with various quantum dots like CdSe, PbSe, PbS or ZnO in the preparation of such devices. The energy levels of the host material and the inorganic phase can be controlled through chemical derivatization of the semiconducting polymers and the size or type of the nanocrystals, respectively [277]. It therefore becomes possible to independently position both the donor and acceptor levels in order to attain high device efficiencies at technologically relevant wavelengths. As recently reported [240,278,280], PbS quantum dots have been utilized to sensitize MEH-PPV into the technologically relevant infrared part of the electromagnetic spectrum.

In all of these devices, charge transfer between the QDs and the polymer is of utmost importance. For an effi-

cient charge transfer between the nanocrystals and the polymers, it is important to control the dispersability of the nanocrystals in the polymer films as well as the morphology and interface of the polymer–QD hybrid materials [232,279]. The dispersability of the QDs in the polymer is directly related to the chemical nature of the ligand on the QD surface, and it is often important to strip the nanocrystals from surface ligands altogether [225]. Some of the surface ligands can be easily stripped by thermal annealing above the glass transition temperature of the polymer matrix. This may, however, result in nanocrystals aggregation. The grafting of electroactive surfactants, such as  $\pi$ -conjugated polymers, could improve the transfer of charges between the nanocrystals and the polymers, as well as the transport of electrons between nearby nanocrystals while maintaining a high dispersability of the QDs inside the polymers. It was shown that end-functionalized poly(thiophene) attached to the nanocrystals enhances the performance of poly(thiophene)/CdSe nanorod solar cells [239]. A phosphonic acid end-functionalized series of regioregular 3-hexyl oligothiophenes was also attached to CdSe nanocrystals [67]. By varying the length of the oligomers, the energy levels between the QDs and the ligands can be adjusted and aligned so as to promote directional energy or charge transfer. The aggregation of QDs in a polymer matrix can also be effectively avoided by using electroactive ligands, such as functionalized oligomeric PPV, attached directly to the nanocrystal surface [80]. To avoid problems with surface ligands, Watt et al. [281–283] developed a method based on the formation



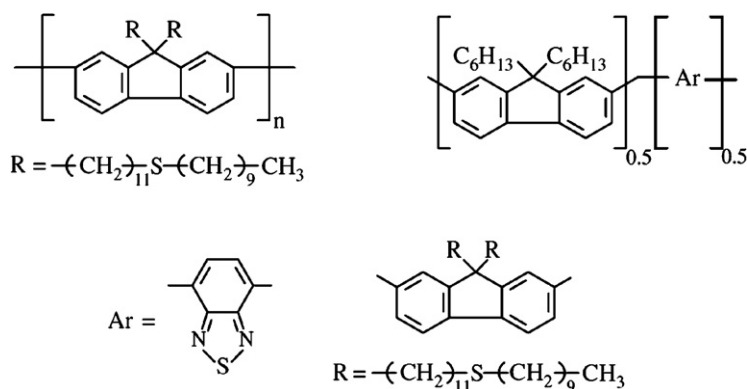


Fig. 27. Sulfide-containing polyfluorene homopolymers and copolymers [50].

of PbS or PbSe in conjugated polymers such as MEH-PPV and P3HT. The devices fabricated from such materials have shown enhanced power conversion efficiencies through an improved hole and electron mobility [284].

### 7.2.2. Light-emitting devices

Hybrid bulk heterojunction devices, such as light-emitting diodes, made of functional polymers and semiconductor nanocrystals, constitute potentially low-cost alternatives to inorganic LEDs. In an early work, Colvin et al. [226] demonstrated how a layered CdSe/PPV nanocomposite can be used to fabricate light-emitting diodes. LEDs are also fabricated by dispersing the QDs in an appropriate polymer matrix (conductive or semiconductive [285]) and depositing the dispersion onto electrodes as thin films by spin-coating [227,232,286,287], by polymerizing the polymer matrix in the presence of QDs [179], or by employing LbL self-assembly [229,231].

In light-emitting devices, the polymer is usually used as a hole or as an electron transporting material to the QDs, which is one of the major prerequisites for such devices. The role of the polymer can also be extended to the effective passivation of the nanocrystal surfaces for

efficient charge injection into the nanocrystals. A rapid charge transfer from polymers to QDs was found to be the main reason for the strong desired quenching of the conjugated polymer luminescence [288,289] although as an alternative mechanism efficient energy transfer from the polymer to the QD can also occur [290,291]. Charged nanocrystals can reduce the aggregation behavior of conjugated polyelectrolytes in thin films via strong electrostatic interactions, thus lowering of the photoluminescence QY due to energy loss via nonradiative decays can be avoided [292]. The size-dependent optical properties of the nanocrystals allow one to use the same fabrication method to obtain different emission wavelengths. Electroluminescent QD/polymer devices emitting in the visible and infrared range of the electromagnetic spectrum have been reported [285,293–295]. Furthermore, full color and white light emission from II–VI semiconductor QD/poly(laurylmethacrylate) nanocomposites was observed [179]. White light LEDs were also realized by blending PVK with CdSe/CdS QDs. The white light emission was in this case due to an incomplete energy transfer from the polymer to the QDs [296].

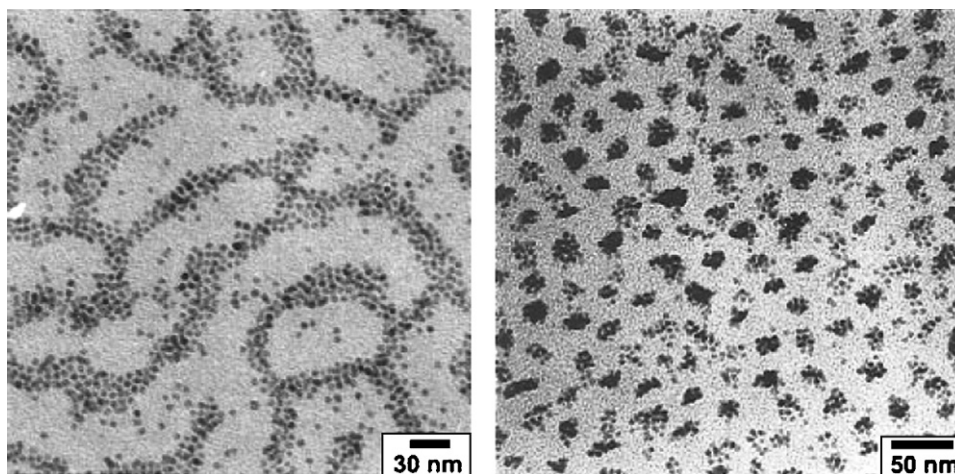


Fig. 28. TEM micrographs of 4.5 nm QDs sequestered to specific domains in (a) a phosphine- and phosphine-oxide-functionalized block copolymer thin film and (b) a microtomed bulk material. Reprinted with permission from [299]. Copyright (1997) American Chemical Society.

In a recent development, Yang et al. have synthesized a series of sulfide-containing polyfluorene homopolymers and copolymers (Fig. 27) [50]. The polymer was shown to effectively replace the TOPO ligands and bind to the QD via the sulfur atom. The oligomeric PPV chains on the QD surface had a profound influence on the optical properties of the PPV/QD blends. While the polymer emission dominated in blends of PPV with ligand-functionalized QDs, it was the emission from the nanocrystals that dominated in the case of blends with PPV-functionalized QDs. Such a behavior was attributed to enhanced energy transfer between the conjugated ligand and the quantum dot, facilitated by the direct coupling of the PPV chains to the QD surface [297]. Moreover, single quantum dot measurements revealed that the “blinking” of the quantum dots, i.e. the intermittent behavior of the luminescence, can be suppressed by controlling the PPV surface coverage [298].

In another effort to control the particle morphology in the polymers, Mattoussi et al. [232] employed a dual-function copolymer consisting of an electron-conducting part and a passivating part containing phosphine chemical groups. TOPO-coated CdSe QDs were sequestered into phosphine-containing domains of the diblock copolymer. The phosphine groups effectively passivated the surfaces of bare and coated QDs, and fluorescence monitoring showed that this prevented the luminescence quenching of the QDs from occurring [299,300]. Under suitable conditions, the copolymers underwent microphase separation and the QDs were predominantly located within the phosphine-containing microdomains (Fig. 28).

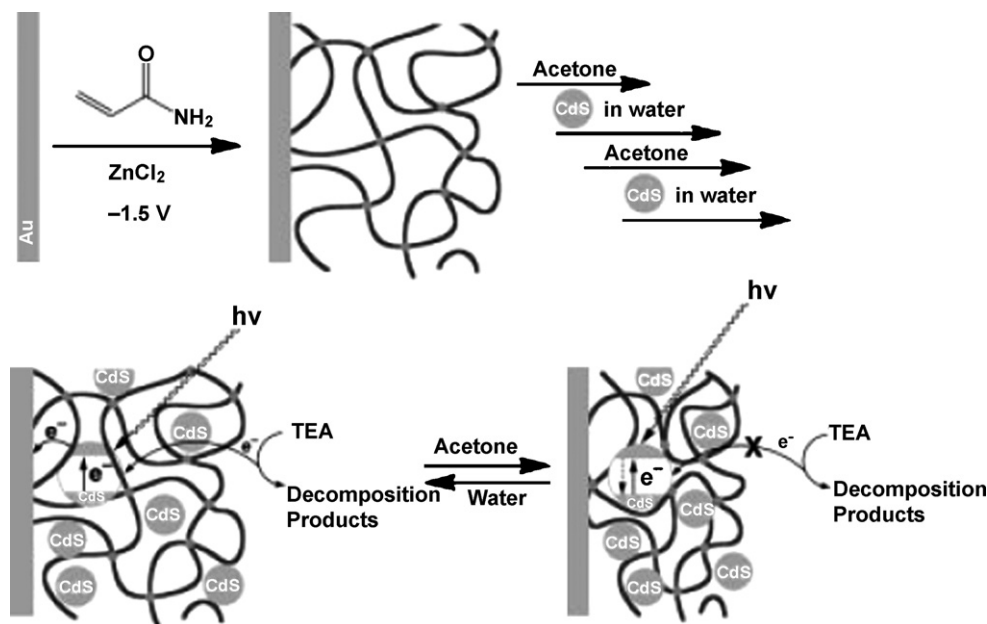
### 7.2.3. Photorefractive materials

Photorefractive materials are based on a spatial modulation of the refractive index in an electro-optically active

material due to the redistribution of charge carriers that are photogenerated under non-uniform illumination. In order for this to take place, the following steps are required: (1) photogeneration of charge carriers, (2) diffusion or drift of charges, (3) trapping of the charges in the region of low light intensities, and finally (4) change in the refractive index due to the excess of charges. In photorefractive materials, QDs may serve as photosensitizers [244–248,301]. Photorefractive materials that are active in the visible range can be realized by mixing polymers such as PVK with, e.g. CdS, CdSe, or PbS nanoparticles below the percolation threshold (<15%). Winiarz et al. [246] and Choudhury et al. [302] have reported QD/polymer photorefractive materials with a spectral response at the telecommunication wavelengths. These materials were obtained by incorporating narrow bandgap semiconductor (HgS) nanocrystals into PVK.

### 7.3. Sensing applications

Quantum dots were often used in various sensing schemes. Most of these schemes involved QD/protein bioconjugates and energy transfer processes for chemical sensing, less often for physical sensing. Despite its many advantages, the combination of polymers with QDs for sensing applications is far less explored. Properly structured QD/polymer materials can induce biocompatibility to the QDs, which may otherwise be cytotoxic [303]. In combination with active biological materials, like enzymes, effective sensors of chemical or biological compounds can be fabricated. For example, the LbL concept can be easily combined with biomaterials for biosensing [304,305]. Constantine et al. [305] used organophosphorous hydrolase (OPH) polycations in an LbL assembly with glycolic acid-modified CdSe QDs for the detection of paraoxon, a



**Fig. 29.** The incorporation of CdS QDs into electropolymerized acrylamide films by the “breathing-in” method. First, the acrylamide monomers are electropolymerized at the gold surface. The quantum dots are then incorporated into the polymer film by the “breathing-in” method, which is based on a cyclic swelling and de-swelling of the polymer film in suitable solvents [307]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

toxic organophosphorus compound used in pesticides and insecticides. Paraoxon can be hydrolyzed by OPH, releasing *p*-nitrophenol, which quenches the emission of the QDs.

Sensing approaches based on QD/responsive polymer thin films were also realized [306]. CdS–nanoparticle/polyacrylamide hybrid thin films were prepared on Au electrodes and the solvent-induced, switchable photoelectrochemical functions of the matrices were studied [307]. The polymer films were prepared by electropolymerization of polyacrylamide on the electrode followed by the incorporation of CdS nanoparticles into the gel by swelling (Fig. 29). In this method, sometimes called the breathing-in method, the gel repeatedly shrinks in one solvent and subsequently swells in solutions of other solvent containing suspended nanocrystals. By repeating this procedure, the amount of nanocrystals in the films can, to a certain extent, be controlled. The QDs are trapped in the gels by what is presumed to be physical entanglements with the gel network.

## 8. Conclusions and outlook

The investigation and preparation of well-defined polymer–QD nanocomposites is currently a rapidly expanding field of research. The research efforts during the last decade have led to a host of new strategies for the fabrication of QD/polymer hybrid nanomaterials. Regardless of the final hybrid structure, three main groups of methods used to obtain polymer–nanocrystal materials can be identified. The first group of methods relies on the direct synthesis of the nanocrystals in the presence of polymers. The polymers act as stabilizers of the growing crystals, or provide a restricted spatial environment for the control of the particle size and size distribution. The reaction site, i.e. the place where the nanocrystal seeds form, could be controlled to some extent by proper engineering of the polymer's functional groups, morphology and self-assembly. The second group of preparation methods deals with the polymer and the nanocrystal syntheses separately and the hybrids are obtained subsequently by using various molecular assembly strategies, like layer-by-layer, simple mixing, and other methods of conjugation. These methods take advantage of the recent developments in the reliable and reproducible synthesis of large amounts of uniformly sized nanocrystals. The resulting high-brightness QDs are then incorporated into the polymers. Finally, the third group of methods is based on the direct functionalization of the nanocrystals with macromolecules. This approach allows for obtaining precisely engineered, designer molecular nanomaterials.

Regarding direct synthesis of the nanocrystals in the presence of polymers most of the novel and exciting hybrids are hard, if not impossible, to synthesize in situ. Thus decoupling the synthesis of the nanocrystals from that of the polymers seems desirable. During the last few years, new QDs with unique properties have been synthesized. Although the synthesis of dedicated polymers with tailored properties has outpaced the progress in the nanoparticle synthesis, so far essentially only a few polymers (and their derivatives) like PS, PMMA, PNI-

PAM, PVK, or MEH-PPV have been considered. This means that instead of tailoring polymers for in situ synthesis of QDs, one should rather focus on the development of suitable approaches for the incorporation of high-quality QDs into engineered polymers exhibiting molecularly controlled architectures. This also underlines the importance of the understanding and control of secondary and higher order structures in the corresponding hybrids. The rich chemistry and physics of block copolymers, for example, offers the possibility to obtain nanocomposite materials with morphologies otherwise impossible to obtain with homopolymers. Thus spatial control of QDs inside the polymer matrix on different lengthscales ranging from nanometers to micrometers calls for more attention.

Although some progress has been made in direct functionalization of QDs with polymers, whether by coating the QDs by presynthesized polymers or by growing polymers directly from the QD surface, many issues remain to be solved. For example, the grafting density of polymers on the QDs should be better controlled for it plays a major role in the final properties of the assemblies, as demonstrated by single QD fluorescence experiments [308]. Our knowledge of the electronic processes across the QD/polymer graft interfaces is still limited and more research work should be performed on such single QD systems. If electroactive polymers are to be grafted to/from the QDs surface, in addition to grafting density, the polymer chain length, its polydispersity, grafting homogeneity and conformation are of importance. Corresponding structural control will be indispensable in the design of optoelectronic devices.

The integration of polymer–QD nanocomposites into optoelectronic devices, or in devices interfaced with biomacromolecular components for diagnostic and therapeutic applications, are only just starting to emerge. More detailed investigations and optimization procedures are still needed before widespread commercialization. Integration of QD/polymer hybrid structures in devices is device-specific and corresponds to the next level of engineered structural hierarchy. Issues include the method of attachment (covalent, physical, supramolecular, etc.), device/QD polymer hybrid interfacing bottom up (molecular engineering) or top down (e.g. spin-coating), signal transduction, environmental sensitivity, retaining biofunction in a non-invasive manner, etc. For example, there is an ongoing debate on the toxicity of nanoscale materials in general, and that of the QDs in particular. It is known that surface chemistry largely determines the toxicity of QDs [309]. Coating QDs with polymeric shells holds a great promise in reducing the nanoparticles cytotoxic effects [310].

The field of QD/polymer assemblies is surely to continue to grow. Most of the development in polymer–QD materials has happened during the last decade and there is a lot of room for research. Parallel development in polymer and QD synthesis and novel fabrication methods would result in novel performance materials with truly unique properties. For this to happen, researchers from diverse fields of science like chemistry, physics, and biology should work in unison. This review is intended for these researchers to be able to identify common grounds and challenges which lay ahead.

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