



Review

Polymer Coated Semiconducting Nanoparticles for Hybrid Materials

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Received: 22 January 2020; Accepted: 5 March 2020; Published: 11 March 2020



Abstract: This paper reviews synthetic concepts for the functionalization of various inorganic nanoparticles with a shell consisting of organic polymers and possible applications of the resulting hybrid materials. A polymer coating can make inorganic nanoparticles soluble in many solvents as individual particles and not only do low molar mass solvents become suitable, but also polymers as a solid matrix. In the case of shape anisotropic particles (e.g., rods) a spontaneous self-organization (parallel orientation) of the nanoparticles can be achieved, because of the formation of lyotropic liquid crystalline phases. They offer the possibility to orient the shape of anisotropic nanoparticles macroscopically in external electric fields. At least, such hybrid materials allow semiconducting inorganic nanoparticles to be dispersed in functional polymer matrices, like films of semiconducting polymers. Thereby, the inorganic nanoparticles can be electrically connected and addressed by the polymer matrix. This allows LEDs to be prepared with highly fluorescent inorganic nanoparticles (quantum dots) as chromophores. Recent works have aimed to further improve these fascinating light emitting materials.

Keywords: polymer coated nanoparticles; solubility; self-organization; fluorescent nanoparticles; dispersion in polymers; quantum dot LEDs

1. Introduction

The use of nano-objects in the real macroscopic world requires—besides their preparation—also their macroscopic processing, organisation, and orientation. This is because any device in the “real world” is in the micro- to milli-meter range and thus contains many nanoparticles. This requires the homogeneous dispersion of the nano-objects in solvents (aqueous or non-aqueous water based) or organic polymeric materials. However, this is often hindered by massive segregation of the nano-objects from the surrounding matrix [1]. Thus, concepts to improve the compatibility of nano-objects with the surrounding matrix become important (see Section 2). In addition, self-organisation of the nanometre sized objects is attractive in dispersing them in a controlled way and to orient anisotropic nanoparticles in a uniform way. This can be realised, if the nanoparticles become individually dispersed in a mobile matrix allowing their self-organization (as compared to agglomerates, in which the multitude of interactions hinder a reorientation). It can be achieved in colloidal crystals [2–4] and lyotropic (solvent induced) liquid crystals (LC) [5,6] (see Section 3). At least the topic of a “functional coating” becomes important and will be discussed in Section 4 (QD-LEDs), where the focus is put on semiconducting properties. In combination with semiconducting polymers as a matrix it is then possible to address the nanoparticles electrically and to prepare quantum dot LEDs (that are polymeric LEDs with quantum dots as chromophores). So, altogether concepts to achieve a solubilization of nanoparticles (Section 2), their organization (Section 3), and the successive electrical addressing of fluorescent nanoparticles (Section 4) are the topic of this review.

2. Concepts for the Functionalization of Inorganic Nanoparticles to Improve Their Solubility and Processability

In this context it is advisable to start by considering the general concepts for the stabilization of colloids in a matrix [7–10]. This relies on either electrical charges or a steric stabilization to overcome the strong adhesion forces among the nanoparticles [11–13] (see Figure 1). These concepts are, in addition, already used in “nearly any” synthesis of nanoparticles, which is performed in the presence of detergents, to prevent aggregation and to stabilize the nanoparticles formed. In this context an electrostatic stabilization is most often used, which can result from an excess of oxides or cations in the nanoparticle. However, for applications in combination with electric fields (discussed later) it is advisable to use steric stabilization and not electrostatic stabilization to avoid water as solvent. In addition, electrostatic stabilization is less effective for a dispersion in polymeric materials. This makes concepts for a steric stabilization, like “hairy rods” most attractive. Even though this concept was developed for stiff main chain liquid crystalline polymers, it is also applicable for inorganic nanoobjects. [14] The concept implies, that a stiff insoluble core is solubilised by linking long chains (“hair”) onto its surface, which are soluble in the solvent. As “hair” are often used alkyl chains [15–17], which can stabilize sphere- or rod-like shaped nanoparticles. They are also in use for delaminated clay fragments [18,19], which possess a plate-like shape.

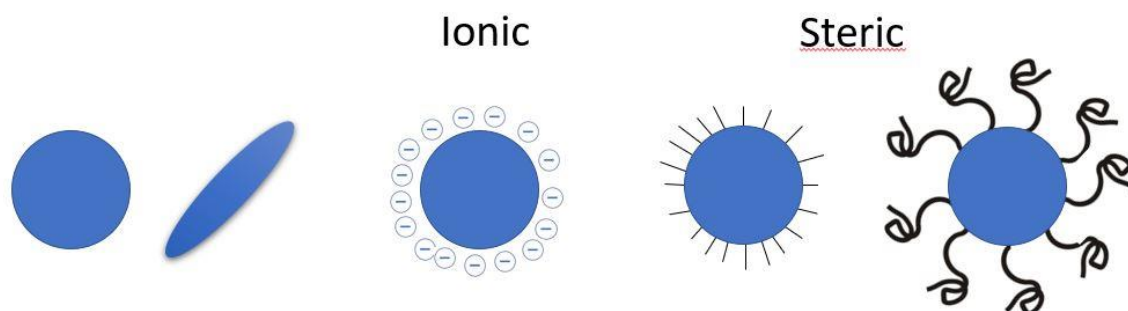


Figure 1. Schematic drawing of spherical and shape-anisotropic nanoparticles (left) and ways of stabilization by ionic and steric stabilization [8,10,20,21].

Polymeric surfactants [7,9,18–20,22,23] offer here advantages for the solubilisation of inorganic nano-objects because polymers themselves are objects of nanometre dimensions (for comparison: the alkyl chain in a detergent may possess 18 C–C bonds, while a polymer chain of a degree of 100 has 200 C–C bonds, which bring it, even in the coiled conformation, to the size of many nms). Therefore, polymers for steric stabilization match the size of inorganic nano-objects much better than simple alkyl chains. Thus, polymer coated surfaces are stabilised sterically up to a distance of nanometres and not only for angstroms as with alkyl chains. In addition, polymer chains have, in the coiled conformation, a lot of free volume inside, which can be filled by solvent. This large interaction volume between solvent and functionalised surface leads to good solubility in solvents for the polymer.

As result it is possible to disperse inorganic nanoparticles as individual objects in various solvents, which are good solvents for the polymers used for coating [20,24], which applies also to the use of compatible polymers. It is thus possible to disperse them homogeneously in polymer films as “solid” solvents. The preparation of highly concentrated solutions also becomes possible. This can finally open the door for the incorporation of fluorescent nanoparticles in semiconducting polymers and for their electrical addressing [24,25].

To coat inorganic nanoparticles with a dense and stable layer of polymer chains two strategies exist, which are either grafting to or grafting from [26–35] (see Figure 2). From a polymer perspective the grafting to approach offers here the advantage that the polymer chains used for grafting can be characterized very well. By the use of multiple anchor groups it becomes possible to avoid adsorption–desorption equilibria and to achieve a stable fixation.

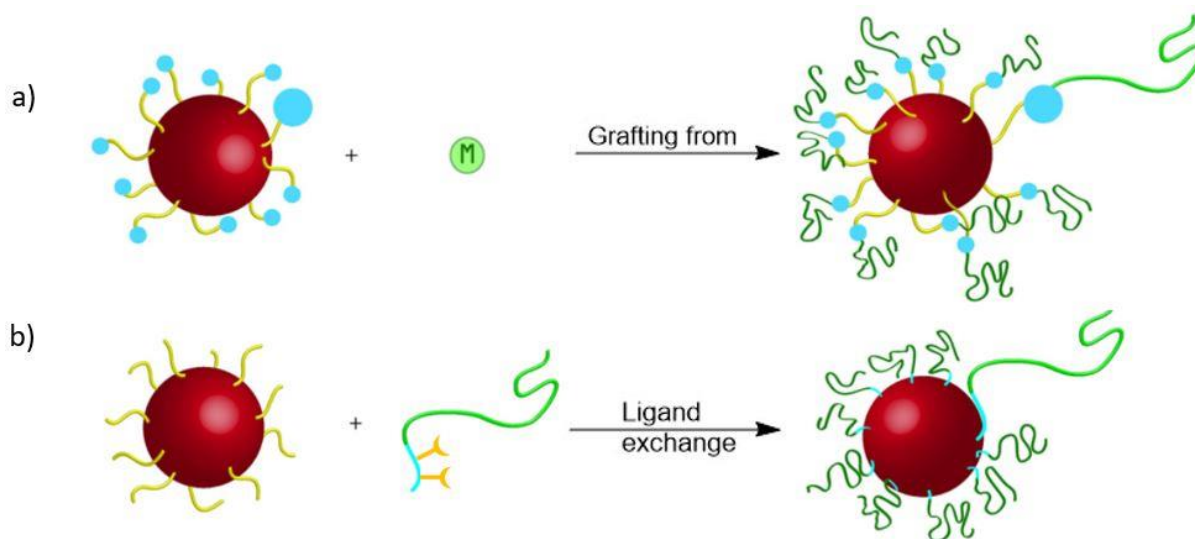


Figure 2. The coating of nanoparticles can either be done by a grafting from (a) or a grafting to (b) process. In the last case the ligand exchange is shown; reproduced with permission from [24]; published by Wiley-VCH, 2015.

Recently a block copolymer synthesis via RAFT polymerisation in combination with a reactive ester intermediate to introduce the anchor groups attracted much interest [20,21] (see Figure 3). It can be used to introduce different anchor structures to the same block-copolymer, which are suitable for grafting to oxidic or chalcogenidic nanoparticles [36,37]. This is important because oxidic nanoparticles attract much attention because of their magnetic or semiconducting properties, whereas nanoparticles based on selenides (often with a sulfidic shell) are prominent as fluorescent nanoparticles. In addition the new polymers can be designed to have multiple anchor units for surface attachment. Through the multi-dentate fixation of the polymer onto the surface adsorption–desorption equilibria reactions are avoided. In this way not only sphere- or rod-like nanoparticles, but also more complex structures like tetrapods [38] have been successfully coated and dispersed.

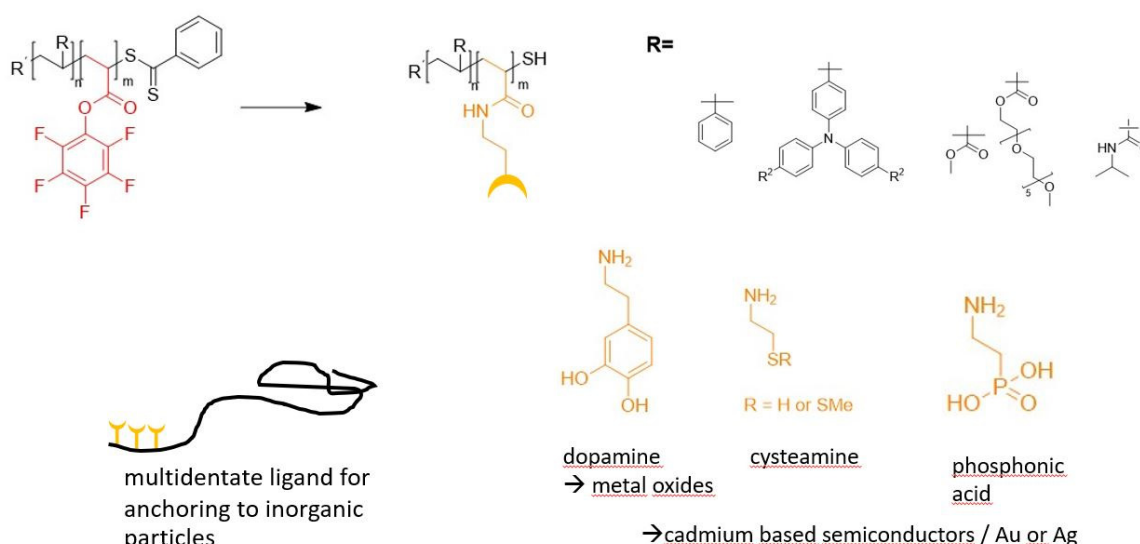


Figure 3. Recently established synthetic route [20,21] to blockcopolymers with multidentate block for the ligand exchange on nanoparticles.

Such inorganic nanoparticles coated with polymer chains can be dispersed as individual nano-objects [7,9,39,40]. This can be seen e.g., from AFM- and TEM-measurements of this films

(see Figure 4A). AFM makes it thereby also possible to differentiate between the inorganic core (hard) and the softer polymer corona and to prove thus directly the core-shell structure of the hybrid materials. The direct proof that there are individually dispersed nano-objects comes mostly from light scattering experiments [39,41] (see Figure 4B). Here both dynamic light scattering, which measures the hydrodynamic radius, and static light scattering, which measures the radius of gyration, give similar results, which correspond to the size of the individual object. Some differences between both measuring technics are, however, to be expected, because the hydrodynamic radius (dynamic light scattering) includes the size of the swollen polymer brushes, whereas the radius of gyration is strongly dominated by the inorganic core, which has a higher refractive index increment (see [39] for a detailed discussion).

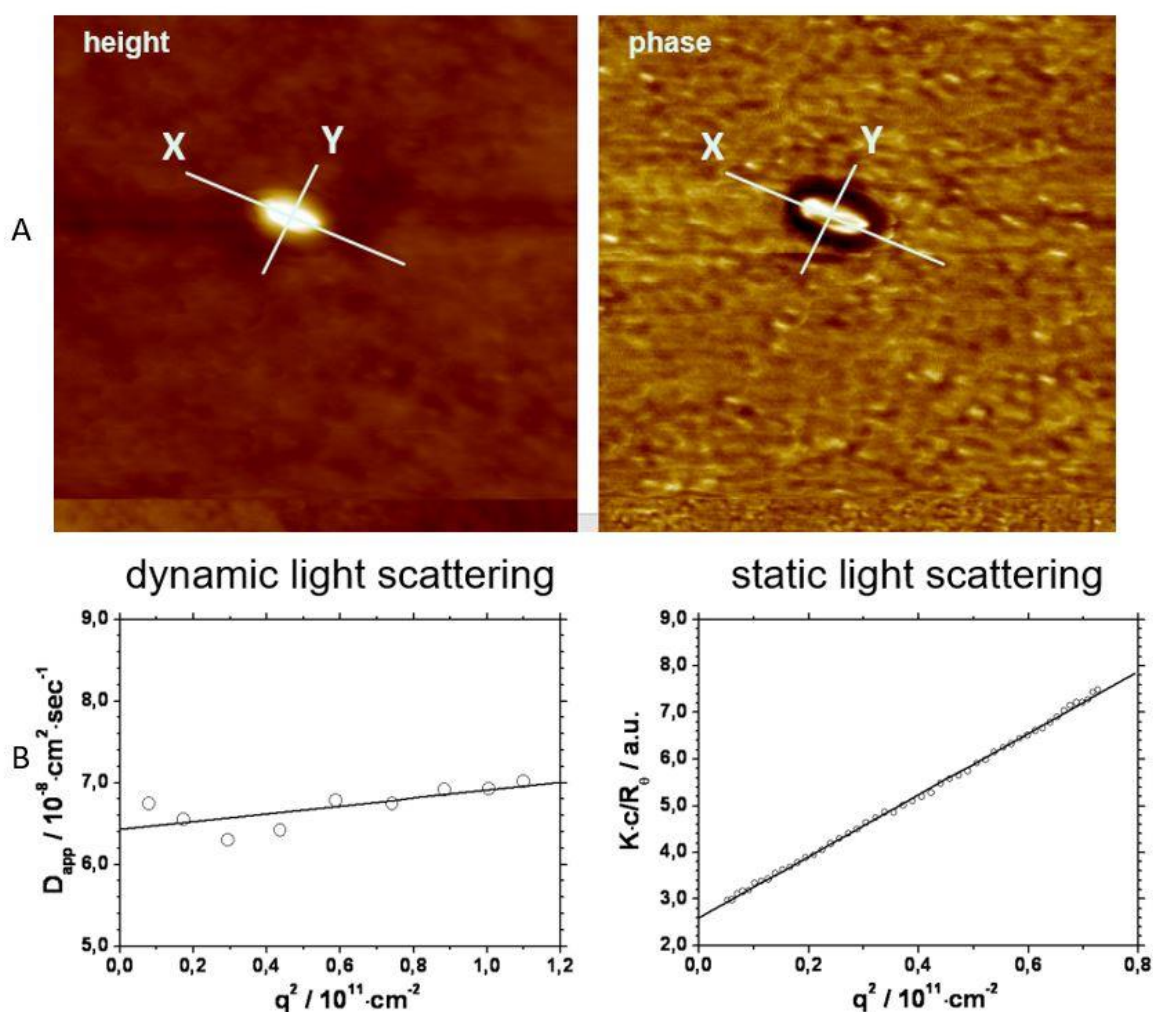


Figure 4. Visualization (A): upper line, AFM) and characterization by light scattering (B): lower line) of properly coated, individually dispersed inorganic nanoparticles (see [39] for more information); reproduced with permission of the ACS [39], published by the ACS, 2008.

During the last decade, remarkable progress has been made in colloidal synthesis [42–46] and the polymer coating [47–52] of nanoparticles with well controlled shapes, which range from simple dots [53–57] to rods [58–61] and to more complicated structures such as tetrapods [62–65], hyperbranched structures [66–68], and wires [69–71] among others. For most of these geometrical structures the solubilization enhancing effect of a polymer coating has already been shown. A large variety of semiconductor materials, e.g., metal sulfides [11–13], metal selenides [72–74], metal

tellurides [75,76], metal oxides [77–79] and lead halide perovskites [80] have been investigated in relation to this topic. They can be coated using the anchor groups presented in Figure 3.

Depending on the solubility of the polymer chains it is also possible to prepare nano-particle solutions, which change their solubility reversible with temperature [39] (see Figure 5a). Alternatively, it becomes possible to include photocleavable links to the polymer chain and to split-off the solubilizing polymer chains on irradiation [81] (see Figure 5b). The solubility can also be changed after preparation of the solution by external stimuli. This might be especially interesting for the dispersion of nanoparticles in polymer matrices, because their viscosity is high and thus solution and dissolution is slow. It is thus possible to stabilize intermediate states of dispersion like finely percolated structures [24], which are interesting for photovoltaics (see below for a more detailed discussion)

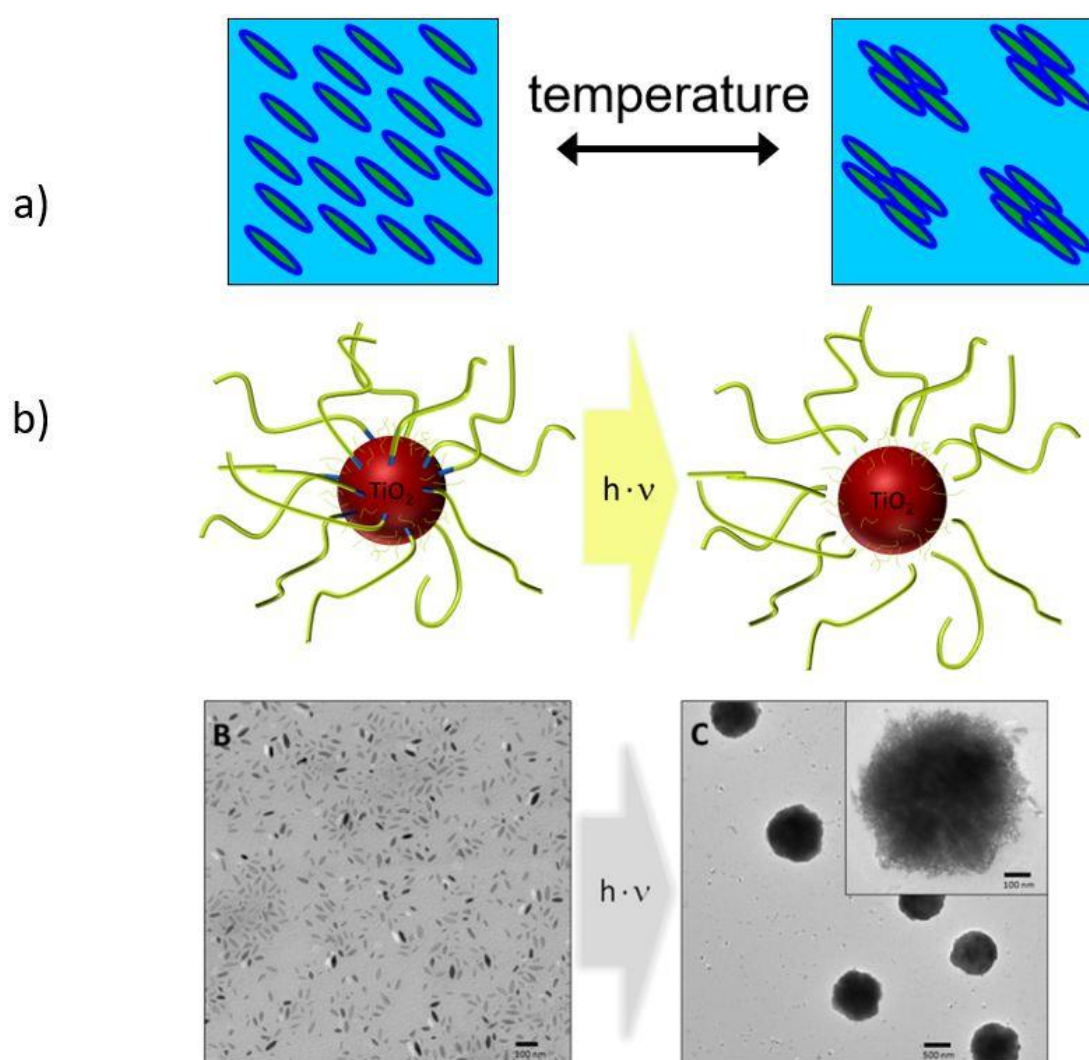


Figure 5. Ways to destabilize polymer coated nanoparticles with an external stimulus and to induce a coagulation. (a) Nanoparticles coated with a polymer with an lower critical solution temperature coagulate during temperature increase [39]; (b) Nanoparticles coated with polymers with a photosensitive group within the polymer backbone allow it to split-off the stabilizing polymer corona [81]; lower part reproduced with permission of [81], published by Wiley-VCH, 2014.

Semiconducting polymers (mostly conjugated polymers) and fluorescent inorganic nanoparticles have been investigated separately for some time. The combination of both materials is, however, highly interesting as it can lead to nanocomposites whose properties are much superior to those of their constituents [82]. These hybrid materials are being considered in several applications, mostly in

light emitting diodes and photovoltaic cells. Latest reviews about this topic can be found in [83–87]. Semiconducting hybrid systems offer the potential to combine the benefits of inorganic nanocrystals (NCs) such as tunable optical properties, optical stability, and high electron mobility [82,86] with the advantages of semiconducting polymers like light weight, flexibility, ink jet printing, roll-to-roll production, solvent processability over a large area and with low costs [83,88–92]. Because it is possible to tune the optical band gap of NCs very accurately from the ultraviolet to the near-infrared, they can be used to prepare very bright quantum dot light emitting diodes (QLEDs, see Section 4) or solar cells consisting of p-type donor polymers and n-type acceptor inorganic nanoparticles which absorb a significant range of the solar spectrum.

Controlling the morphology is a crucial aspect for optoelectronic applications. For QLEDs a homogeneously dispersed structure is most desirable. Therefore, intimate contact between NCs and polymers (no demixing) is essential. Preparation techniques such as kinetic entrapment [93] and in situ polymerization [94] are known to generally stabilize highly dispersed states in nanocomposites.

Solar cells need a percolated structure to facilitate the macroscopic transport of holes and electrons to the appropriate electrode, even though they benefit from improved dispersion (short exciton diffusion lengths). To prepare a percolated structure a controlled demixing is required, which must be stopped (to prevent further coarsening) before the demixed structures become larger than several hundred nm (see [23] for discussion). In this context the concepts discussed in the context of Figure 5 [39,81] are suitable to induce a demixing.

3. Controlling Orientation, Dispersion, and Percolation of Inorganic Nanoparticles in a Polymer Matrix

As discussed in the first paragraph, polymer chains can be used to cover inorganic nanoparticles, which makes them well soluble as individual objects and allows the preparation of highly concentrated solutions even in a polymer matrix. Through this, it is possible to fill polymeric materials with a high concentration of inorganics [7,39–41,95]. Furthermore, even functional inorganic nanoparticles can be combined with a functional semiconducting polymer matrix.

In the case of shape anisotropic inorganic nano-objects their good solubility can also give rise to the formation of liquid crystalline phases. That is because above certain “critical” concentrations [20,21,39] the shape anisotropic nano-objects act as mesogens and self-organize [6,7]. This can be also attractive for opto-electronic applications. Generally, the formation of lyotropic liquid crystals [14,96,97] from rigid-rod objects as result of form-anisotropy is well understood [98,99] and such phases offer the potential to orient anisotropic nanoparticles.

Historically lyotropic LC-phases in water have been observed for various rigid-rod objects like V_2O_5 ribbons [100,101], tobacco mosaic viruses [102], and TiO_2 nanorods [103,104]. Aqueous solutions offer the opportunity to stabilise nano-objects electrostatically by surface charges. Thus lyotropic (solvent induced) liquid crystalline phases from V_2O_5 solutions in water have been known for a long time [22] under proper pH and salt conditions. However, the charges used to stabilise the system require water as solvent and disable any electronic use. Therefore, ion free mineral liquid crystals from uncharged anisotropic nanoparticles in organic solvents are attractive and can be made following the concept of grafting to polymer chains to the anisotropic object.

Using this concept, smectic and nematic phases could be prepared recently in highly concentrated solutions of TiO_2 nanorods [20], which were coated with block copolymers (see Figure 6). Polarizing optical microscopy showed birefringent, mobile textures, while TEM measurements of samples prepared from concentrated solutions showed the parallel orientation of the rod like nanoparticles, which are the shape anisotropic mesogens of the system. This work has been extended to various other semi conducting nano-rods from oxidic and chalcogenidic semiconductors like TiO_2 , ZnO , SnO_2 or $CdSe$, ZnS , and $CdTe$ [21], which required different anchor blocks (see Figure 3). This concept was also applied successfully to induce a liquid crystalline orientation in dispersions of carbon

nanotubes [105–107]. A comparable ordering of plate like nanoparticles can also be obtained and is used to make artificial nacre [95].

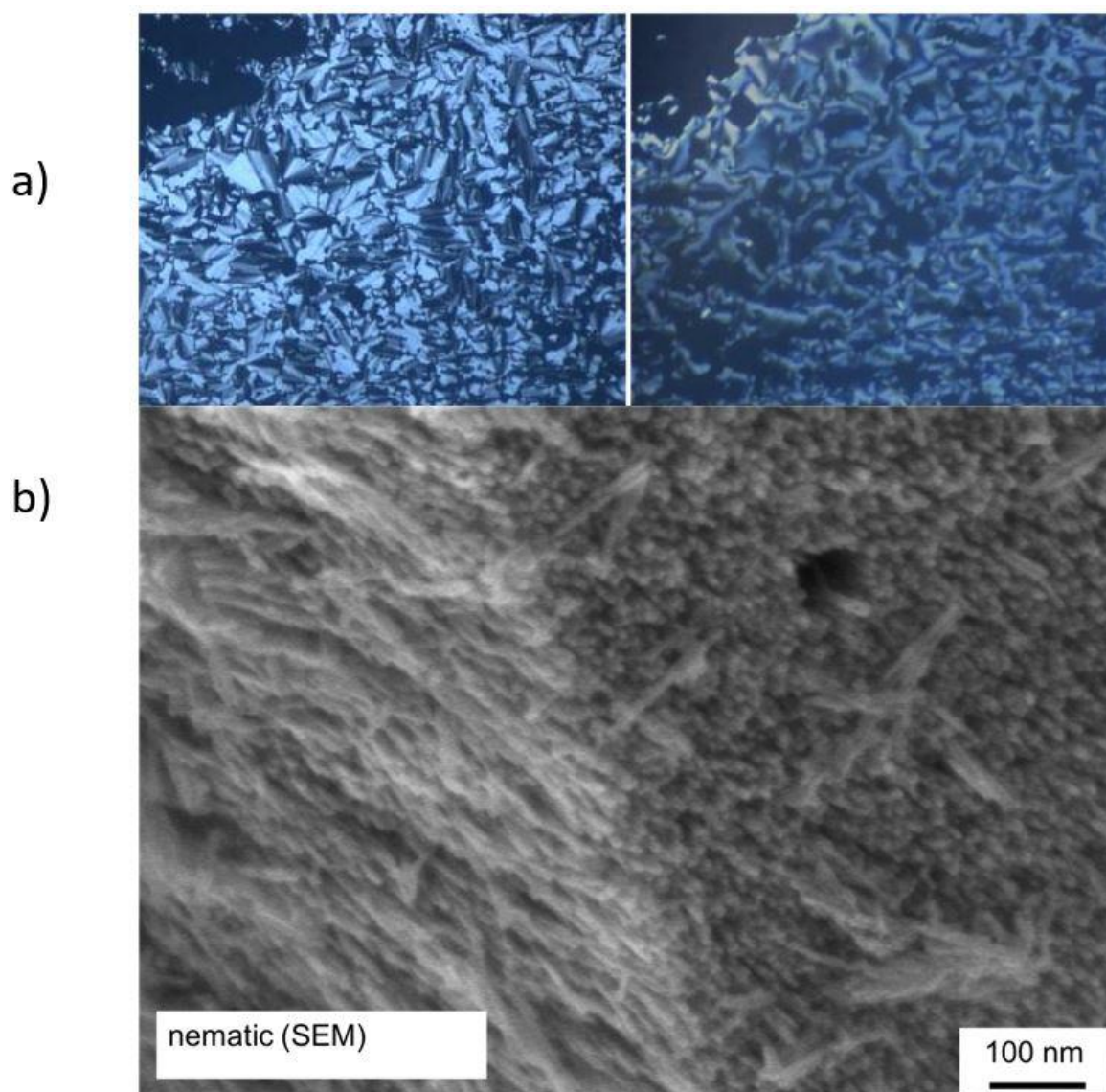


Figure 6. Liquid crystalline phases formed from shape anisotropic inorganic nanoparticles in highly concentrated solution [20]; (a) polarizing microscopy showing smectic and nematic textures with increasing temperature. (b) SEM microscopy of the dried phase consisting of TiO_2 nano-rods; reproduced with permission of [20], published by Wiley-VCH, 2007.

Generally, the possibility to orient shape anisotropic nanoparticles and especially semiconducting ones is interesting for materials science and especially for photovoltaics [108–111]. In this context Alivisatos and co-workers [15] could recently show that rod-shaped nanoparticles oriented perpendicular to the electrodes improving the efficiency of solar cells [112]. In their case they had to orient the semiconducting inorganic nanorods however by a complicated growing process, away from the substrate. Liquid-crystalline phases, would allow an orientation of the whole phase. For non-properly coated nanoparticles, it is, however, difficult to obtain the high concentrations needed to obtain them. The situation is, however, different for the systems and the polymer coating discussed here.

Recently it was found that polymer coated TiO_2 nanorods could be solubilised and oriented also in an organic hole conducting matrix where they orient into a liquid crystalline phase by self-assembly [113]. Moreover, it is possible to orient this liquid crystalline phase uniformly in an

external electric field. [114] Thus it becomes possible to orient the central part of the liquid crystalline phase perpendicular to the electrodes (see Figure 7, lower part). The resulting structures have the correct orientation for an organic photovoltaics setup, in which the oriented TiO_2 nanorods transport the electrons to one electrode while the holes migrate through the organic hole conducting material.

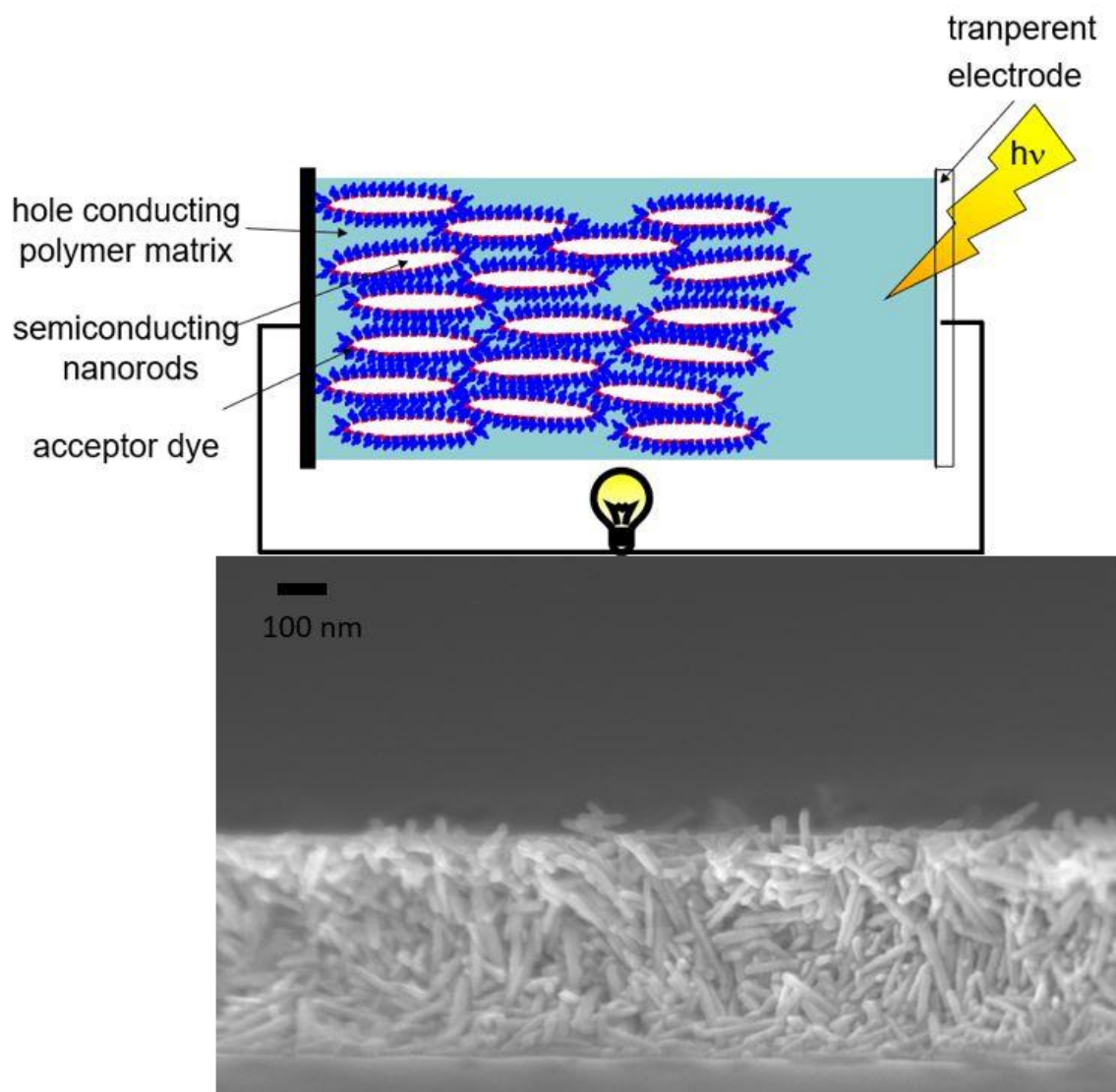


Figure 7. Schematic representation of a photo-voltaic cell optimized for an effective transport of the negative charge to the electrode and an assembly of ZnO nano-rods on an electrode; lower part reproduced with permission of [114], published by Wiley-VCH, 2010.

Two more aspects should be mentioned in the context of the electrical coupling of inorganic nanoparticles and an organic matrix. First, by coating an inorganic nanoparticle with a semiconducting polymer, a p-n junction is established on the level of the core-shell nano-object (see Figure 8). This allows charge transfer and charge migration on the nano-level to be studied [115–117]. So it became possible to determine charge separation and charge transport under irradiation for polymer coated hybrid systems [115–117]. Figure 8 shows, how the polymer corona charges positively under irradiation, while the inorganic core from TiO_2 accumulates electrons (negative charges).

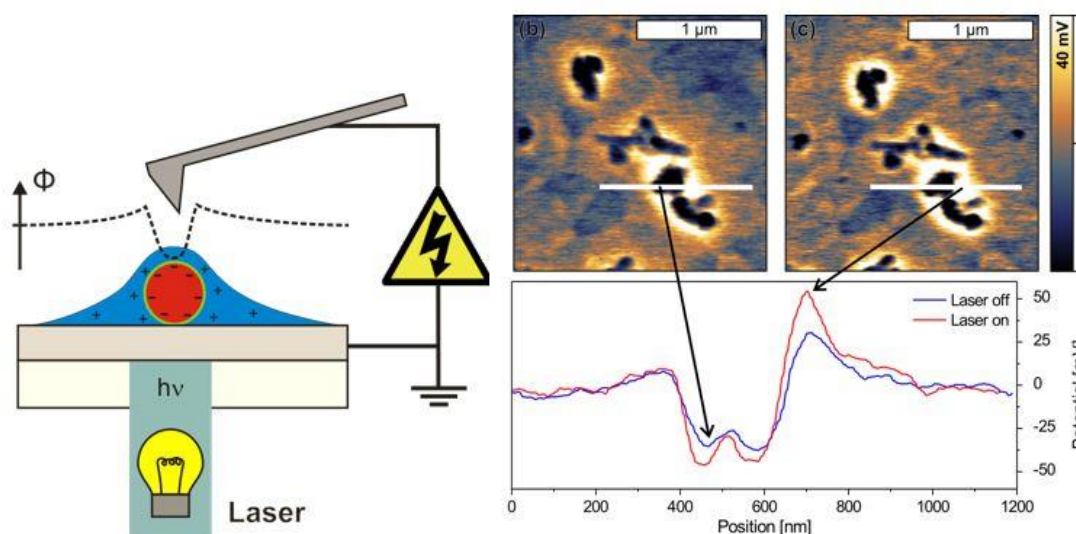


Figure 8. Schematic presentation of Kelvin-probe AFM measurements (left), which allow a determination of charging of nanoobjects and measurements (right), which prove the transfer of electrons from the coated semiconducting polymer to the TiO_2 nanoparticles (see [115–117]); right part reproduced with permission of [115], published by the ACS, 2010.

Second, the polymers grafted to the inorganic nanoparticle can be a precursor for graphitic material, into which they decompose during heating (see Figure 9a). This allows the coating of redoxactive inorganic nanoparticles with graphite or, if the process is done in a composite, the dispersion of many nanoparticles in a graphitic matrix. This can be beneficial to electrically address nanoparticulate electrode materials in lithium or sodium ion batteries [118–120] (see Figure 9) where it helps to improve the electrode performance.

So, to summarize the result of Section 3: The high solubility in “classical” solvents and polymers (as solid solvents), which can be achieved with the polymer coating of inorganic nanoparticles, allows liquid crystalline phased rod shape anisotropic nanoparticles to be prepared easily. These phases can then be used to orient the nanoparticles macroscopically by an external electric field. In addition, the coating with functional polymers makes an electrical coupling to an external matrix possible, this opens up the possibility for electric addressing of fluorescent inorganic nanoparticles like quantum dots (QDs). This will be discussed in Section 4.

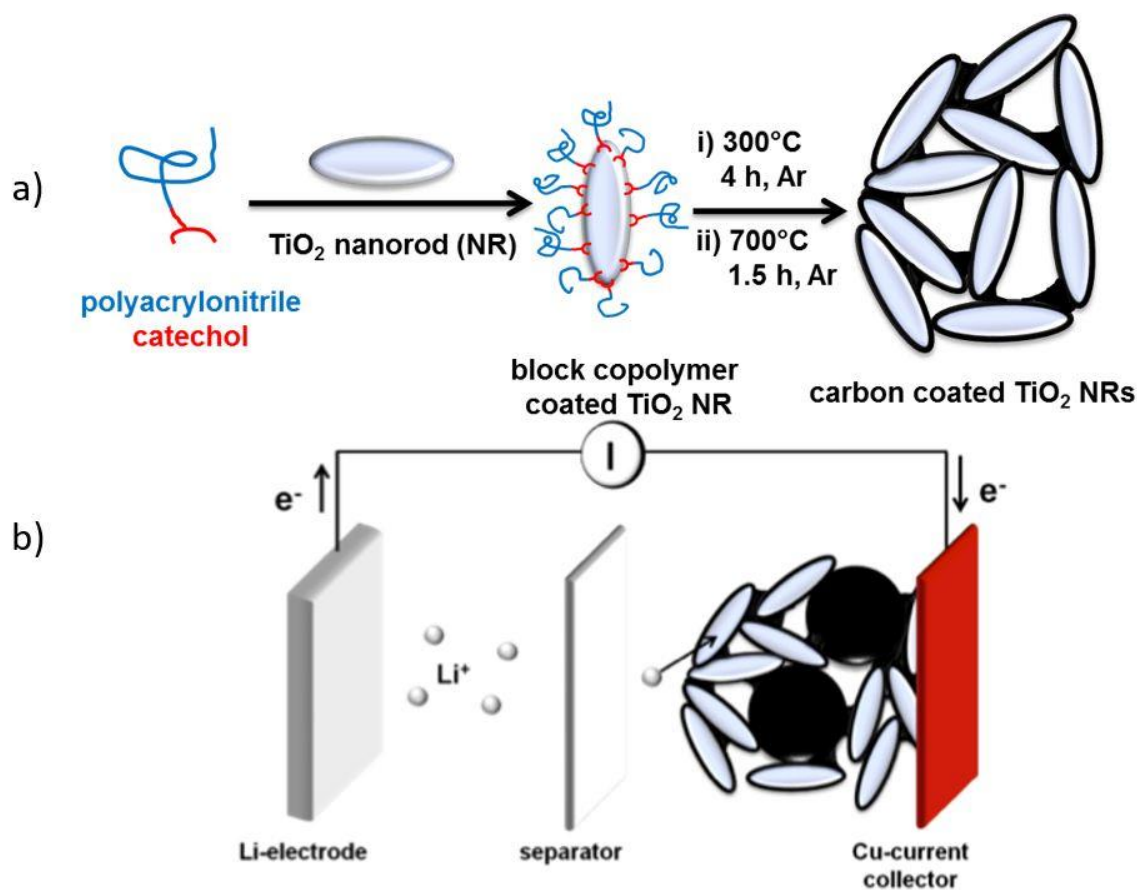


Figure 9. Coating of TiO₂ nano-rods with block copolymers with a graphitable polyacrylonitrile block and their conversion into a nanocomposite with nano-rods embedded in graphite [118] (a) and the use of this nanocomposite as anode (b); reproduced with permission of [118], published by Wiley-VCH, 2013.

4. QD-LEDs

Generally, in semiconducting nanoparticles the electronic properties (e.g., band gap) depend on their size. This is especially obvious for fluorescent nanoparticles, for which the wavelength of fluorescence varies with size. Such fluorescent nanoparticles are called quantum dots (QDs). They possess often a high fluorescence efficiency. So, they are attractive as chromophores in LEDs. Thus recently, quantum dot based light emitting diodes (QLEDs) became competitive alternatives to organic light emitting diodes (OLEDs) in terms of colour purity, luminescence intensities, and external quantum efficiencies (EQEs) [121–123]. The narrow emission profile, the high stability of quantum dots (QDs), the high photoluminescence quantum yields (PL QYs), and the easily tunable emission wavelengths make them attractive as quantum dot LEDs (QLED) [124]. By understanding the basic device physics and optimizing the device structure it was possible to improve the device performance and efficiency of QLEDs, so much that they can be compared to organic LEDs [122,125–133]. For this study semiconducting polymer hybrids QD, which allow a homogeneous dispersion in the matrix of a semiconducting polymer and an efficient charge transport into the QDs were very helpful [116,134–136].

Chemical structures of a combination of semiconducting polymers and QDs are presented in Figure 10.

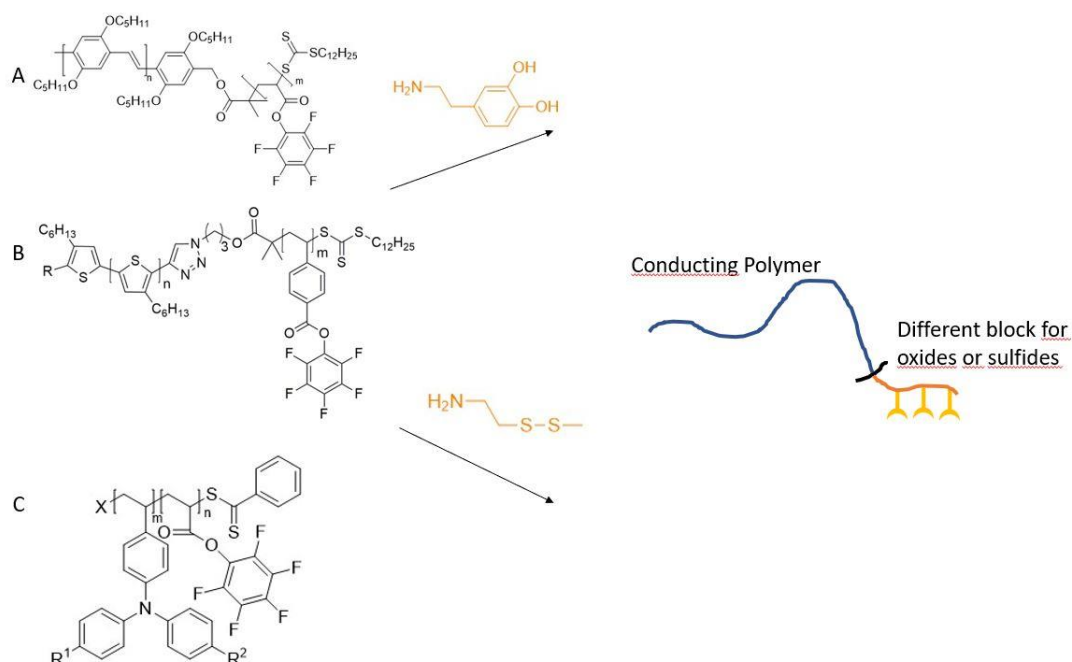


Figure 10. Block copolymers based on poly(phenylene-vinylene) [116] (A), polythiophene [136] (B) and poly(arylene ether amine) v [134] (C) and an anchor block for oxidic or sulfidic quantum dots.

The strong affinity between the surface of the inorganic part and the anchoring block of the polymers leads to a dense coating of the QDs and this allows a good dispersion (uniform distribution) within the semiconducting polymer matrix (Figure 11a). In addition to that the electro-luminescence observed in such hybrid systems is that of the pure QD (Figure 11b). This proves that all excimers formed from the positive and negative charges in the polymer matrix reach the QD for emission. With these systems it becomes possible to study the influence of the morphology of hybrid emission layers (e.g., QD concentrations or mean inter-dot distances) simply by varying the mixing ratios between the QDs and semiconducting polymers (see Figure 11) [24,135]. Using different semiconducting polymers, the charge carrier transport through the semiconducting polymers can be adapted. This allows us to raise the mean QD-to-QD distance or the thickness of the QD active layers without declining the charge transport properties [137,138].

In this context it becomes also attractive to use shape anisotropic fluorescent nanoparticles (see above) to optimize emission [139].

To optimize such QLEDs concerning the external quantum efficiency (EQE), CdSe/Cd_xZn_{1-x}S core/shell Type-I heterostructured QDs with a core radius of 2.0 nm and a total radius of 4.5 nm were used. Such a structure confines both hole and electron wave functions within the CdSe core. In addition, this specific type of QD was extensively used in previous QLED and QD-semiconducting polymer hybrid studies [127,138]. For further improvement it is necessary to consider the band gap alignment as presented in Figure 12. Crucial for QLEDs with CdSe QDs are especially their low HOMO and LUMO values. They make it, on one hand, difficult to transport positive charges (holes) into the QD and lead, on the other hand, to an easy overcharging of the QDs with electrons. This general problem can be reduced either by optimizing the setup and the injection layers [140,141], or, in the case of the homogeneous dispersion in bulk, by lowering the HOMO level of the conductive polymers grafted to the QDs [24,137,138]. Figure 12 shows the energetic situation (band gap position of the sublayers in the QLED) together with some polymer structures recently synthesized to optimize the transport of positive and negative charges.

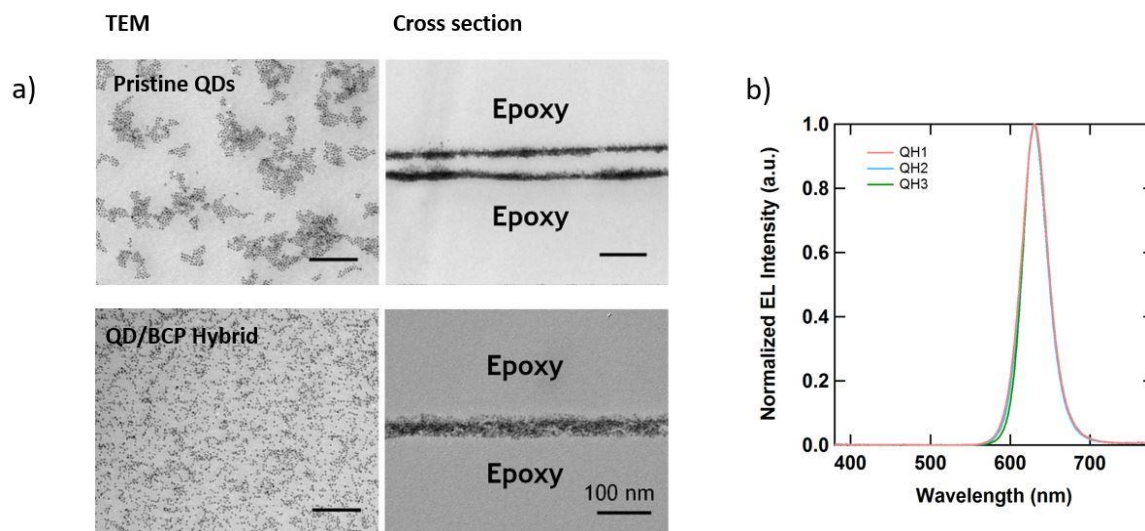


Figure 11. CdSe QDs as light emitting material in a matrix of semiconducting polymer for the preparation of an QLED; (a) dispersibility as viewed from the top and the side [135] (note the homogeneous dispersion of the polymer coated hybrids); (b) electroluminescence from 3 hybrid systems (QH1 to QH3, see ref. for assignment); they are identical to the electroluminescence of the pure QDs; reproduced with permission of [135], published by Wiley-VCH, 2009.

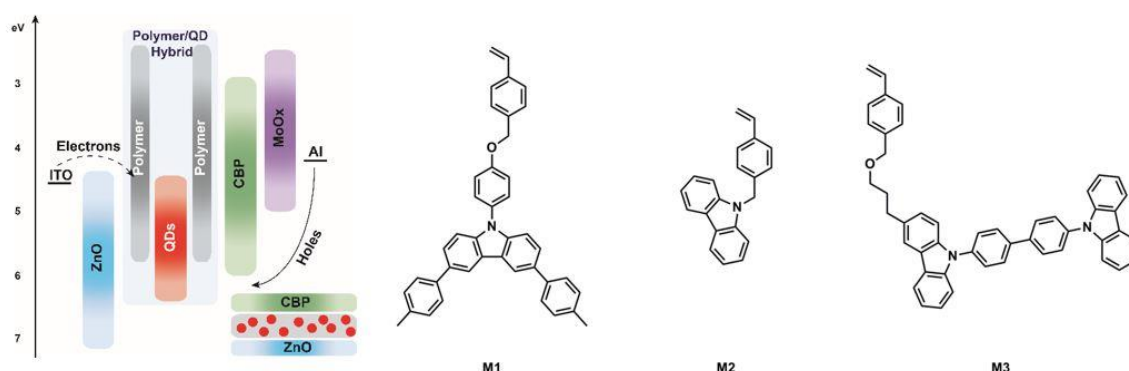


Figure 12. Scheme of the band gap alignment in an QLED with inverted device architecture (left) as well as 3 new monomers for the preparation of a semiconducting blockcopolymer; see [138] for more details.

Recently the significance of the morphology of QD emission layer on the device performance was studied in a systematic comparison [25] and it could be shown that the homogeneous dispersion of QDs, as it can be obtained with hybrid systems, is advantageous. For this purpose, QD emission layers of different morphologies consisting of QD-only films, QD/semiconductor polymer blends or QD-semiconducting polymer hybrids, were compared (see Figure 13). The optoelectronic performance of QLEDs demonstrates that the hybridization of QDs with semiconducting polymers significantly enhances the emission efficiency of QD emitters and this can be explained by (i) the improved charge carrier balance concerning the QDs and (ii) the optimized morphology. Pure blends suffer from their inhomogeneous structure due to segregation of QDs and polymer (see also Figure 11). Thus, in parts of the film the charges will never meet a QD, while in others the situation resembles QD-only films. QD-only films are, however, very fragile and cannot be expanded in thickness; they bring the QDs in close proximity to each other, which increases the electronic coupling between the QDs and leads to quenching. Thus, the efficiency of the QD emission layer can be increased by increasing the mean inter-dot distance as happens naturally in the hybrid QD emission layers. This oppresses the quenching between QDs. So, QD-semiconducting polymer hybrid emission layers benefit from both aspects and

show a substantially enhanced device efficiency (peak EQE of 5.6%) and brightness (peak luminance of 21,707 cd m⁻²) [25] compared to the cases of QD-only (2.0% and 16,843 cd m⁻²) or physically blended QD/polymer emission layers (1.7% and 4207 cd m⁻²).

Hybrid QLEDs vs. Blend QLEDs

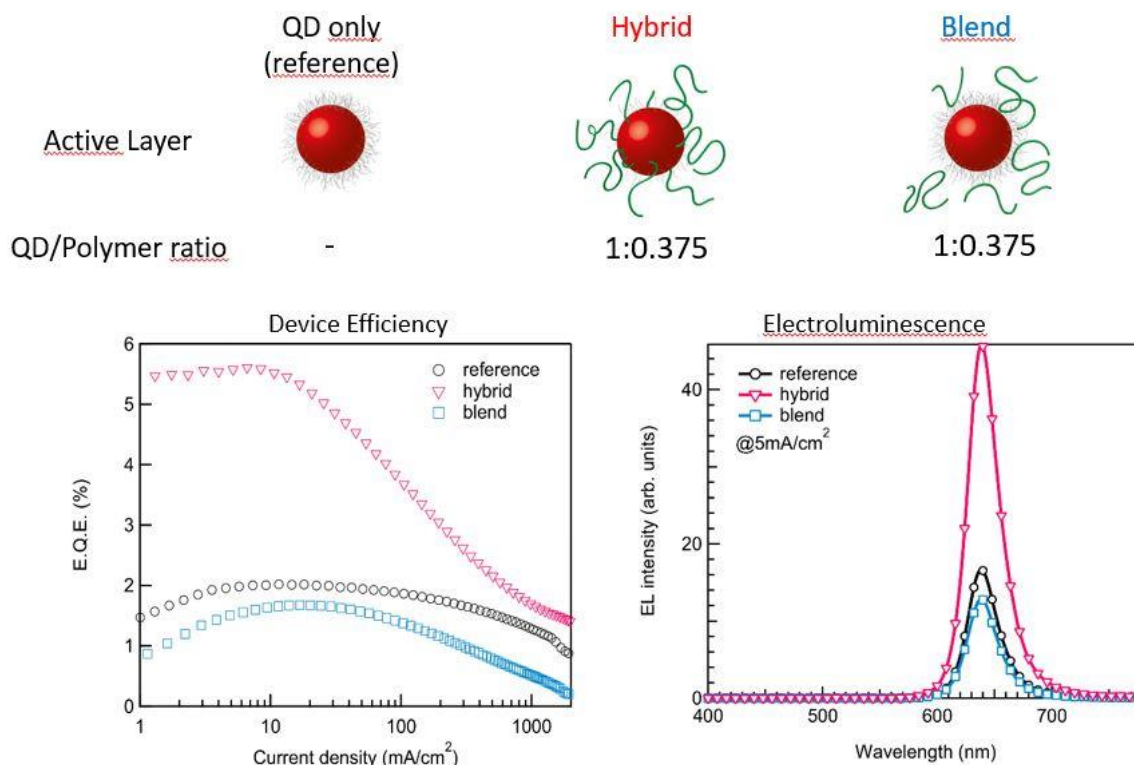


Figure 13. Results of the comparison of CdSe QLEDs with a single layer of fluorescent QDs (left, reference) as well as polymer coated hybrids and blends of unfunctionalized QDs and polymer; see [25] for more details; reproduced with permission of [25], published by Wiley-VCH, 2016.

Such hybrid structures can also be made from InP QDs (see Figure 14). Such QDs have found a lot of interest in circumventing the use of toxic Cd in CdSe. From the chemical side it is relatively easy to coat such InP QDs with semiconducting polymers, because InP quantum dots themselves are usually coated with ZnSe/S as inorganic shell to stabilize the InP core [127]. Therefore, the chemistry needed to graft polymers to them is identical to the established CdSe QD, which uses the same shell material (Figure 14a). In this case successful grafting, homogeneous dispersion of the QDs, and an improved external quantum efficiency could also be demonstrated. The electroluminescence is again identical to that of QD-only devices (Figure 14b).

Quite recently some new concepts to improve the performance of QD-LEDs by the use of polymer hybrids were introduced. This concept starts with the idea, that the QDs act as chromophores in the semiconducting matrix, which is needed for charge transport. Usually the need to localize the charges (positive and negative) inside the chromophores for excimer formation requires that the QDs have a lower band gap than the matrix. However, under these conditions they will naturally act as traps, reduce the charge carrier mobility [142], and worsen charge transport and effectivity. Now there is a possibility to circumvent this problem. It requires the blocking of charge transfer, because in this way the creation of traps can be eliminated. The transfer of energy from the matrix (excimer formation within the semiconductor) to the chromophore can then still be done by Foerster transfer [142]. This

concept could be realized recently [142] (see Figure 15). It was possible by coating of the CdSe QDs with polystyrene. Polystyrene has such a large band gap so that neither electrons nor holes can easily cross a thin shell of it. So, the CdSe QDs no longer act as traps, which improves the charge transport in the matrix of the semiconducting polymer. Furthermore, it leads to a voltage independent electroluminescence spectrum of the quantum dots.

InP/ZnSeS Quantum Dots

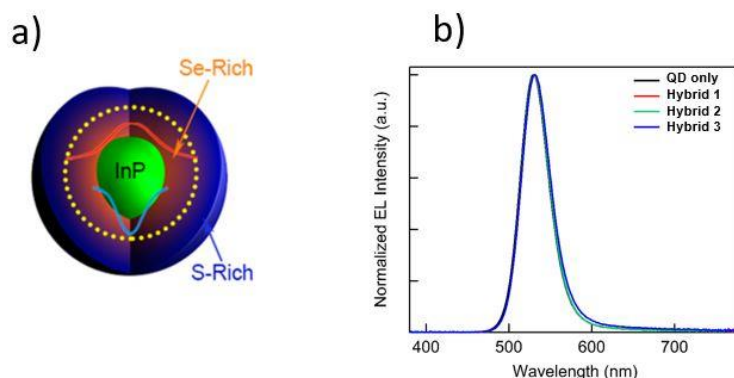


Figure 14. Structure of InP QDs coated with a ZnSeS shell (a) as well as the electroluminescence of QLEDs (b) prepared from such QDs after coating with a semiconducting polymer (a block copolymer from M2 in Figure 12).

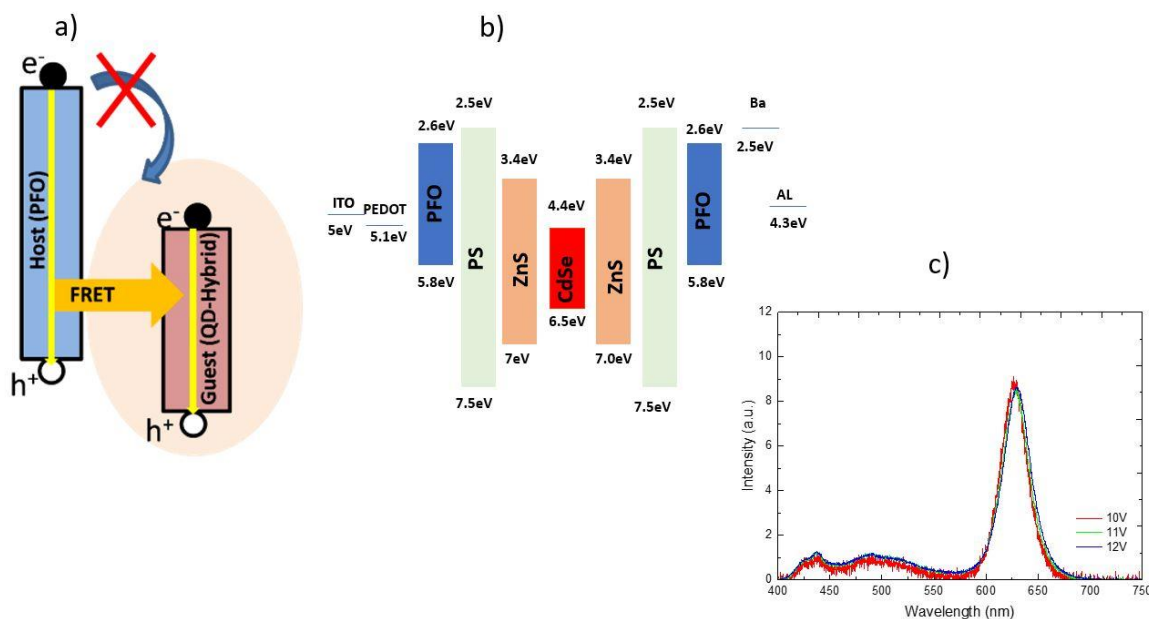


Figure 15. Schematic representation (a) of the general concept of preventing traps for charges by placing fluorescent guests inside a semiconducting polymer; coating the QD with a thin polystyrene shell (see energy diagram in (b)) can block the transfer of charges to the QD; the transfer of energy from the semiconducting matrix to the QD can, however, still proceed via Foerster transfer. The resulting electroluminescence (c) is voltage independent. See [142] for more information.

5. Summary

This paper summarizes recent work on the preparation of inorganic–organic hybrids from a materials perspective. For this purpose, it presents, at first, concepts to improve the solubility (or more broadly, the compatibility) of inorganic nanoparticles in organic solvents or polymers as matrix. It has been shown that with a proper polymer coating it is possible to dissolve (disperse) the nanoparticles as

individual objects and to modify this, later on, with external stimuli. The dispersion as individual objects becomes thereby not only possible in solvents, but also in polymers (as solid solvents) and even in highly functional, semiconducting polymers.

Starting with good solubility (compatibility) two further aspects are discussed. The possibility to prepare highly concentrated solutions of shape anisotropic nano-objects make it easy to obtain lyotropic liquid crystalline phases. They also allow a macroscopic orientation of the shape anisotropic nano-objects.

Alternatively, semiconducting inorganic nanoparticles can be electrically connected to a polymer matrix. This is advantageous for energy storage in batteries and it allows polymer LEDs to be prepared with highly fluorescent inorganic nano-particles (QDs) as chromophore. Recent works have aimed to further improve these fascinating light emitting materials.

Funding: Most of the research of the author -in relation to this topic- was funded by the German Science Foundation, DFG (IRTG 1404)

Acknowledgments: Dominik Fuchs is thanked for helping in the preparation of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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