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 matrixes has stepped forward for superior photostability, thermal stability, and chemical durability while simultaneously sustaining high quantum yields. Here, we review three basic methods for loading the macrocrystals with nanocrystals, namely relatively slow direct embedding, as well as accelerated methods of vacuum-assisted and liquid—liquid diffusion-assisted crystallization. We discuss photophysical properties of the resulting composites and 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.

Since their first description in the early 1980s, 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,† chemistry,‡ physics,§ and electronics.† 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 by the 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.§ 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 have been reported 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.6,7 Moreover, electronic displays employing NCs as color converters have been developed and commercialized, for example, by Samsung,§ 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 matrixes (macrocrystals), which enables high QYs in powder form and solid films together with significantly improved photo- and thermal-stability of the NC emission. The powders macrocrystals containing NCs have further been shown to possess excellent compatibility with the epoxies widely used for encapsulating color converters. 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.12,9 As an interesting application, the NCs in macrocrystals have been very recently proposed as sensitive thermometers using strong variations observed in their emission spectra as a function of temperature.13

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In this article, we summarize recent developments on the NCs embedded in macrocrystals. 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 light LEDs, which were developed employing a model-experimental feedback approach. We also summarize the studies on exciton transfer and plasmonic interactions in these macrocrystals. At the end, an overview of the advantages and limitations of the NCs in macrocrystals together with a future outlook are presented.

To date, CdTe NCs in water,\textsuperscript{15} CdSe/ZnS NCs in water and nonpolar solvents with an alloyed gradient shell\textsuperscript{16} and Au NCs in water\textsuperscript{17} have been successfully incorporated into macrocrystals. In addition, the incorporation of Cd-free InZnP/ZnS NCs in water has been reported as well.\textsuperscript{18} Salts including NaCl,\textsuperscript{11,19} KCl,\textsuperscript{11} KBr,\textsuperscript{11} borax,\textsuperscript{20} and LiCl\textsuperscript{21} have been employed as host matrices along with organic crystalline hosts including sucrose\textsuperscript{22} and anthracene.\textsuperscript{22} The NCs were embedded in 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, nonaggregated incorporation of the NCs. If the colloidal stability is low, using a host with lower ionic strength if dissolved in solution\textsuperscript{19,20} or reducing the time needed for the crystallization might be helpful.

The first method is based on the incorporation of watersoluble NCs (e.g., CdTe) into conventional ionic salt crystals\textsuperscript{11} such as NaCl, KCl, KBr, or nonionic molecules such as sucrose.\textsuperscript{12} Using ionic salts, the NCs in macrocrystals 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$_2$O 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 with NCs. However, a change from the cubic to the octahedral shape of the crystals 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 known to alter the shape of NaCl crystals from cubic to octahedral.\textsuperscript{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 of the synthesis of CdTe NCs emitting in the green to orange spectral regions, an 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, a reproducible incorporation of such NCs is feasible.\textsuperscript{24}

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 nonionic organic molecule forming large crystals—has been shown to allow for the simultaneous incorporation of CdTe NCs together with Au NCs.\textsuperscript{25} Because the incorporation of citrate-capped metal NCs into ionic hosts was not possible due to the induced aggregation, the utilization of sugar enabled plasmonic interactions to occur between semiconductor and metal NCs, which will be further discussed in the applications section of this review. Alternatively, borax (Na$_2$B$_4$O$_7$·10H$_2$O) has been successfully used to immobilize core–shell NCs after a ligand exchange with MPA. Because borax has a reduced ionic strength in comparison to alkali halides, a higher NC colloidal stability in the crystallization mixture could be realized. In addition, larger amounts of NCs have been incorporated into macrocrystals.\textsuperscript{20} To incorporate the NCs dispersed in organic solvents while avoiding a phase transfer, anthracene has been employed by utilizing its solubility in chloroform which can simultaneously disperse oleic acid capped NCs.\textsuperscript{22}

The second method provides a fast pathway for the incorporation of NCs dispersed in organic solvents into the inorganic or organic matrix without a prior ligand exchange. With this technique, NCs dispersed in organic solvents are directly incorporated into the organic solvent-soluble salts such as LiCl.\textsuperscript{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, redispersed in THF, and mixed with LiCl-saturated THF solution. Subsequently, the solvent was evaporated quickly in a vacuum chamber resulting in a complete macrocrystal formation within a few minutes.

The third method is the LLDC\textsuperscript{18} relying on the solubility difference of inorganic salts in solvents with different 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 1 day decreasing the time needed to embed NCs in macrocrystals by more than

![Figure 1. Incorporation techniques used to embed NCs into macrocrystals. The first method is the direct incorporation via slow solvent evaporation, which relies on the mixing of NCs with salt or organic molecule solutions and then on evaporating the solvent slowly to obtain crystals. The second method is a vacuum-assisted NC incorporation, which is based on dispersing the NCs in a polar organic solvent, which subsequently disperses the salt, and then on evaporating this solvent in a vacuum chamber. With this method, the duration of the NC incorporation 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 solvent 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 refs 11, 20, and 22 (American Chemical Society 2012, 2015, and 2015, respectively).](image-url)
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 CHCl₃ to H₂O 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 25 (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).

1 order of magnitude in comparison with the crystallization techniques based on the slow evaporation of solvent. 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 the cocrystallization with salts without a prior phase transfer into water was achieved. Here, NaCl-saturated methanol was added to the NCs in chloroform forming crystal seeds which were then redispersed in pure methanol. In the second step, NaCl dissolved in H₂O was injected under the seed-methanol layer and stored for 15 h.

In many cases, a crystalline matrix affects significantly the PL spectra and PL QY of the incorporated NCs. Upon embedding the NCs into a crystalline host, a slight red shift of the PL spectra is typically observed which can be explained with the variation of the dielectric medium surrounding the NCs. The shape of the PL spectra, on the other hand, is not altered. As can be seen in 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, can be attributed to the formation of a thin CdCl₂ layer. This additional thin layer seems to passivate dangling bonds on the NC surface and by this reduce the nonradiative relaxation routes, as described by Sargent et al.

In another study, we performed comparative investigations of CdSe/ZnS NCs embedded in NaCl macrocrystals and CdTe NCs in borax to test the hypothesis of surface defect curing related to the formation of a chloride layer. In both cases, CdCl₂ cannot be formed on the NC surface. According to Figure 2b, CdSe/ZnS NCs exhibit a typical drop in the PL QY during the phase transfer from organic media to water, which is 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 nonradiative processes. This additionally suggests that the formation of CdCl₂ 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 the PL QY was also investigated. 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). Thus, the utilization of LiCl matrices allows for realizing color-converting powders with PL QYs higher than 70%.

The incorporation of the NCs into macrocrystals builds up a barrier against oxygen and humidity penetration that eventually improves the emission stability of the NCs at elevated temperatures and when exposed to high photon fluxes. By applying different test routines, the emission stability of the NCs in the macrocrystals was investigated in different studies. For example, Adam et al. treated the samples 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, whereas the NCs in macrocrystals preserve their intense PL even after 24 h of storage without any noticeable deterioration.

As the host matrix proved to be exceptionally rigid, it is indeed very unlikely that ambient oxygen could penetrate through the salt to 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 already 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 that were carefully prepared to exhibit optical densities comparable with the NCs in 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. However, the NCs in macrocrystal sample showed a remarkable photostability for 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 macrocrystals and NCs associated with the surface of the macrocrystals. It should be emphasized that the shape and position of the PL spectra are not altered by the intense phototreatment. This can also be seen in Figure 3c, which shows the change in the emission spectrum of the white light LED (w-LED) prepared employing color conversion layer.
The emission stability of the NCs in LiCl was also studied at elevated temperatures. For this purpose, green-emitting macrocrystal powders were integrated on a blue light-emitting diode driven at 100 mA. The results presented in Figure 3d demonstrate that the LiCl matrix acts as a strong barrier against oxygen diffusion toward the NCs and helps the NCs to retain their initial emission intensities. However, the same NCs exhibited a significantly weaker emission stability when they are integrated on LEDs without inorganic salt encapsulation. These findings clearly show that incorporating NCs into crystalline matrices significantly contributes to the stable emission of the 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 reactivity of the encapsulants, for example, epoxy resins typically used for integration of color converters on LEDs. In addition, the macrocrystals can be powdered without any deterioration of their original QY. The powders can be mixed and the tuning of the final emission spectra may be achieved by carefully controlling their amounts (Figure 4a). As a result, highly stable and efficient LEDs with superior photometric performance can be obtained.

Although w-LEDs using CdTe NCs embedded in macrocrystals as color conversion layers with promising photometric performance were demonstrated in early work, those devices could not fulfill all of the demanding requirements for indoor lighting at the same time. 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.

According to the underlying model, 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 emitting materials were used with special emphasis given on generating a warm white light to simultaneously achieve CRI > 90, LER > 330 lm/Wopt 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/Wopt at a CCT of 2720 K was fabricated. Therefore, this LED, with its emission spectrum and chromaticity coordinates displayed in Figure 4b and c, respectively, balanced for the first time these strongly related figures of merit for NC-based color converters exceeding state-of-the-art in literature.

In addition to w-LEDs based on 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. 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. 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

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Figure 3. (a) True-color images of the stability test of NCs in 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; 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 NC–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 a 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 20 (American Chemical Society 2015). (d) QY variation of NC-embedded LiCl crystals and a 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).

Based on NCs in macrocrystals as described in ref 20. To avoid strong heat generation and to observe the effect of the intense photon flux, the LED was placed on an aluminum plate for passive cooling and was operated at a 1 kHz on/off rate which kept the temperature of the LED below 35 °C. As expected, the intensity of the w-LED emission decreased only slightly during 96 h of operation. The effect of the salt-encapsulation on the emission stability of the NCs was also studied by Hsu et al. In this work, CdTe NCs in water were integrated into a 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. It should be noted that all above-mentioned macrocrystals were grown under ambient conditions. A preparation under inert atmosphere could be beneficial for commercialization reasons, preventing the incorporation of dissolved O2. This might be a crucial step for a further increase of the photostability.
environment so that the effects related to the surrounding medium are mitigated or fully eliminated by the host medium. The plasmonic interaction in the macrocrystals containing metal NCs was demonstrated for the first time by Erdem et al.\textsuperscript{13} 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 centimeter-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 coimmobilized within sucrose and the PL QY of the NCs was found to increase by 58% owing to the plasmonic interaction.

The luminescent powders of NCs in macrocrystals also provide interesting opportunities for studying excitonic interactions on the nanoscale. Soran-Erdem et al.\textsuperscript{22} studied exciton dynamics by incorporating non polar red-emitting NCs into anthracene crystal which is a well-known organic semiconductor. 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 as revealed from TEM images was below 20 nm within the LiCl matrix suggesting that the nonradiative energy transfer should also be possible in their powders. On the basis of this hypothesis, Erdem et al. hybridized nonpolar green- and red-emitting NCs within LiCl salt.\textsuperscript{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.\textsuperscript{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 over 70 lm/W\textsubscript{elect}.

Recently, Kalytchuk et al. utilized the temperature dependent emission change of the NCs in macrocrystals for remote temperature measurements.\textsuperscript{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 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 enabling the detection of the temperature with high precision in these solid-state materials.

In this Perspective article, we have given an overview of the procedures leading to a broad range of NC-integrated macrocrystals and evaluated their potential as the next-generation color conversion materials for pure color and white luminaires. Moreover, macrocrystal matrixes proved to be 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 addressed in order to exploit their widespread application. Until now, no clarification of structure–property relationships has been reported which requires more detailed studies including a systematic variation of host materials and NCs of various well-known surface chemistries. Acceleration of the fabrication procedure as well as introducing of new host matrices may help to extend the applicability of the method. Indeed, KH₂PO₄ single crystals as well as introducing of new host matrixes may help to extend the applicability of the method. Indeed, KH₂PO₄ single crystals may incorporate organic molecules and inorganic oxide nanoparticles, whereas BaSO₄ can be used for quick incorporation of large amounts of NCs. According to our expertise, the issue of the limited NC loading in the crystalline matrix can be considered as crucial for applications where high absorption cross sections are desired (e.g., color conversion). In addition to already mentioned first steps made in this direction, the recently introduced method of pressing of salt pellets should be mentioned. On the basis of the phenomenon of cold flow, this method allows the fabrication of high quality optically transparent salt pellets heavily loaded with NCs. The incorporation of oligomer nanoparticles of organic molecules, and of newly emerging nanoparticles such as carbon dots are also interesting aspects demonstrating the versatility of the methods described in this perspective. Future studies should include the use of anisotropic quantum structures like quantum rods and platelets, especially in combination with an oriented incorporation of them into the host matrixes. Furthermore, the use of Cd-free NCs for the embedding in salts is still challenging although highly desired for potential commercialization. It needs to be investigated in more detail with an emphasis on retaining the PL QY over all intermediate steps. The retaining or even improving of the PL QY and light outcoupling from the devices (e.g., LEDs) are required to reach not only high spectral qualities 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 matrixes 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 an interesting direction of research on these materials that still remains unexplored. When the works presented here and the unexplored potential of these materials for science and engineering applications are considered, we believe that NCs in macrocrystals 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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