Review

Polymer-Nanocrystal Hybrid Materials for Light Conversion Applications

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Abstract: In this mini-review we report on current developments of hybrid materials based on semiconductor nanocrystals integrated into polymer matrices for direct light conversion, their present limitations, as well as their high potential for future applications.

Keywords: semiconductor nanocrystals; polymer nanocrystal hybrid materials; light conversion; white light generation

1. General Introduction

1.1. Semiconductor Nanocrystals

Semiconductor nanocrystals (NCs) with sizes ranging between 2 and 10 nm present unique size-dependent optical properties based on the quantum size effect [1,2] opening new doors for application in photovoltaics (PV) [3,4], lasing [5,6], light emitting diodes (LEDs) [7] and other opto-electronic devices [8,9], thermoelectric applications [10], memory devices [11] and fluorescence biological labeling [12–14].

Tailoring the properties of these materials can be achieved by simply tuning the particle size without introducing any changes in the chemical composition, or by changing the material composition.

Various shapes starting from spherical NCs, also called Quantum dots (QDs), rods, wires and tetrapods are available by adjusting the synthesis reaction parameters [15]. By reducing the semiconductor size down to the NC regime, a characteristic blue shift of the band gap appears, and a widening of the band gap with a discrete level structure develops as a result of "quantum size effect" in these structures [2]. In Figure 1 the absorption and photoluminescence spectra of CdSe QDs of different sizes are shown demonstrating this effect.

Figure 1. Left, absorption spectra of differently sized CdSe NCs. Right, corresponding PL spectra representing deeper red, red, orange, yellow, green and blue (from right to left) emitting CdSe cluster [16] and NCs [17,18] under UV excitation at 380 nm.
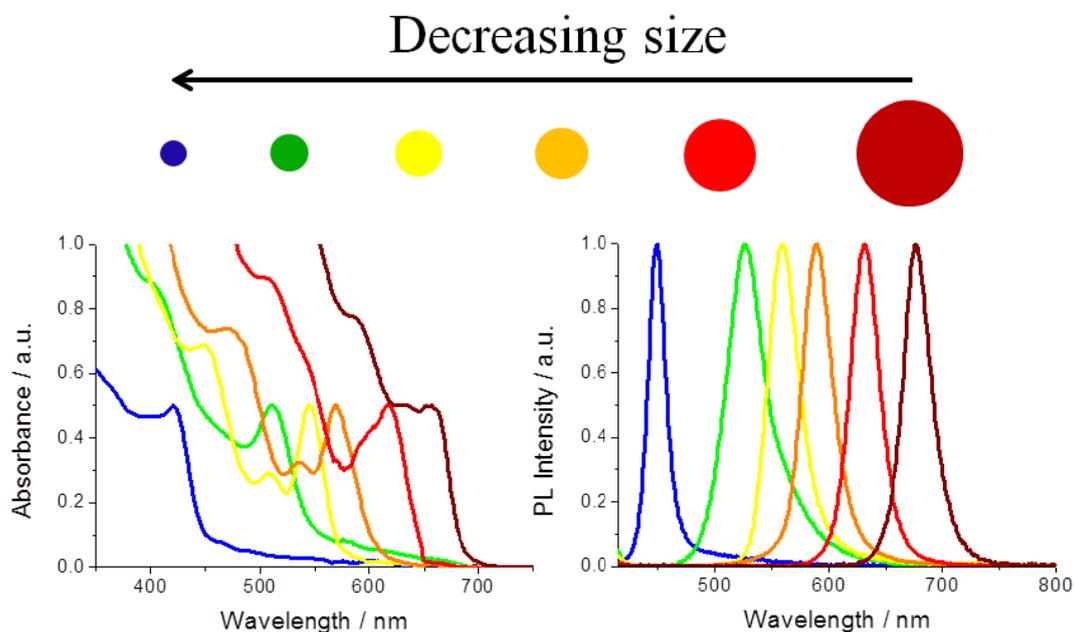
Figure 2. Size- and material-dependent emission spectra of several colloidal semiconductor NCs in a variety of sizes. The blue spectra represent different sizes of CdSe NCs with diameters of 2.1, 2.4, 3.1, 3.6, and 4.6 nm (from right to left). The green spectra represent InP nanocrystals with diameters of 3.0, 3.5, and 4.6 nm. The red spectra are related to InAs NCs with diameters of 2.8, 3.6, 4.6, and 6.0 nm (The image is reproduced from [12] with permission).
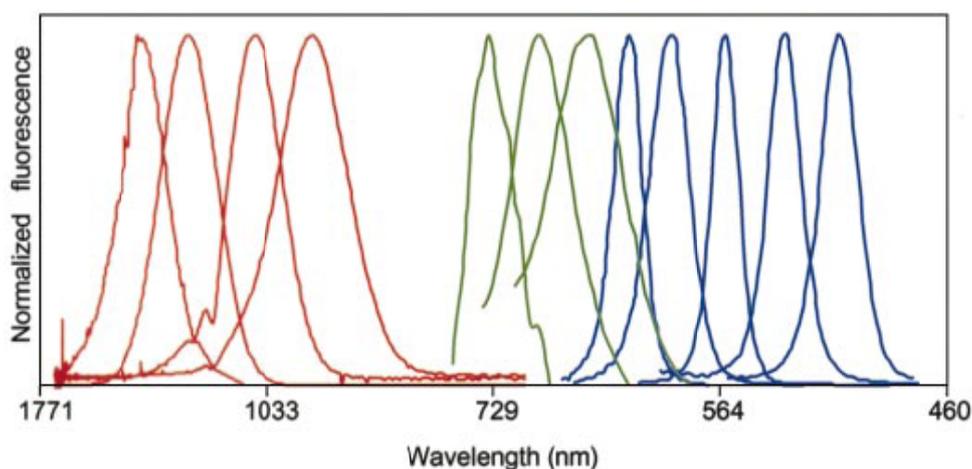
By changing the material composition as well as the size of the individual NCs the range for PL emission can be tuned covering the entire optical spectrum starting from UV to the NIR (Figure 2). The high quantum yield (QY), extraordinary photostability, pure color and the PL emission tunabilty of semiconductor NCs make them an obvious target of investigation for applications of white light generation. Examples for light emitting NCs are ZnO, CdS, CdSe, CdTe and CdSe core, core-shell or core-multishell structures which absorb UV or blue light and convert it into light of longer wavelengths.

1.2. Semiconductor NCs/Polymer Nanocomposites

Colloidal semiconductor NCs can form various hybrid materials by e.g., being integrated into different host materials including polymers. The incorporation of NCs into solid matrices from their growth solution is of interest for technologically useful applications as well as for fundamental studies of NC-matrix interactions. Polymers offer opportunities for flexible, lightweight, and mechanically stable NC nanocomposites [19]. Semiconductor NC-polymer composites combine the advantages of both components and have been realized for light emitting displays [7], light conversion layer [20] such as LED covers or in solar concentrators [21], optical bar coding [22], photocatalyst [23] and photovoltaics [4]. The main challenge in the preparation of NC-polymer composites is preventing a macroscopic phase separation and the aggregation of NCs in the hybrid material which would lead to film inhomogeneities and fluorescent quenching effects limiting the respective optical device performance.

Colvin *et al.* reported on the first hybrid NC-polymer light emitting diodes (LEDs) in 1994 [7]. A thin layer of CdSe NCs was deposited on a conductive support, and combined with a 100 nm thick soluble poly(p-phenylenevinylene) PPV derivative layer. Since then, a lot of progress has been achieved for optimizing all parameters of NC-polymer hybrid LEDs. The introduction of CdSe@CdS core-shell NCs made a significant improvement for the NCs-polymer hybrid LED [24]. The efficiency was increased twenty times by increasing the efficiency of the radiative recombination and device internal quantum efficiency, while the lifetime was increased as well by a factor of hundred. Other potential application for NC-polymer based LEDs are offering large area lighting systems and backlighting for flat panel displays. Such applications require LEDs emitting multi-color light or white light. Recently, Wood *et al.* fabricated a full color AC-driven display based on inject-printed NCs/polymer composites [25]. Semiconductor colloidal NCs integrated in solvent based polymers have a potential to compete with other technologies such as OLEDs and full-color quantum dot displays [26]. The lifetime of hybrid organic-NC based LED devices is still limited to some extend by the instability of the metal contacts and degradation of organic components under high current operation conditions [11]. In order to avoid such limitations, some non-conductive polymers are combined with semiconductor NCs forming a photoluminescent conversion layer for commercially available e.g., blue LEDs [20,27]. In the following we concentrate on the description of NC-polymer hybrid materials based on non photoactive polymers for light conversion applications.

The first down-conversion LED was achieved by coating a transparent CdSe@ZnS core-shell polylaurylmethacrylate (PLMA) hybrid composite on the surface of a GaN light-emitting diode. Saturated-color light with different wavelengths has been generated by tuning the size of NCs (Figure 3).

Figure 3. GaN LED emitting blue light originally at 425 nm covered with a NC-polymer hybrid film. Due to the light conversion layer the emission is changed to ~590 nm (the images are reproduced from [20] with permission).
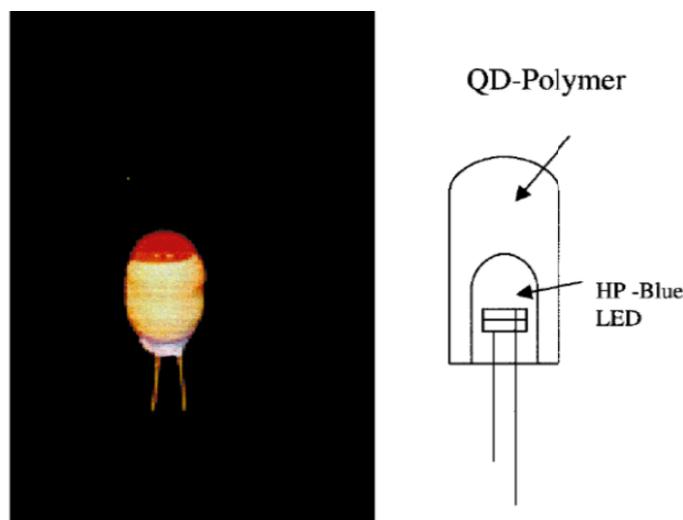
2. Semiconductor NC Polymer Hybrid Materials Based on Non-Photoactive Polymers

The development of blue and UV emitting diodes based on GaInN or GaN led to a new revolution in lightning. In combination with different materials as phosphors full color displays and white light emitting devices could be achieved [27,28]. These days LEDs are the most promising candidates for replacing traditional energy-inefficient incandescent bulbs and halogen lamps. With new generations of more energy-efficient RGB LEDs or white LED illumination systems, around 90% of the energy could be saved compared if conventional light bulbs are used [29]. There is an alternative approach to generate white light emission, based on the combination of blue, green and red emitting LEDs. Multichip LEDs offer a good color rendering index and high energy efficiency [27]. Hoverer, it demands very high production costs and requires a complicated lighting and electronic system to adjust the light intensity. Therefore, the phosphor conversion LED is the most promising approach for achieving a simple and low cost white light emission. Because of this, most common commercial white LEDs are based on blue-GaInN LEDs together with yellow emitting Ce activated yttrium aluminum phosphor (YAG:Ce). YAG:Ce phosphors absorb a significant part of the blue light from the GaInN chip and convert it into yellow light. The mixing of blue and yellow light generates white light. However, the broad and red-deficient emission spectrum of the YAG:Ce phosphor and the color purity varies with the input power limiting the color rending index (CRI) to ~80. The correlated color temperature (CCT) of such YAG:Ce phosphor based LEDs are limited to 4,000–8,000 K, which corresponds to the emission of neutral- and cool-white light [30]. Especially, the illumination efficiency of the device is currently limited by the efficiency of the converting phosphor and the thermal instability. To overcome these problems, various phosphors have been examined in white LED applications. NC based phosphors are a new and emerging alternative for the existing YAG:Ce based phosphors. The NCs minimize light scattering and can be uniformly dispersed into many kinds of polymers for easy packaging and handling. The shortcomings of thermal quenching and reabsorption could be overcome by using transparent polymer hosts and the realization of multilayers where each

layer contains one light emitting NC components. For example, white light emission with CRI over 90 was achieved by a novel CdSe NCs biphenylperfluorocylcobutyl (BP-PFCB) polymer hybrid layer [31]. Figure 4 shows the typical emission spectrum of a commercially available white light emitting converter LED in comparison with a commercial UV LED covered by an NC-polymer hybrid film leading to white light emission with a CRI value of 93.

Figure 4. (**a**) Emission spectrum of a commercially available white light emitting LED from Osram AG (PARATHOM PAR16, CRI is 72.7, CCT is around 6,200 K). (**b**) Absorption and emission spectra of CdSe based white-light emitting NC mixtures (CRI is 93). The dashed lines represent the absorbance spectra, while the continuous lines show the emission spectra of the CdSe NCs. The red spectra are NCs solvated in toluene; the blue spectra are 12% w/w NCs in BP-PFCB. The feature at 400 nm (blue solid line) is an artifact due to the tail of the excitation source's emission, and the emission feature at 730 nm is a 2nd order diffraction peak introduced by the detection setup. The inset is a true color photograph of a 365 nm LED coated with a CdSe NC-BP-PFCB hybrid film (Figure 4(b) is reproduced from [31] with permission).
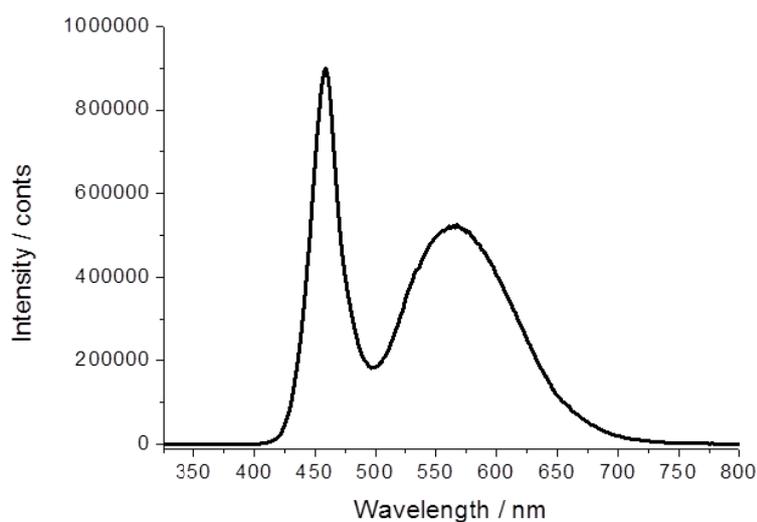
(**a**)
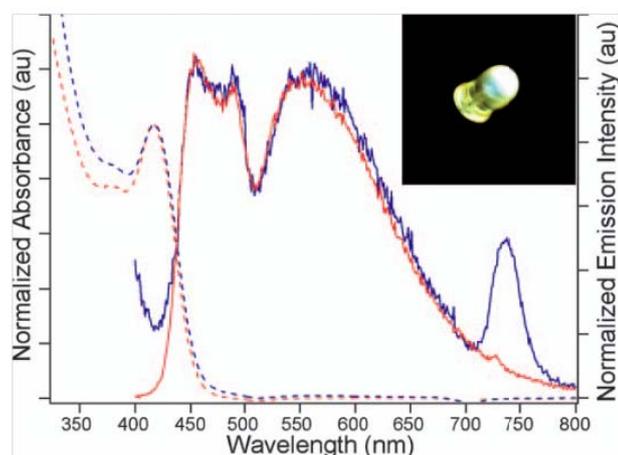
(**b**)

The chemical structure of various polymers utilized as polymeric hosts for luminescent semiconductor NCs are shown in Figure 5.

> **Figure 5.** Chemical structures of suitable polymer hosts for the integration of semiconductor NCs. Poly(methyl methacrylate) (PMMA), PLMA, Nylon, Poly(lauryl methacrylate-*co*-ethylene glycol dimethacrylate) (P(LMA-*co*-EGDM), Cellulose triacetate (CTA), and BP-PFCB.

PMMA

P(LMA-co-*EGDM*)

PLMA

CTA

Nylon

BP-PFCB
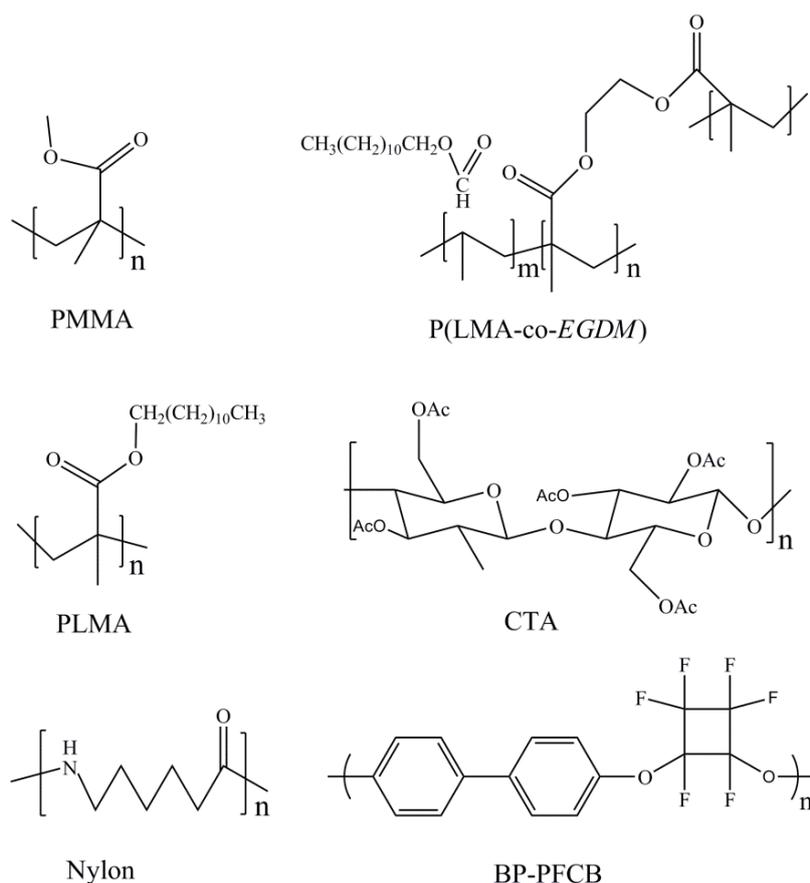
3. Synthesis Approaches for NC Polymer Based Hybrid Materials

There are in principle three distinguishable approaches for obtaining polymer NC hybrid materials.

3.1. Integration of as Synthesized Semiconductor NCs into Polymers by Physical Mixing

Physical mixing of NC solutions and polymer solutions is a first obvious approach for obtaining NC-polymer hybrid materials, especially for thin films. Even when serious chemical attacks to the NC surface are avoided during the solution mixing, PL QY is often reduced by the agglomeration of NCs due to phase segregation processes. An example is shown in Figure 6. Physical mixing is often used with organic soluble polymers, such as PMMA [29,31], cellulose [23,32] and so on. In order to maintain or even increase the PL QY, additional protective shells e.g., out of CdS [32], ZnS [20] and/or silica [33] are utilized for covering the core NCs. Bomm *et al.* [32] prepared CdSe@CdS NCs and cellulose triacetate (CTA) nanocomposites with a PL OY of 52% by using this physical mixing

method. CdSe@CdS core@shell nanorods (NRs) were dispersed in a mixture of $CH_2Cl_2/CHCl_3$ (1:1) containing 2.5 wt % CTA by ultrasound treatment. The nanorod/polymer-solution was drop-casted on a 3 mm thick glass-substrate. The 9–15 μm thin CTA nanocomposite layers containing were obtained directly on glass. Figure 6 shows TEM images of such a CdSe@CdS NRs/CTA nanocomposite film.

Figure 6. (**a**) TEM image of a cellulose triacetate (CTA) nanocomposite layer containing 2 wt % CdSe@CdS core@shell nanorods (NRs) (**b**) TEM image of (a) at higher magnification showing the agglomeration of NRs in the polymer film (The figures are reproduced from [32] with permission).
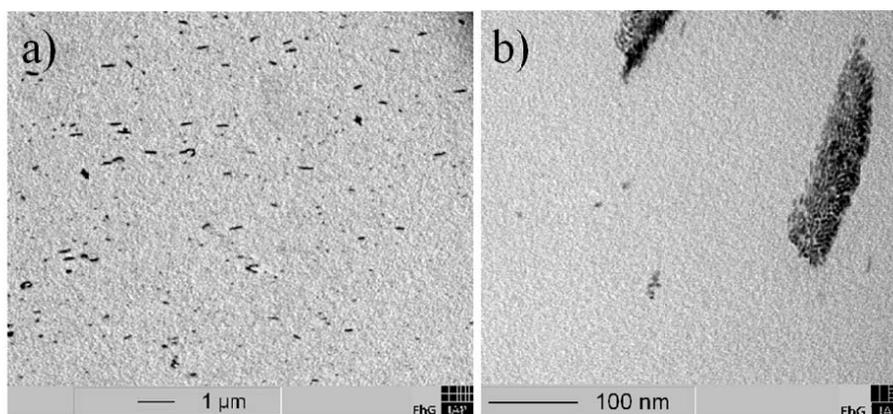
3.2. In-Situ *Synthesis of Semiconductor NCs in the Presence of Polymers*

Typically, here the preparation procedure is divided into two steps. In a first step, organometallic precursors for NCs are introduced into polymer matrices by simple mixing the precursors and the polymer together in a common solvent. In a second step, the mixtures of NC precursors and polymer are exposed to gas or chalcogenide solution [34] and/or simply heated up. Since the infinite crystal growth are limited by the polymer matrices, only nanometer-sized semiconductors crystals are obtained and remain in the polymer composite. Haggata *et al.* report on a method for the preparation od CdS, ZnS, CdSe and ZnSe NCs in a polymer matrix [35–37]. A carefully controlled reaction temperature and suitable choice of solvent was found to have a dramatic effect on the size of the resulting particles. CdS, CdSe, ZnS or ZnSe NCs for example can be formed after $ZnMe_2$ was introduced in a soluble pyridyl polymer adduct (a polymer that contains nitrogen and dimethylcadmium or dimethylzinc) and after reacting with H_2Se or H_2S ZnS and ZnSe NCs were formed respectively. The formation of the resulting NCs-polymer hybrid materials are shown schematically in Figure 7.

Within this *in-situ* synthesis method a control over the size and shape of semiconductor NCs within the polymer matrices was not achieved, and the photoluminescence QY of the NCs was quite low. For example the photoluminescence QY of CdSe NCs obtained by this method was less than 10%, containing a high degree of defect states visible by an additional broad red-shifted luminescence signal in the PL spectrum.

Figure 7. Formation of the 2PySiPB adduct and the reaction of the polymer adduct with hydrogen sulfide. In a 1st step, organometallic precursors of (ZnMe$_2$) and a 2-methylpyridyl derivative were mixed together in the solvent. In a 2nd step, the formed polymer adduct was exposed to H$_2$S. The reaction of ZnMe$_2$ and H$_2$S had been carried out in the presence of polymer and yielded to ZnS NCs (The figure is reproduced from [35] with permission).
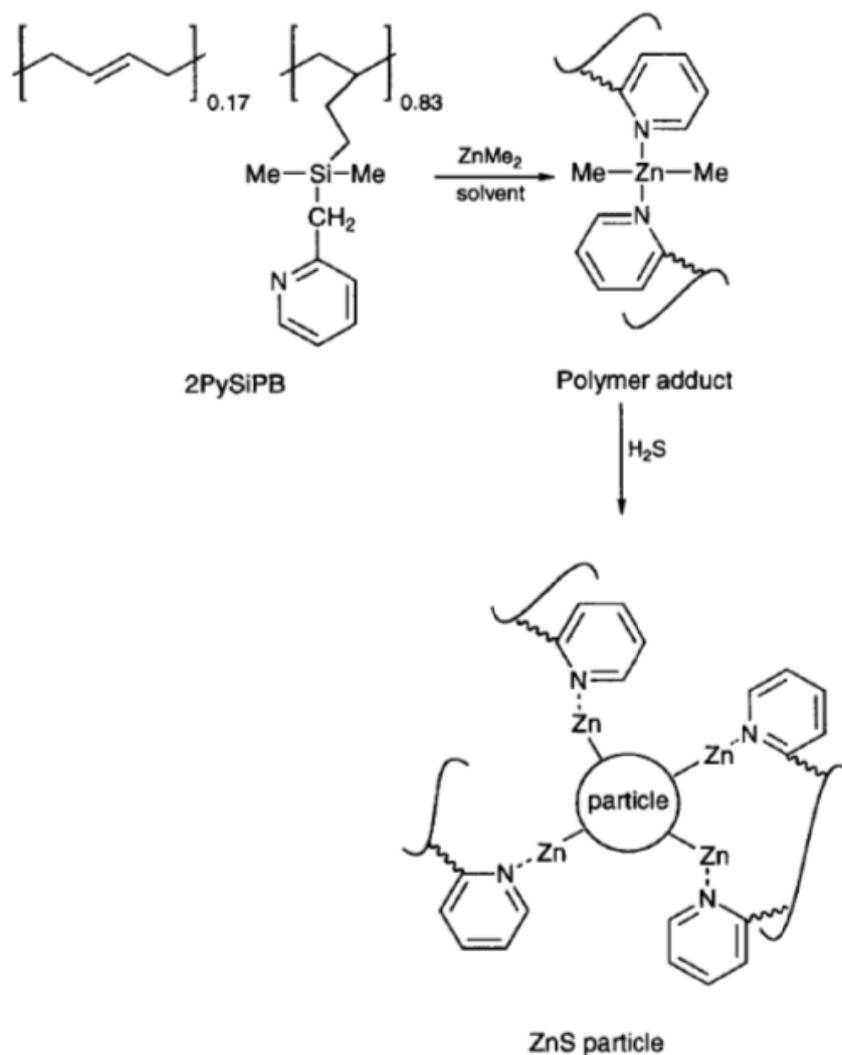
3.3. Polymerization Reaction in the Presence of Semiconductor NCs

Here, the direct polymerization of organic monomers in the presence of NCs is performed to form the NC-polymer hybrid material *in-situ*. The chemical attack from e.g., radicals during polymerization reactions and the aggregation of NCs within the polymer are the main causes for the photoluminescence quenching of semiconductor NCs in this hybrid material. Often the NCs are synthesized with an additional protective shell out of a higher bandgap material [20,32] or out of silica [33]. An optically transparent polymer is also required for utilizing the hybrid materials for light conversion. Bawendi *et al.* have succeeded in fabricating transparent polymer composites out of CdSe@ZnS NCs and PLMA by radical polymerization of monomers. In their case the long alkyl side branches of PLMA could efficiently avoid the aggregation and phase separation of NCs [34].

Additionally the protecting trioctylphosphine (TOP) ligand was also used to prevent the agglomeration and chemical attack on CdSe/ZnS QDs. Woelfle *et al.* introduced a poly(methyl methacrylate) (PMMA) compatible ionic liquid to protect the CdSe/ZnS QDs [38]. However, the chemical attack during the thermal polymerization process could not be completely avoided. In both cases the resulting nanocomposites exhibited photoluminescence QYs of less than 40%.

Recently, Bomm *et al.* reported a new method to incorporate CdSe@CdS core @shell nanorods into P(LMA-*co*-EGDM) by UV-polymerization lauryl methacrylate (LMA) monomers with the cross-linking agent ethylene glycol dimethacrylate (EGDM) monomers in the presence of the CdS@CdS NRs [32]. They found that a high concentration of a liquid UV-initiator led to a significant decrease of PL QY. 70% PL QY was observed for this hybrid material by using only 0.1 wt % of a UV-initiator. Figure 8 shows the effect of the concentration of the UV-initiator on the PL behavior of the nanocomposites. A decrease in PL QY is observed for high UV-initiator concentration. After incorporation of NCs into polymer, to maintain the optical properties of NCs in the hybrid materials is of outermost importance for light conversion application. As we mentioned before, the NCs phase separation and agglomeration, which could significantly reduce the transparency and PL QY of the NCs/polymer hybrid, should be avoided. NCs should be homogenously distributed in the polymer matrix without forming agglomerates. TEM investigation were carried out on this CdSe@CdS NR/P(LMA-*co*-EGDM) nanocomposites confirming the absence of agglomerates within the hybrid material (Figure 9).

Figure 8. Absorption and PL spectra of CdSe@CdS NR/P(LMA-*co*-EGDM) composites containing 0.05 wt % NRs (aspect ratio 6:1) with low (0.1 wt %, solid line) and high (0.5 wt %, dotted line) concentrations of the UV-initiator. (The figure is reproduced from [32] with permission).
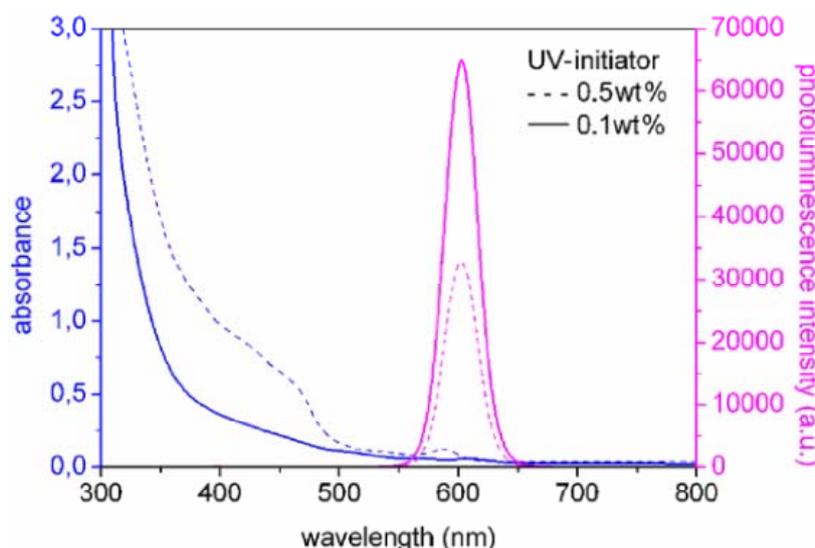
Figure 9. (**a**) TEM image of CdSe/CdS nanorods (aspect ratio 6) after synthesis. (**b**) TEM image of a CdSe/CdS NR/P(LMA-*co*-EGDM) composite film. (The images are reproduced from [32] with permission).
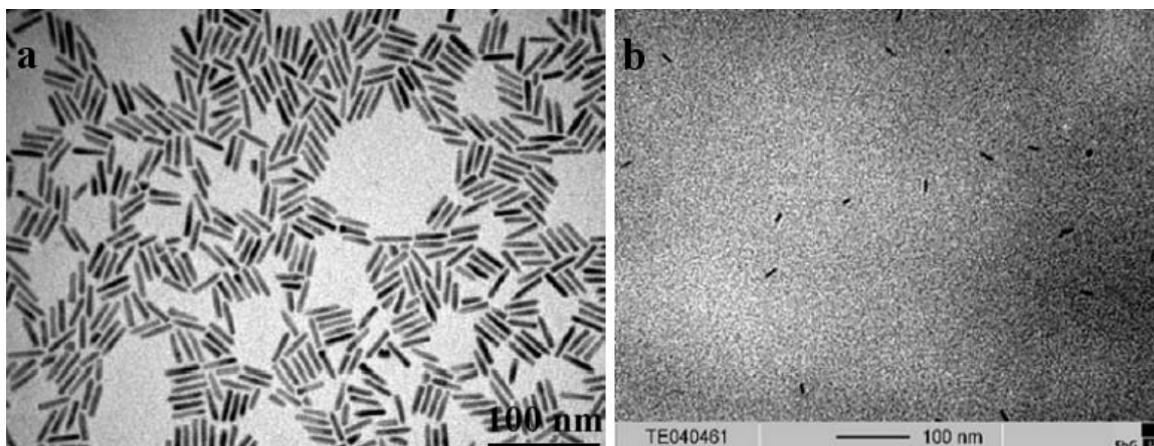
Without an additional protecting shell for the CdSe core material, the QY of CdSe-PMMA or CdSe-BP-PFCB hybrid materials is rather limited. Very recently, we developed a simple reproducible and up-scalable one pot approach for the incorporation of crude CdSe core QDs into nylon without the need of further purification steps. 60% PL QY was reached by this CdSe core NCs nylon composite [18]. No significant loss in PL intensity was observed for the hybrid material compared to NC solutions and no additional protective shell was needed for the NCs which makes the process easy and up-scalable and. In Figure 10(a) the principle of the *in-situ* polymerization process of nylon in the presence of CdSe QDs is shown. The resulting hybrid material is moldable in any shape, transparent and highly luminescent (Figure 10(b)). As it is depicted in Figure 10(a), the polymerization of 6-aminocaproic acid monomers was performed at 220–250 °C in the presence of as-prepared unpurified TOPO and HDA capped core CdSe QDs using a straight forward process under nitrogen atmosphere [18]. The excess ligand molecules are separated during solidification due to phase separation between the QD-nylon phase and the ligand phase and can be easily removed. Therefore even unpurified crude QDs can be used directly after synthesis without applying any extra purification step. Differently sized QDs can be incorporated into the nylon polymer resulting in different color emitting hybrid materials and laser scanning microscopical (LSM) investigation of the hybrid films revealed a homogenious PL emission at the microscopic level [18]. The transparency of the resulting product can be increased by fast cooling of the liquid phase. The QD hybrid materials can be processed while kept in liquid phase above 150 °C and different forms and shapes are available. After incorporation of the QDs into the polymer matrix, no significant loss of PL QY was observed.

Another successful approach for obtaining functional NC-polymer hybrid films is the attachment of polymerizable capping ligands directly onto the NC surface, which can lead to a strong binding of NCs to the resulting polymer matrices. Zhang *et al.* capped octadecyl-p-vinyl-benzyl dimethylammonium chloride (OVDAC) on CdTe NCs in aqueous solution via electrostatic interactions [39]. CdTe NC-polymer bulk composites were obtained after the radical polymerization reaction was induced by azobis-isobutyronitrile (AIBN) as initiator. The phase separation and agglomeration of the NCs from the polymer host was avoided by the strong attachment of CdTe NCs to the polymer matrix during

polymerization. This approach can be used for a wide range of monomers, such as styrene and methyl methacrylate based ones.

Figure 10. (**a**) Schematic illustration of the *in-situ* polymerization reaction of 6-aminocaproic acid in the presence of as synthesized CdSe QDs leading to the CdSe QD-nylon hybridmaterial, (**b**) A photograph of a thin transparent QD-nylon hybridfilm with and without UV excitation at 312 nm is displayed.
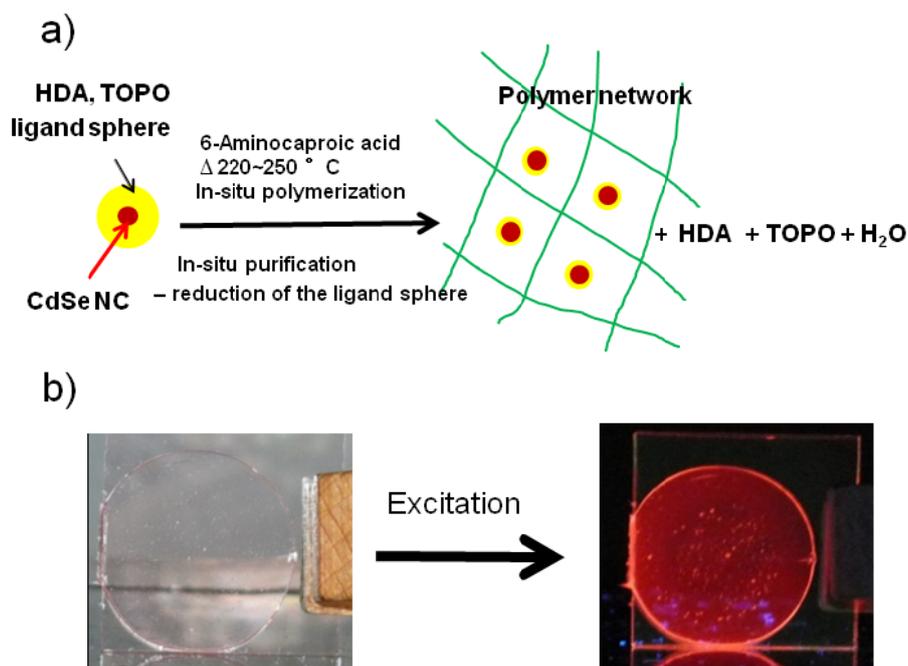
4. Applications of Luminescent NC-Polymer Hybrid Materials

4.1. White Light Generation

Nowadays, 20% of the electricity is globally consumed for lighting [30]. Especially, for indoor applications in homes, office, *etc.*, the lighting is responsible for half of total electricity consumption [30]. The widespread use of solid state based lighting is predicted to save 50% of the energy consumption for lighting [30]. Theoretically, the white LED could reach a high CRI value around 90 and a luminous efficiency higher than 350 lm/W. However, CRI of the commercial white LEDs are limited up to 80 for now [40,41]. A warm white LED with a CRI of 89 and a luminous efficiency of 274 lm/W$_{opt}$ at a CCT of 3,100 K has been obtain by using nitride-based Eu^{2+} phosphors in combination with a blue LED [40] which is the best result achieved so far. Nizamoglu *et al.* reported a photometric model and proposed a new design for white light LEDs [30,42]. They experimentally demonstrated warm-white LEDs combined with nanophosphors based on CdSe@ZnS core-shell NCs on a LED chip to achieve luminous efficiency higher than 350 lm/W$_{opt}$ with a CRI of 89.2 at a CCT < 3,000 K. This result demonstrates that semiconductor NCs have a promising high capability for the generation of warm white light. During the last decade, lots of efforts were devoted for optimizing the white light emission

by NC-/hybrid materials. Current research focuses on two directions, one is to increase the quality of the emission color (CRI and CCT), and another is to obtain higher luminescence efficiency.

For obtaining a good emission color, the most common approach is mixing different emitting NCs in the polymer. Chung *et al.* reported a white emission by using mixtures of differently sized CdSe core NCs incorporated in PMMA as a phosphor [27]. The white LED was fabricated by covering a 460 nm emitting blue LED with a CdSe NC-PMMA nanocomposite layer. Two white light emitting realizations were presented, the first one was based on a single phosphor film containing CdSe NCs emitting at 580 nm and the second one was based on a dual phosphor film containing CdSe NCs emitting at 555 and 625 nm respectively. In the single phosphor realization the CRI is with 15.7 very low. The CRI value was increased to 61.1 after choosing the dual phosphor realization. In order to avoid the reabsorption effect by mixing differently emitting NCs together in one polymer layer, a double layer approach was introduced where the longer emission wavelength NC-polymer layer was coated on top of the shorter emission wavelength NC-polymer layer. However, limited by the low PL QY of CdSe NCs, the luminous efficiency of white LEDs were lower than 6 lm/W at an operating current for the blue LED of 20 mA. The design of NCs with a broad emission signal is an alternative approach for achieving white light spectra. Schreuder *et al*, examined thirteen dissimilar polymers as potential encapsulates for special designed broad emitting (white-light emitting) NCs [31]. They found that encapsulates based on cyclosiloxane or bisphenol-A type epoxy structures caused extensive aggregation of the NCs even at low loading levels (less than 0.5% w/w) due to the solubility difference between the polymers and the NCs. Biphenylperfluorocyclobutyl (BP-PFCM) exhibited the most robust, color stable, and homogenous encapsulation properties enabling a high loading of NCs as well. White-light emitting CdSe NCs encapsulated in the BP-PFCB polymer were coated on various UV-LEDs creating a white light source with chromaticity coordinates of (0.324, 0.322) and a high color-rendering index of 93 with a luminescence efficiency below 1 lm/W since the original PL QY of such white-light emitting CdSe NCs is already very low. The luminescence efficiency of such CdSe NCs-BP-BFCB nanocomposite covered LEDs increased up to 5.3 lm/W by optimizing the thickness of the hybrid films and the utilization of different types of UV LEDs [43]. A lot of researchers also choose the CCT which is a criterion for the quality for warm white light as overall quality parameter for optimizations. Chandramohan *et al.* demonstrated a warm white light (CCT of 3,436 to 4,500 K) emitting LED with a CRI of 87.4 using green-light-emitting CdSe NC-PMMA hybrid materials covering a InGaN/GaN based blue emitting LED [44]. Very recently, Chung *et al.* fabricated a warm (CCT of 3,237.4 K) white light emitting LED with a CRI of 83.8 and a luminescence efficiency of 4.14 lm/W by combining blue LED emitting at 430 nm with a nanocomposite film based on (Poly[(9,9-dioctyl-2,7-divinylenefluorenylene)-alto-*co*-(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene)] (PFPV) and $CuInS_2$-ZnS nanoparticles [45].

In order to improve the overall luminescence efficiency, a lot of research groups try to increase the PL QY of the light converting hybrid material. Weaver *et al.* for example studied the fluorescence quenching behavior during the incorporation of CdSe@ZnS NCs into cyanoacrylate, epoxy and silicone [46]. They found that excess of amines in the NCs solution passivated the NCs surface and preserved the PL QY of the NCs-polymer composites. Yu *et al.* reported on a white light LED with a luminescence efficiency of 44.2 lm/W by mixing a relatively high amount of CdSe NCs (20% by weight) into PFPV [47]. Since the luminescence efficiencies achieved for light conversion layers so far

are still low, efforts have to be dedicated for the development of NCs/polymer composites with high QY. Low cost and high PL QY hybrid materials would be the key parameters for NC based white light conversion materials towards their utilization and for commercializing. First commercially available NCs/polymer based white light converter plates are already on the market (Figure 11).

Figure 11. Photograph of Quantum LightTM optics from the company QD Vision, Lexington, MA, USA for converting cold white light emitting LEDs into warm white light sources (Image source: www.qdvision.com, 2010, copyright QD Vision).
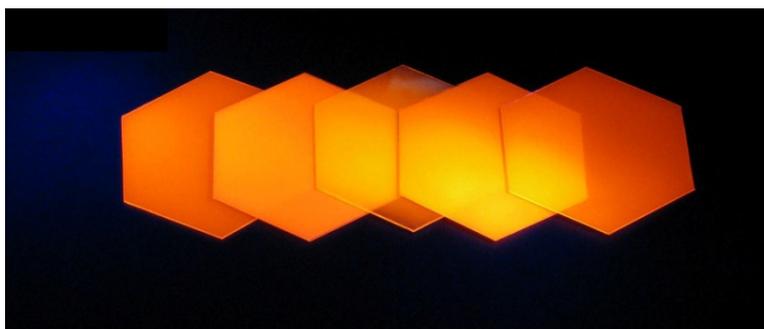
4.2. Light Conversion Layers in Concentrator Solar Cells

One main driving force of photovoltaic (PV) research and development is attaining higher power conversion efficiencies at lower costs. Compared with expensive prices of high efficient PV modules, it is preferable to convert incident light from the solar spectrum collected at large areas to monochromatic light and concentrate the converted light onto a small area of a high efficient solar cells with optimized power conversion efficiencies for the chosen monochromatic light . Based on this concept, luminescent solar concentrators (LSC) were developed in the late 1970s as an alternative approach to lower the costs of PV. The achievable efficiency of LSCs is dependent on how well it is spectrally matched with the attached absorbing fluorescent material. Recently, Goldschmidt *et al.* reported two independent methods to increase the collection efficiency of LSCs. One is to combine two different dyes to enlarge the utilizable spectral range. The other is to increase the collection efficiency by using a photonic structure acting as a band stop reflection filter in the emission range of the dye. Figure 12 demonstrates the principle of a multi-fluorescent concentrator cell based on Goldschmidt's concept [48].

However, over 60% of the total solar photon flux occurs at wavelengths above 600 nm, which is beyond to the absorption range of most organic dyes. Novel luminescent photo stable materials with absorptions reaching to the infrared are needed for increasing the efficiency of LSCs. Semiconductor NC based hybrid materials have good potential to match this need. NCs can provide excellent PL QY with sufficient long term stabilities. For example PLQE of 85% has been reported for core-shell NCs [49], and PL QY of 70% for the transparent NCs/polymer composites so far [32].

Figure 12. Principle of a multi-fluorescent concentrator. The light collection unit consists of a stack of different absorber layers. An additional photonic structure helps to minimize reflection losses. The photonic structure acts as a band stop reflection filter. It allows light in the absorption range of the dyes to enter the collector, but reflects light in the emission range. Therefore a larger amount of light is trapped in the collector and guided to the high efficient spectrally matched solar cells mounted at the edges (The figure is reproduced from [48] with permission).
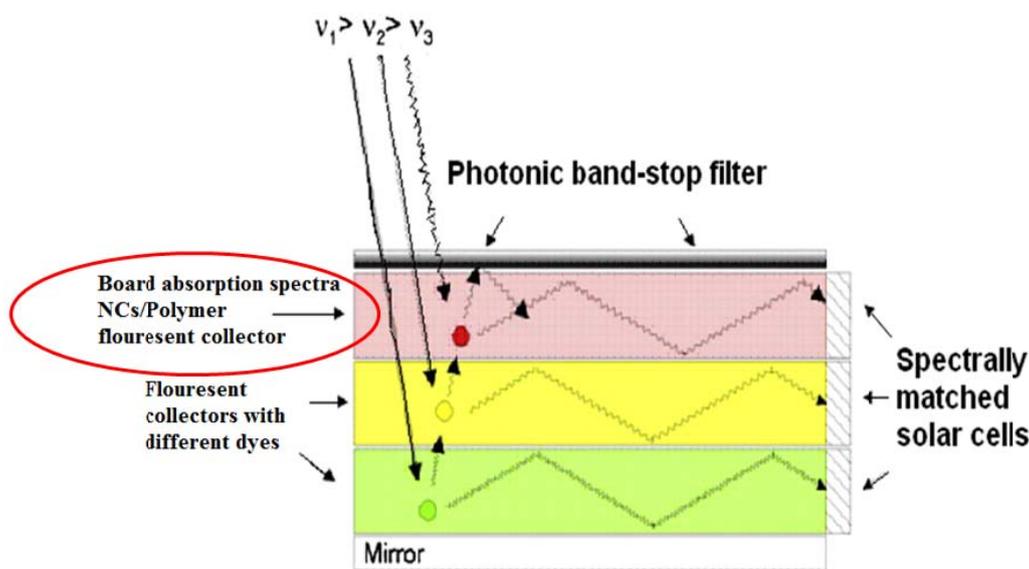
4.3. Light Conversion Layers for Enhanced Plant Growth to Increase Biofuel Production

The improvement of energy conversion and storage is one of the major tasks to achieve further optimization of the global energy management. In addition self-sufficient energy harvesting technologies are currently developed to obtain autonomous and flexible small devices harvesting energy from the environment similar to photosynthesis. The overall energy conversion efficiency of photosynthesis is below 1%. One reason is that chlorophyll as main absorber in plants for photosynthesis does not use the fully visible spectrum but rather the blue and red light only. Figure 13(a) shows the absorption of chlorophyll a and b demonstrating the loss based on incomplete absorption of the visible light range. Recently there have been tremendous efforts undertaken to utilize biofuels for transportation by e.g., mixing some biofuel content to petrol. Since biofuel production is competing with food production, negative consequences such as increasing food prices enhancing the poverty of millions of people have already been observed. Enhancing plant growth especially of plants not competing with the food chain is of outermost importance to damp and hinder these negative developments. Due to the broad range absorption properties of semiconductor NCs and the tunability of their absorption and emission properties over a wide range, NCs/polymer hybrid materials could be used as solar absorbing and light converting layers matching to the absorption characteristics of chlorophyll (Figure 13(b)). This would lead to a better utilization of the incident solar light for plant or algae growth for the production of biofuels. As one can see in Figure 13(a), the absorption spectrum of chlorophyll is very narrow, only blue and red light is useful for the photosynthesis. For example CdSe NCs can absorb the energy of the

green, yellow and orange spectrum the light and convert it into the emission of red light matching to the absorption maximum of the respective chlorophyll (Figure 13(b)).

Figure 13. (**a**) Absorbance spectra of chlorophyll a (green) and b (red) in solution. The spectra of chlorophyll molecules are slightly modified *in vivo* depending on specific pigment-protein interactions (The image is reproduced from [50] with permission), (**b**) Absorption and PL spectra of differently sized CdSe NCs matching to the absorption of the chlorophylls respectively. The excitation for the NC emission was performed at 380 nm.
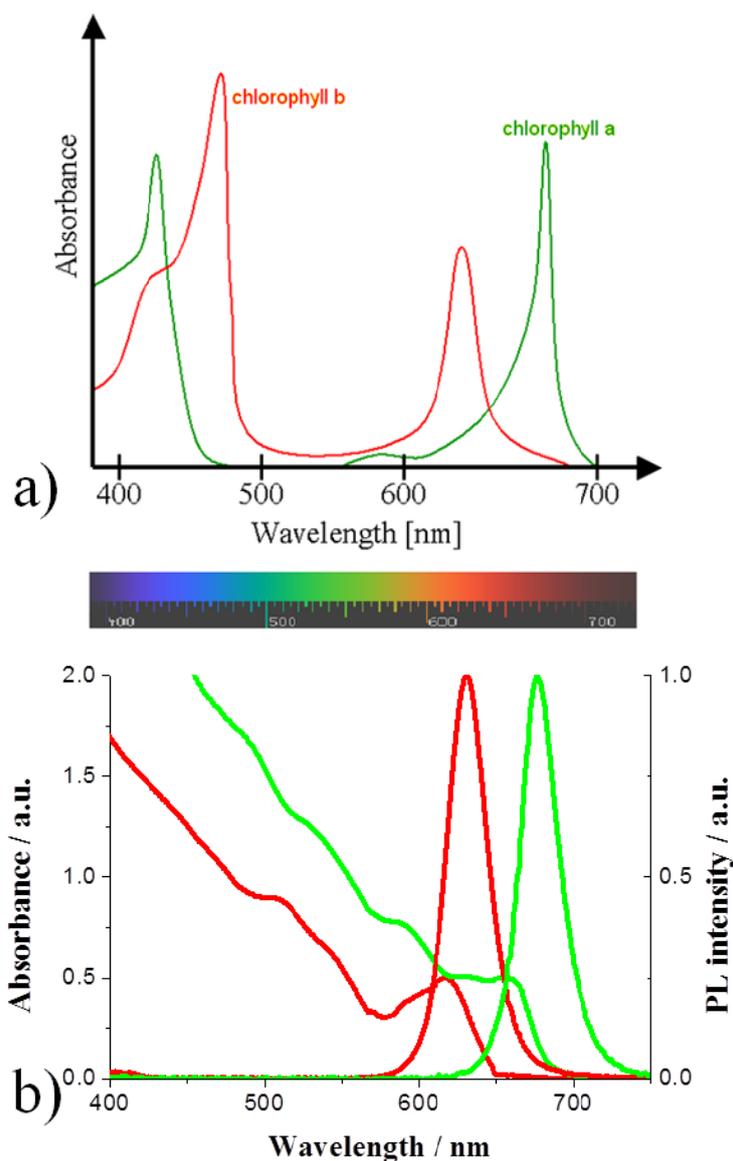
5. Outlook

The development of semiconductor NCs-polymer hybrid materials continues. Once the excellent photo stability, high QY and tunable sized-dependent PL properties of NCs are maintained in NC-polymers hybrid materials they can be utilized in a wide range of applications including LED conversion layers, absorber layers in fluorescent concentrator solar cells and light converting layers for enhanced plant and algae growth for increasing the biofuel production. Further applications might be

high sensitive fluorescence detection screens or the development of fluorescence standards for three dimensional confocal laser scanning microscopy. Since cadmium and lead based materials are considered toxic and therefore not environmental friendly, the development of cadmium and lead-free NC materials are of high importance for future applications. Luminescent NCs based on $Y_2O_3@Eu_2O_3$, $InP@ZnS$, $MnSe@ZnSe$ might be promising materials to be incorporated into polymers for various light conversion applications [28,33,51].

Acknowledgments

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