Colloidal Nanocrystals Embedded in Macrocrystals: Methods and Applications

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ABSTRACT

Colloidal semiconductor nanocrystals have gained substantial interest as spectrally tunable and bright fluorophores for color conversion and enrichment solids. However, they suffer from limitations in processing their solutions as well as efficiency degradation in solid films. As a remedy, embedding them into crystalline host matrices has stepped forward for superior photostability, thermal stability, and chemical durability while simultaneously sustaining high quantum yields. Here, we review three methods for preparing these mixed macrocrystals, discuss their photophysical properties, present their application in light-emitting diodes as well as their utilization for plasmonics and excitonics. Finally, we present a future outlook for the science and technology of these materials.

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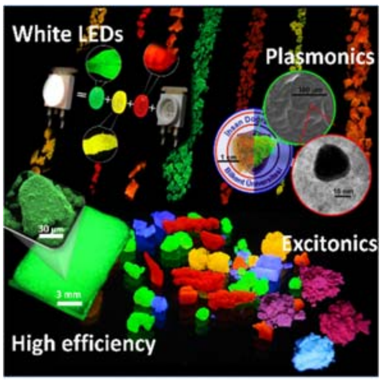

Incorporation of colloidal nanocrystals into crystalline host matrices allows for robust light-emitting solids possessing high quantum efficiency and emission stability. Here, we summarize the techniques for preparing these materials and their applications and present a future outlook on the topic.

KEYWORDS

Mixed macrocrystals, colloidal nanocrystals, quantum dots, light-emitting diodes, lighting, displays

Since their first description in the early 1980's, most of the scientific research has been focused on the reproducible colloidal synthesis of high efficiency, narrow-band emitting semiconductor nanocrystals (NCs) covering the electromagnetic spectrum from ultraviolet (UV) to infrared (IR). Today these materials find applications in various branches of biology,[1] chemistry,[2] physics,[3] and electronics.[4] In the field of photonics, NCs attract significant interest for use in light-emitting diodes (LEDs) and displays because they allow for high photoluminescence (PL) quantum yields (QY), for their narrow-band emission accompanied with broad-band absorption spectra characteristics of semiconductors. Furthermore, NCs offer tunable emission spectra by controlling their size, shape, and composition and engineering their architecture. Especially, their narrow emission bands lead to advantages important for quality lighting in white LEDs and displays because they provide the ability to design the emission spectrum with increased color purity in luminaries and color definition in displays.[5] These strengths of the NCs also make them promising alternatives to rare-earth ion based phosphors, which are traditionally used in white LEDs used in lighting and displays.

To date high-performance white LEDs using NCs for color-conversion that simultaneously enable successful color rendition capability and optimal overlap with the human eye sensitivity function along with a warm-white shade have been reported.[6,7] Moreover, electronic displays employing NCs as color converters have been developed and commercialized, e.g., by Samsung,[8] Sony,[9] and Amazon.[10] Despite their successful deployment, NCs still typically suffer from decreasing QYs in their solid films within polymeric encapsulants and low emission stability on LED chips driven at high currents. The rigid conditions during the direct hybridization process of NCs with these host materials are known to degrade the NC emission. Furthermore, the diffusion of oxygen and humidity through the encapsulating materials is another important concern especially when the NCs are subjected to heat, for example, when intimately integrated with LEDs and these hybrid devices are driven at high current densities. As a remedy to these problems, a new promising method has been recently proposed by Otto et al.[11] for the incorporation of the NCs into crystalline host matrices, which enables high QYs in powder form and solid films together with significantly improved photo- and thermal-stability of the NC emission. The powders of these mixed macrocrystals have further been shown to possess excellent compatibility with the epoxies widely used for encapsulating color converters by the industry. This is an important strength of this material system for the LED and display producers. In addition, these NC-macrocrystals have been shown to provide a robust platform for studying environment-sensitive interparticle interactions such as plasmonics and excitonics[12,13]. As an interesting application, the macrocrystals of NCs have been very recently proposed as sensitive thermometers using strong variations observed in the emission spectrum of the macrocrystals as a function of temperature [14].

In this article, we summarize recent developments on the mixed macrocrystals of NCs. First, we briefly review the techniques to produce these materials and discuss their main photophysical features. Subsequently, we present the latest demonstrations of pure-color LEDs and white LEDs, which were developed employing a model-experimental feedback approach. Then follow studies on exciton transfer and plasmonic interactions in these macrocrystals and the utilization of the macrocrystals as thermometers is summarized. At the end, an overview on the mixed macrocrystals together with a future outlook is presented.

To date, CdTe NCs in water[15], CdSe/ZnS NCs in water and nonpolar solvents with an alloyed gradient shell[16] and Au NCs in water[17]have been successfully incorporated into macrocrystals. In addition, the incorporation of Cd-free InZnP/ZnS NCs in water have been reported as well.[18]

Salts including NaCl,[11,19] KCl,[11] KBr,[11] borax,[20] and LiCl[21] have been employed as host matrices along with organic crystalline hosts including sucrose[12] and anthracene[22]. In these previous works, the nanoparticles were embedded into the host matrix using one of the three main strategies reported in the literature, which are schematically displayed in Figure 1: (i) direct incorporation of NCs via slow solvent evaporation, (ii) vacuum-assisted NC incorporation, and (iii) liquid-liquid-diffusion-assisted-crystallization (LLDC). For the crystallization process, the colloidal stability of the NCs within the concentrated solution of the host material needs to be high enough to ensure proper, non-aggregated incorporation of the NCs. If the colloidal stability is low, using a host with lower ionic strength in solution[12,20] or reducing the time needed for the crystallization might be helpful[18,21].

The first method is based on the incorporation of water-soluble NCs (e.g. CdTe) into conventional ionic salt crystals[11] such as NaCl, KCl, KBr or non-ionic molecules such as sucrose[12]. In these works, using ionic salts, the mixed macrocrystals of NCs were obtained by blending a saturated salt solution with a batch-specific amount of the NCs. The solutions were kept at 30 °C to promote the evaporation of H_2O and the crystallization was finished when the parental solutions turned colorless. Although some influence of the colloidal species on the growth and structure of ionic crystals is expected, no remarkable effects were observed in the experiments, which can be ascribed to the low loading values of the NCs within the macrocrystals. However, a change from the cubic structure to the octahedral shape was observed when NaCl was utilized as the host matrix. Such different morphology of the host material can be attributed to the free stabilizing agents (TGA or MPA) within the NC-salt solution mixture, which are well known to alter the shape of NaCl crystals from cubic to octahedral.[23] Furthermore, MPA-stabilized NCs turned out to be generally more stable in saturated salt solutions than their TGA-stabilized counterparts. As TGA-capping allows for a better control on the synthesis of CdTe NCs emitting in green to orange spectral regions, efficient incorporation of strongly emitting TGA-capped CdTe NCs into salt matrices is possible. By adjusting the pH of the saturated salt solution, using KCl as a host matrix, and adding small amounts of additional free stabilizer, reproducible incorporation of such NCs is feasible.[24]

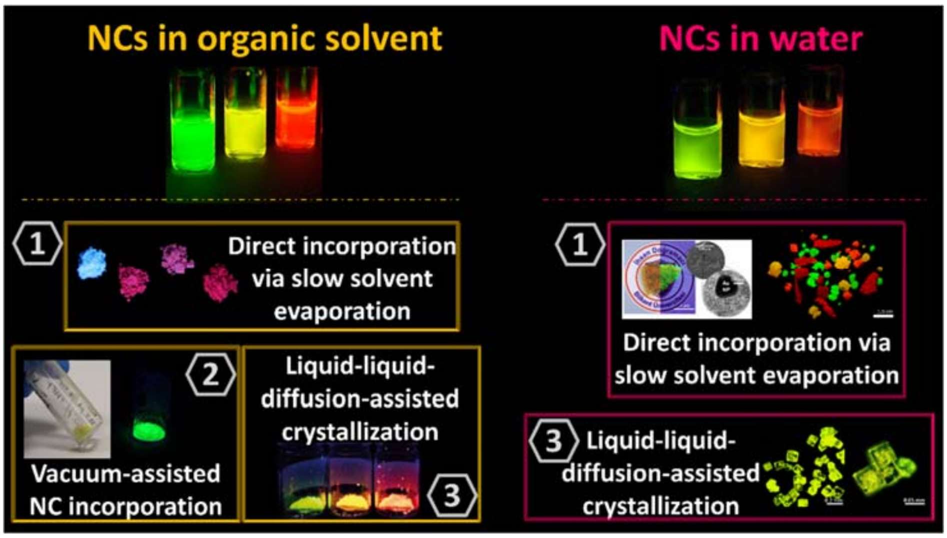

Figure 1. Incorporation techniques used to embed NCs into macrocrystals. The first method is the direct incorporation via slow solvent evaporation, which relies on mixing NCs with salt or organic crystalline molecule solution and then on evaporating the solvent slowly to obtain crystals. The second method is vacuum-assisted NC incorporation, which is based on dispersing the NCs in a solvent, which subsequently disperses the NCs, and then on evaporating this solvent within a vacuum chamber. With this method NC incorporation duration is decreased from days to minutes compared with the slow evaporation technique. The third method is the LLDC. In this method, the diffusion of an orthogonal solvents is employed to decrease the solubility of the salt in water enabling the immobilization of the NCs on the salt crystals. Reproduced with permission from Ref. [18] (©John Wiley and Sons, 2015), Ref. [12] (©Springer Verlag, 2015), Ref. [21]

(©Royal Society of Chemistry, 2015), and Ref. [11,22,25] (©American Chemical Society 2012, 2015, and 2015, respectively).

As a variation of this approach, to reduce the ionic strength of the saturated salt solutions, alternative host matrices were employed. For example, sugar, which is a non-ionic organic molecule forming large crystals, has been shown to allow for the simultaneous incorporation of CdTe NCs together with Au NCs.[12] Since the incorporation of the citrate-capped metal NCs was not possible using ionic hosts due to the induced aggregation, the utilization of sugar enabled plasmonic interactions occurring between semiconductor and metal NCs, which will be further discussed in the applications section of this review. Alternatively, borax ($Na_2B_4O_7 \cdot 10H_2O$) has been used to immobilize core/alloyed-shell NCs following a ligand exchange with mercaptopropionic acid (MPA). Since it has a reduced ionic strength in comparison to alkali halides, higher NC colloidal stability in the crystallization mixture could be realized. More importantly, higher amounts of NC incorporation into macrocrystals have been reported.[20] To incorporate the NCs dispersed in organic solvents, anthracene has been employed by utilizing its solubility in chloroform, which can simultaneously disperse oleic acid capped NCs.[22]

The second method provides a fast pathway for the incorporation of NCs dispersed in organic solvents into the inorganic or organic molecules without a prior ligand exchange. In this technique, NCs dispersed in organic solvents are directly incorporated into the organic solvent-soluble salts such as LiCl[13,21]. In these reports dry tetrahydrofuran (THF) was used to dissolve LiCl, which is also a relatively good solvent for the NCs. In order to incorporate NCs into LiCl, the NCs were dried, re-dispersed in THF, and mixed with LiCl-saturated THF solution. Subsequently, the solvent was evaporated quickly in a vacuum chamber, resulting in a complete mixed macrocrystal formation within a few minutes.

The third method is the LLDC[18] relying on the solubility difference of inorganic salts in solvents with various polarities. In this technique, due to the reduced solubility of NaCl in water by the interdiffusion of the orthogonal solvent, the crystallization can be completed in less than one day lowering the time needed to produce mixed macrocrystals by more than one order of magnitude in comparison with the crystallization techniques based on the slow evaporation of solvent.[11,19] Therefore, a mixture of NC solution and NaCl was placed below a layer of methanol, allowing the methanol to diffuse into the NC-layer and be stored for roughly 15 h. Moreover, by adapting a two-step seed-mediated LLDC, the direct application of oil-based NCs for co-crystallization with salts without a prior phase transfer into water was achieved. Here, NaCl-saturated methanol was added to the NCs in chloroform forming initially mixed macrocrystal seeds, which were then redispersed in pure methanol. In the second step, NaCl dissolved in H_2O was injected under the seed-methanol layer and stored for 15 h.

The most significant effects of the NC incorporation into a suitable crystalline matrix appear on the PL spectra and PL QY. Upon embedding the NCs into a crystalline host, a slight red shift of the PL spectra is observed, which can be explained with the variation of the dielectric media surrounding the NCs. The shape of the PL spectra, on the other hand, is not altered. As it can be depicted from Figure 2a, all CdTe NCs show an enhancement in the PL QY following the incorporation into NaCl. This enhancement, which is larger than the expected refractive index-induced change[26,27], can be attributed to the formation of a thin $CdCl_x$ layer. This additional thin layer seems to passivate dangling bonds on the NC surface and reduce the non-radiative relaxation routes, as described by Sargent et al.[28,29]

In another study, Müller et al. performed comparative studies of CdSe/ZnS NCs embedded in NaCl macrocrystals and CdTe NCs in borax to verify the hypothesis of surface defect curing related to the formation of a chloride layer. In both cases, $CdCl_x$ cannot be formed on the NC surface. According to Figure 2b, CdSe/ZnS NCs exhibit a typical drop in PL QY during the phase-transfer from organic media to water[26], which remains almost unaffected by the incorporation into the NaCl host. For the borax-encapsulated CdTe NCs, the PL QY increases only slightly upon incorporation. Variations of the PL QY, which remain below the expected refractive index-induced changes, indicate an increase of non-radiative processes. This suggests that the formation of $CdCl_x$ at the NC surface, which can occur for CdTe in the presence of NaCl, possibly contributes to the salt-crystal induced PL enhancement. The effect of the nonpolar NC incorporation into LiCl crystal powders on PL QY was also investigated[21]. The results showed that the PL QYs of these powders might sustain the values in the dispersion if the concentration of the NCs is correctly adjusted (Figure 2c). This means that incorporating the NCs into LiCl allows for realizing color-converting powders with PL QYs higher than 70%. In addition to the NCs, the effects of the nanoparticle encapsulation within crystalline matrices were studied using organic semiconductor oligomer nanoparticles.[30] In this work, the researchers incorporated orange-emitting oligomer nanoparticles into NaCl and sucrose, and showed that the QY of the nanoparticles in sucrose matrix improves more than six times when incorporated in sucrose while incorporation into salt matrices did not demonstrate a remarkable variation in the QY. With this work, the QYs of these organic nanoparticles were brought to similar levels of the inorganic NCs in solid-film, which makes these nanoparticles suitable for solid-state lighting.

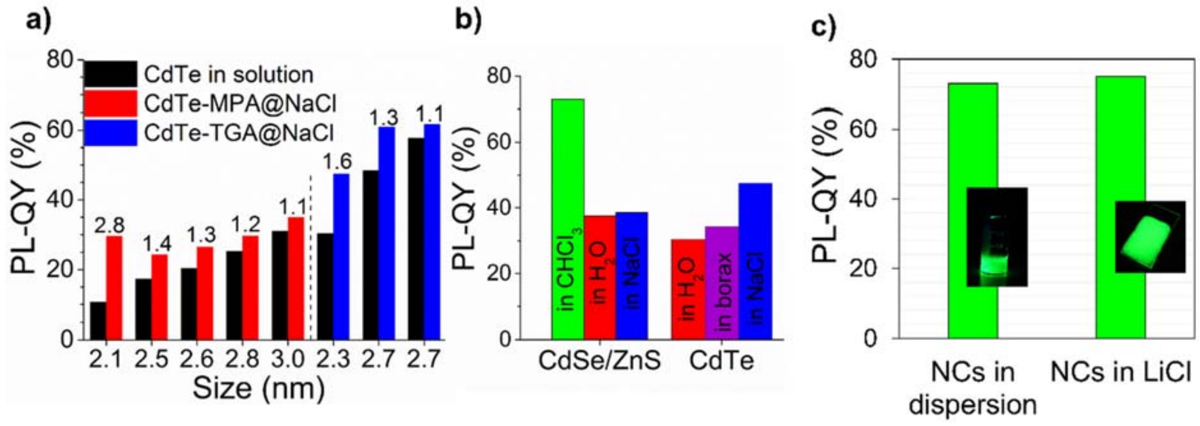

Figure 2.a) PL QY of thiol-stabilized CdTe NCs before (black) and after (red or blue) their incorporation into the salt matrix with the respective enhancement factors given as numbers. Increasing particle sizes lead to higher PL QYs in solution and smaller PL QY enhancement factors for both thiol ligands. b) Relative PL QY of CdSe/ZnS and the respective NC-salt mixtures. CdSe/ZnS NCs were phase-transferred from $CHCl_3$ to H_2O resulting in a PL QY drop, whereas subsequent incorporation into NaCl causes only a negligible change in PL QY. CdTe NCs from one batch were incorporated into either borax or NaCl crystals, yielding almost no change for the former but a strong increase by a factor of 1.5 in the case of using a NaCl host. Reproduced with permission from Ref. [26] (© American Chemical Society, 2014). c) PL QY of NC-embedded LiCl crystals before and after crystallization. Reprinted with permission from Ref. [21] (© Royal Society of Chemistry 2015).

The incorporation of the NCs into macrocrystals builds up a barrier against oxygen and humidity penetration, which eventually improves the emission stability of the NCs at elevated temperatures and when exposed to high photon flux. By applying different test routines, the emission stability of the NC emission within the macrocrystals was investigated in different studies.[11,18,20] For example, Adam et al. stored the mixed macrocrystals in a strongly oxidizing solution and observed the variation of the emission intensity over time. As shown in Figure 3a, the emission of the pure NCs in the strong oxidizing solvent is completely quenched within 24 h, while the mixed macrocrystals preserve their intense PL even after 24 h of storage without any noticeable deterioration.

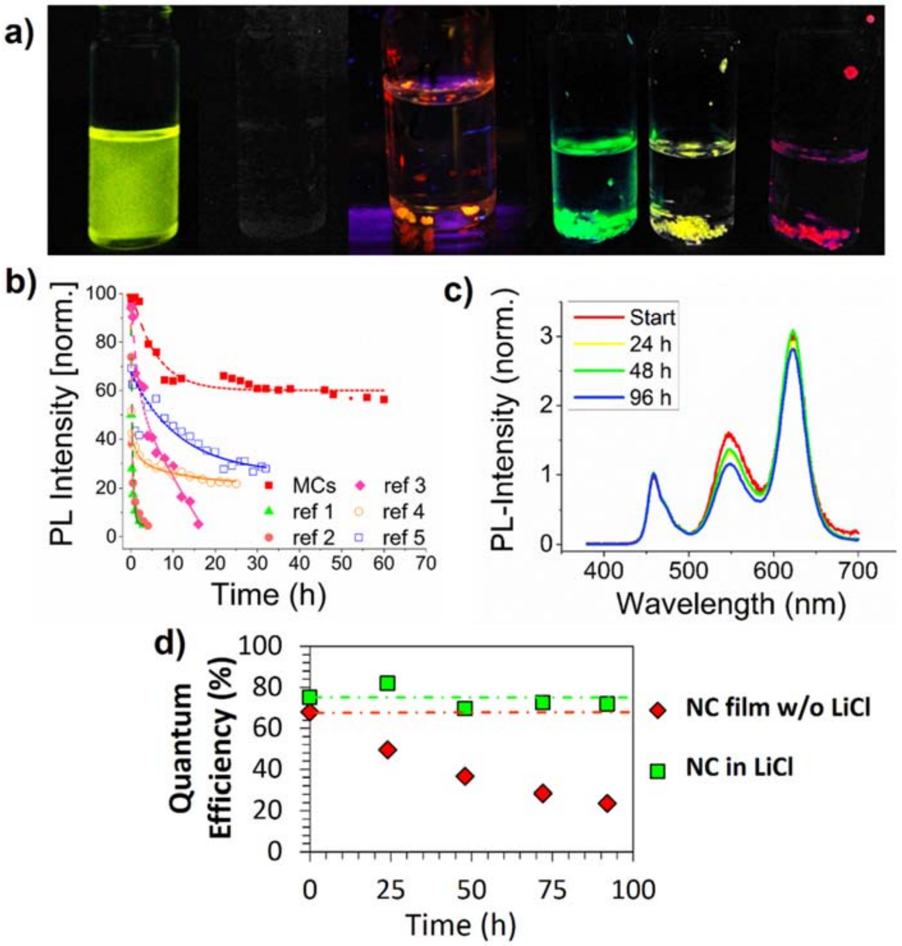

Figure 1. a) True-color images of the stability test of mixed macrocrystals by using benzoyl peroxide as oxidizing agent under 365 nm UV excitation. From left to right: CdSe/ZnS NCs in toluene before and after the addition of benzoyl peroxide for 24 h; mixed macrocrystals containing CdTe NCs and various CdSe/ZnS NC after the addition of benzoyl peroxide in

toluene for 24 h. Reprinted with permission from Ref. [18] (© John Wiley and Sons 2015). b) Evolution of the integral PL intensity of CdTe NCs-NaCl macrocrystals and reference samples containing the same NCs in different matrices or mixtures in the focal point of a 1000 W xenon lamp. Solid lines are solely provided as a guide to the eye. Reprinted with permission from Ref. [11] (©American Chemical Society 2012). c) PL spectra of the w-LED before and during the stability tests. The w-LED was driven at 300 mA and a 1 kHz on/off rate. Reprinted with permission from Ref. [25] (©American Chemical Society 2015). d) QY variation of NC embedded LiCl crystals and NC film (without crystallization) as a function of time on the blue LED driven at high current level for 96 h. Reprinted with permission from Ref. [21] (©Royal Society of Chemistry 2015).

As the host matrix proved to be exceptionally rigid, it is indeed very unlikely that ambient oxygen could penetrate through the salt into the encapsulated NCs. The NCs should consequently offer high photostability when they are protected from the environment. Photostability tests of CdTe NCs in NaCl matrix were carried out in Ref. [11] by placing them at the focal point of a 1000 W Xenon lamp fitted with a water filter for cutting off the near-IR part of the spectrum. CdTe NCs embedded in polymers, mixtures of NC powder with NaCl crystal powder, with glass powder, and with poly(methyl methacrylate) (PMMA) powder were used as reference samples, which were carefully prepared to possess optical densities comparable with the mixed macrocrystal sample. To monitor the stability, the PL spectra of the samples were measured in the course of the phototreatment. As depicted in Figure 3b, the harsh conditions of the illumination used in the tests were found to weaken the emission of all of the reference samples. Their degradation times turned out to be on time scales from minutes to several hours. Nevertheless, the mixed macrocrystal sample showed remarkable PL stability of more than 60 h.

The initial drop of 30-40% in the emission intensity may be assigned to degradation processes involving water and oxygen entrapped in the mixed macrocrystals and NCs associated with the surface of the mixed macrocrystals. It should be emphasized that the shape and position of the PL spectra is not altered by the intense phototreatment while only the total PL intensity decreases. This can also be seen in Figure 3c, which shows the change in the emission spectrum of the white LED prepared employing mixed macrocrystal powders as color conversion layer. To avoid a strong heat generation and observe the effect of the intense photon flux, the LED was placed on an aluminum plate for passive cooling and operated at a 1 kHz on/off rate, which kept the temperature of the LED below 35 °C. The intensity of the mixed macrocrystal emission decreases only slightly, which is in good agreement with the findings on the PL stability of the mixed macrocrystals under intense illumination.

It should be noted that these mixed macrocrystals were grown under ambient conditions. A preparation under inert atmosphere could be beneficial for commercialization reasons, preventing the incorporation of dissolved O_2. This might be a crucial step for a further increase of the photostability. The emission stability of the NCs in LiCl was also studied at elevated temperatures.[21] For this purpose, green-emitting mixed crystal powders were integrated on a blue light-emitting diode driven at 100 mA. Results represented in Figure 3d demonstrated that the LiCl matrix acts as a strong barrier against oxygen diffusion toward NCs and helps the NCs to protect their initial emission intensities. However, the same NCs exhibited significantly weaker emission stability when they are integrated on LED without inorganic salt encapsulation. The effect of the salt-encapsulation on the emission stability of the NCs was also studied by Hsu et al.[31] In this work, CdTe NCs in water were integrated into NaCl matrix and a red-emitting LED was obtained by hybridizing the powders of NCs in salt on a UV LED. The resulting device exhibited a remarkable power conversion efficiency of 72.6%. Furthermore, these NCs were shown to possess high emission stability on LEDs with a half-lifetime reaching 6488 h at low current levels. These findings clearly show that incorporating NCs into crystalline matrices significantly contributes to the stable emission of NCs, which is of great importance for lighting and display applications.

One of the important advantages of these macrocrystals is the protection of the NCs within the host matrix against the chemical effects of the encapculants. In addition, the ability to powder these macrocrystals allows for their utilization on LEDs without any deterioration of their QY and for tuning the final emission spectra by carefully controlling their amounts (Figure 4a). As a result, highly stable and efficient LEDs with superior photometric performance can be obtained by employing them.

Although white LEDs (w-LEDs) using CdTe NCs embedded into NaCl and LLDC-based mixed macrocrystals as color conversion layers with promising photometric performance were previously shown, those devices could not fulfill all of the demanding requirements for indoor lighting at the same time.[11,18] To prepare a w-LED with a high luminous efficacy of optical radiation (LER), a high color rendering index (CRI) and a low correlated color temperature (CCT) close to the incandescent bulb, a model-experimental feedback approach was used.[20]

According to the underlying model,[6] the spectral requirements were defined and evaluated at each intermediate stage to guarantee the exceptional quality of the final device. Three sets of borax-based macrocrystals with CdSe/ZnS NCs with an alloyed gradient shell as green, yellow, and red emissive centers were used with special emphasis given on generating a warm white light to simultaneously achieve CRI >90, LER >330 lm/W_{opt}, and CCT <4500 K. By adjusting the powder amounts of the different color components and thereby tuning the hue of the final device, a warm w-LED reaching a CRI of 91 and a LER of 341 lm/W$_{\mathrm{opt}}$ at a CCT of 2720 K was fabricated. Therefore, this LED, with its emission spectrum and chromaticity coordinates displayed in Figures 4b and 4c, respectively, balanced for the first time these strongly related figures of merit for NC-based color convertors exceeding state-of-the-art in literature.[7,32]

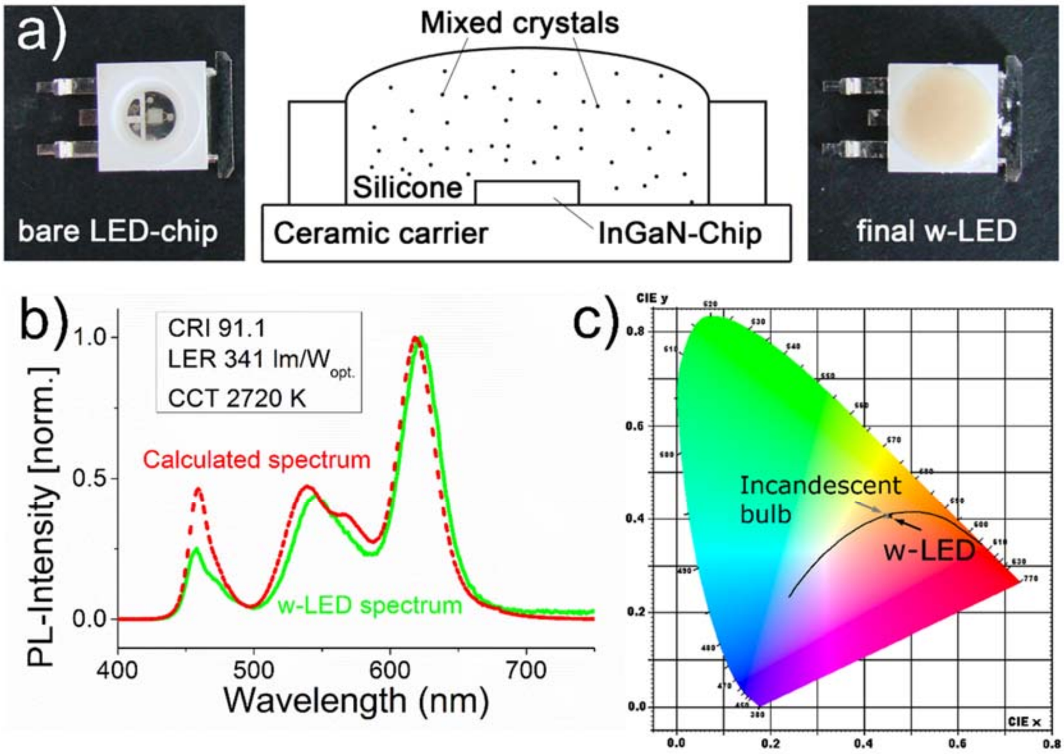

Figure 2. a) True-color image to the bare blue-emitting 1 W InGaN LED chip, schematics of its hybridization with mixed macrocrystals embedded in silicone and the resulting white LED. Reprinted with permission from Ref.[11]. ©American Chemical Society 2012. b) PL spectrum of the w-LED within the visible region (solid line) and the modeled spectrum used (dotted line), while c) shows CIE 1931 diagram with the black-body radiator (black line, CRI 100) as

comparison with the w-LED marked with the black cross and an incandescent bulb (grey cross). Reprinted with permission from Ref. [25]. ©American Chemical Society 2015.

In addition to white LEDs of macrocrystals, their single-color LEDs were also studied. For this purpose, Kalytchuk et al. incorporated CdTe of various sizes into NaCl and obtained green-, yellow-, orange-, and red-emitting powders[19]. These were subsequently integrated with UV LEDs, forming pure-color emitting LEDs. A proof-of-concept blue-green LED was prepared by Erdem et al.[13] In this work, green-emitting core/alloyed shell NCs were immobilized within LiCl. These NCs were shown to protect the initial QY after forming their powders, and their LEDs were prepared by encapsulating them with a commercially available epoxy resin on a blue LED.

Incorporation of the NCs within macrocrystals also enables creating robust and stable platforms for investigating plasmonic interactions. The main advantage of this approach is the isolation of the metal nanoparticles from the ambient environment so that the effects related to the surrounding medium are mitigated or fully eliminated by the host medium. The plasmonic interaction in the mixed macrocrystals of metal NCs was demonstrated for the first time by Erdem et al.[12] Prior to this work, only salt crystals had been employed for embedding colloids into crystals. However, the citrate-capped Au NCs aggregated immediately after the introduction of the salt solutions due to the presence of cations in the solution. As a remedy, a sucrose host was proposed and Au NCs were incorporated within sucrose macrocrystals. The resulting cm-sized crystals exhibited pink color inherited from the plasmonic character of the gold nanoparticles. The absorption spectrum of these crystals clearly showed the plasmonic resonance, which was slightly red-shifted due to the increased refractive index of the sucrose host compared to the nanoparticle dispersion in water. Subsequently, semiconductor and metal

NCs were co-immobilized within sucrose and the PL QY of the NCs was found to increase by 58% owing to the plasmonic interaction.

The mixed macrocrystals also provide interesting opportunities for studying excitonic interactions as they enable to obtain luminescent powders in which exciton transfer takes place on the nanoscale. Soran-Erdem et al.[22] studied exciton dynamics by incorporating non polar red-emitting NCs into anthracene crystals, which is a well-known semiconducting organic crystalline molecule. Since the absorption spectrum of the incorporated NCs strongly overlaps with the emission spectrum of the anthracene host surrounding the NCs, the nonradiative energy transfer was enabled from the host anthracene molecules to the incorporated NCs. Time-resolved fluorescence spectroscopy clearly revealed the existence of this energy transfer with an efficiency reaching ~29%. In this work, the anisotropic optical features of the anthracene were also utilized and otherwise isotropic emitting NCs were shown to exhibit anisotropic emission character when incorporated into the anthracene macrocrystals. Furthermore, these macrocrystals were integrated on a UV LED as color converters. The resulting device had a violet appearance owing to the combination of blue emission from the anthracene host and the red emission from the NCs.

In their previous study, Erdem et al. reported that the distance between the NCs in TEM images was below 20 nm within the LiCl matrix[21] suggesting that the nonradiative energy transfer should also be possible in their powders. Based on this hypothesis, Erdem et al. hybridized nonpolar green- and red-emitting NCs within LiCl salt.[13] The analyses of the emission dynamics revealed a nonradiative energy transfer efficiency reaching ~54%, which is almost twice the value obtained in anthracene macrocrystals.[22] The authors also prepared a proof-of-concept of an excitonically improved light-emitting diode employing these powders. The resulting device exhibited a violet emission and reached a luminous efficiency >70 lm/W_{elect}.

Recently, Kalytchuk et al. utilized the temperature dependent emission change of the mixed macrocrystals for remote temperature measurements[14]. In this work, CdTe NCs of various sizes were incorporated into NaCl and their emission spectra were recorded from 80 to 360 K and strong variations were observed in the emission intensity at different temperatures. The researchers have found out that the temperature coefficient is strongly dependent on the NC size and the smallest NCs exhibit better temperature sensitivity. The investigation of the nonradiative lifetimes revealed that they change significantly as opposed to the radiative lifetimes, which remain mostly constant with temperature. This dependence of the nonradiative recombination was found to be responsible for the variations in the emission spectrum and this enables the detection of the temperature with high precision in these solid-state materials.

In this perspective letter, we have presented a summary of the procedures for a broad range of NC-integrated mixed macrocrystals and evaluated their potential as the next-generation color conversion materials for pure color and white luminaires along with robust platforms for studying interparticle interactions. As these materials are yet at a very early age of exploration, a broad number of interesting aspects need to be investigated in order to exploit their widespread application. Until now, no derivatization of structure-property relationships has been reported, which requires more systematic studies including different host materials as well as NCs of various and well-known surface chemistries, while new salts including $BaSO_4$[33] and KH_2PO_4[34] have been also introduced. In addition, there is still a need for increasing the loading amount and accelerating the incorporation process, which also attract the interest of the researchers.(chang,benad).

Future studies should include the use of anisotropic quantum structures like quantum rods, especially in combination with an oriented incorporation of the quantum structures into the host matrices. Furthermore, the use of Cd-free NCs needs to be analyzed in more detail with an emphasis on retaining the PL QY over all intermediate steps. The incorporation of organic molecules[34] and nanoparticles such carbon dots[35,36] also an interesting aspect which may address the problems of the NCs and offer decreasing the costs. This can also be used for the LED applications, where improved PL QY and light outcoupling from the device are required to reach not only high spectral but also high electrical efficiency.

As another direction, employing these macrocrystals for lasing applications is also an important motivation for increasing the NC concentration in the macrocrystals. Moreover, these robust crystalline matrices might be considered as a suitable platform for investigating nonlinear plasmonics. In addition, engineering the structure of these macrocrystals such as creating photonic crystals is also a possible interesting capability of these materials that still remains unexplored.

Considering the works presented here and unexplored potential of these materials for science and engineering applications, we believe that mixed macrocrystals of colloidal NCs will remain as an interesting material system in the near future for the field of colloidal photonics.

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Notes

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