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Kalytchuk, Sergii; Zhovtiuk, Olga; Rogach, Andrey L.

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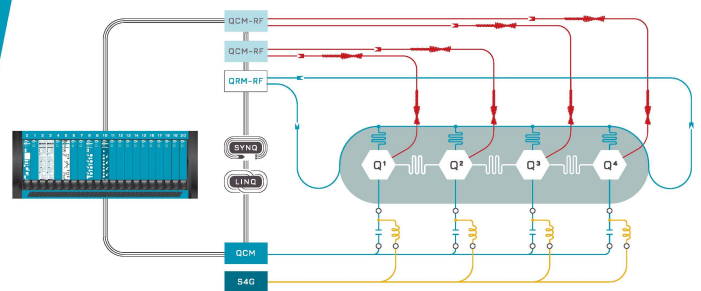
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Sodium chloride protected CdTe quantum dot based solid-state luminophores with high color quality and fluorescence efficiency

Sergii Kalytchuk,^{1,2} Olga Zhovtiuk,¹ and Andrey L. Rogach^{1,a)}

¹*Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong*

²*Clean Energy and Nanotechnology (CLEAN) Laboratory, School of Energy and Environment, City University of Hong Kong, Shatin, N.T., Hong Kong*

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We report on a series of fluorescent powders based on CdTe colloidal nanocrystals embedded into a protective NaCl matrix, which provide solid-state luminophores with emission colors covering the whole green to red spectral region of visible spectrum and enhanced fluorescence quantum yields comparing to the parent CdTe nanocrystals, unravelled by UV-vis absorption and diffuse reflectance measurements as well as by steady-state and time-resolved photoluminescence spectroscopy. Prototypes of hybrid light-emitting diodes of high color quality utilizing this kind of luminophores as a down-converting layer are demonstrated. © 2013 AIP Publishing LLC.

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Semiconductor nanocrystals, also termed colloidal quantum dots (QDs), offer a great potential for electronic and optoelectronic applications because of their unique physical properties, such as tunability of the emission wavelength due to the size quantization effect, high photoluminescence (PL) quantum yield (QY), narrow emission bandwidths, broad absorption profiles, superior photostability, and flexible solution processing.^{1–5} QD-based full-color solid-state luminescent materials have recently received considerable attention, both for backlighting of liquid-crystal displays, which utilizes the optically induced emission of colloidal QDs, and for the next-generation visible and near-infrared optical down-converters for solid-state lighting sources.^{6–14} This is also evidenced by the large number of companies developing colloidal QD-enhanced displays and solid-state lighting sources, such as QD Vision, Nanosys, LG Innotek, Samsung, Philips Lumileds Lighting Company, and Avago. The market for QD-based products is projected to a tenfold increase by 2015, with particularly rapid growth in the optoelectronics sector.¹⁵ Indeed, the first commercial TV from Sony that features quantum dot technology from QD Vision was presented recently.

Most of the optoelectronic and optical devices require QDs-based solid state materials isolated from solution where they have been initially synthesized. However, there are several challenges to realize highly efficient light emitting materials involving solid state QDs. PL QY is often significantly reduced when the QDs are transferred from their parent solutions into solid-state close-packed films,^{16,17} which is commonly ascribed to the non-radiative Förster resonant energy transfer (FRET) of excitons to the neighbour nanocrystals with lower emission quantum yield where they recombine non-radiatively.¹⁸ Their PL QY could be sensitive to heat, light, oxygen, and moisture, and it can rapidly deteriorate upon continuous excitation in a solid state, unlike in the colloidal solution phase where there typically exist an

excess of surface ligands passivating the QD surface. It is thus crucially important to find suitable matrices, which prevent non-desired agglomeration of QDs while preventing reduction of PL QY in solid-state QDs-based materials, compared to their starting colloidal solutions, and ideally even providing its enhancement. The recently introduced fabrication of mixed crystals of CdTe QDs and NaCl (Ref. 19) offers a useful strategy in this respect, combined with advantages of the protection of QDs from the environment. Herein, we have utilized this approach to achieve high color quality emission from solid-state powders of CdTe QDs embedded in an inorganic NaCl protective crystal matrix (which we denote as CdTe QDs@NaCl further below) and demonstrate that their PL QYs can indeed be enhanced as compared to the parent colloidal solutions. We highlight their favourable light-emission characteristics as unravelled by UV-vis absorption and diffuse reflectance measurements as well as by steady-state and time-resolved photoluminescence spectroscopy and demonstrate their use as efficient luminophores for solid-state lighting sources.

Starting colloidal solutions of CdTe QD stabilized by mercaptopropionic acid were synthesized in aqueous solution by the method of Ref. 20. Five samples of CdTe QDs with diameters of 2.3, 2.6, 2.8, 3.0, and 3.1 nm were obtained. Mixed crystals of CdTe QDs@NaCl were obtained according to Ref. 19. 5 ml of as-prepared aqueous CdTe QDs solutions (with a molar concentration of $\sim 6.7 \mu\text{M}$) have been mixed with 25 ml of a saturated NaCl solution in a 30 ml beaker. The solutions were held in a temperature controlled oven at 30 °C for 4 weeks. The mixed crystals of CdTe QDs@NaCl were isolated when the parental solution turned colorless, which indicated the completion of crystallization process. They were rinsed with cold water, dried, and grinded into fine powders using agate mortar and pestle set.

All optical measurements were performed at room temperature under ambient conditions. Fig. 1(a) shows absorption and PL spectra of CdTe QDs in the starting aqueous colloidal solutions, which have been arbitrarily shifted in vertical direction for clarity of presentation. The PL peaks of CdTe

^{a)}Author to whom correspondence should be addressed. Electronic mail: andrey.rogach@cityu.edu.hk

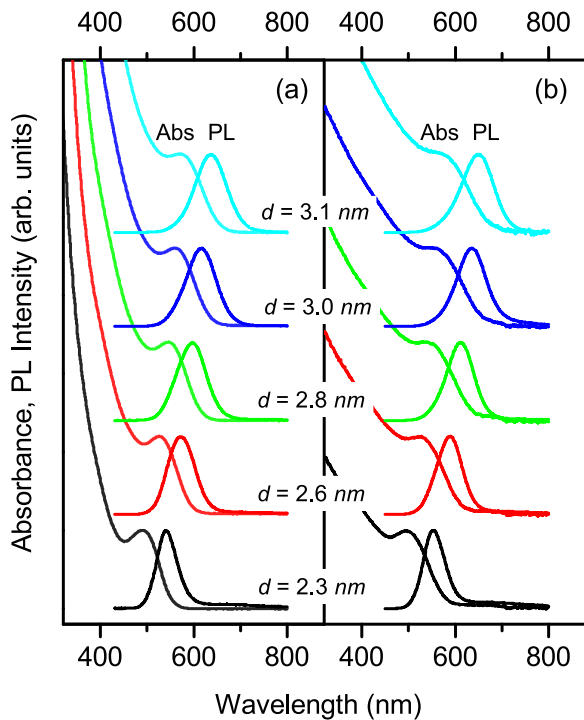


FIG. 1. (a) Absorption and PL spectra of the starting colloidal solutions of CdTe QDs and (b) solid-state diffuse reflectance absorption and emission spectra of CdTe QDs@NaCl powders.

QDs of the five different sizes cover green-to-red spectral region and are centered at 541, 573, 597, 617, and 637 nm, respectively. The band-edge PL peaks are reasonably narrow (FWHM in the range of 50–80 nm), indicating monodispersity of QDs. Fig. 2(a) shows true-color photographs of five differently sized starting colloidal solutions of CdTe QDs under UV light as well as of the corresponding CdTe QDs@NaCl powders. The latter were obtained both under daylight and UV illumination. The CdTe QDs@NaCl powders have only a slight tint of colors under daylight but possess intense size-dependent PL under UV excitation, similar to the parent colloidal solutions of CdTe QDs. Importantly, the incorporation of CdTe QDs into the ionic crystals of NaCl showed no indication

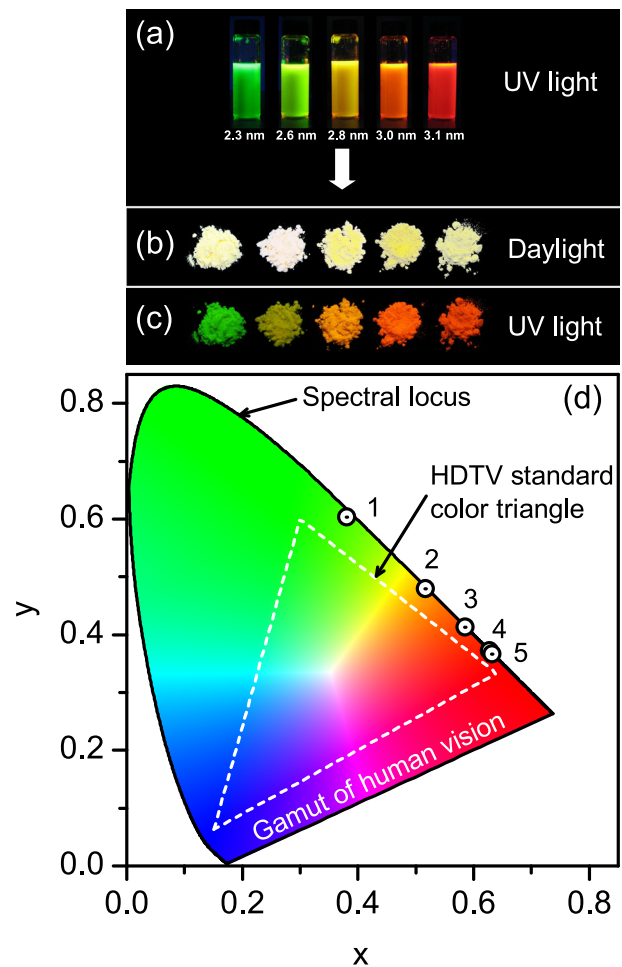


FIG. 2. True-color photographs illustrating emission colors of (a) starting colloidal solutions of CdTe QDs and (c) solid-state CdTe QDs@NaCl powders, taken under UV light ($\lambda_{\text{ex}} = 365$ nm). Panel (b) shows the appearance of CdTe QDs@NaCl powders under daylight. QD sizes gradually change from 2.3 nm to 3.1 nm, as indicated in frame (a). Panel (d) shows CIE coordinates of the emission of the five-colored QDs-based powders with respect to the color triangle of the HDTV standard.

of QDs aggregation, as evidenced by the identical excitonic structures and similarity of the diffuse reflectance absorption spectra of QDs@NaCl powders (Fig. 1(b)) with absorption

TABLE I. Optical characteristics of five starting colloidal solutions of CdTe QDs and the corresponding solid-state CdTe QDs@NaCl powders: wavelength positions of the first absorption maximum λ_{abs} and the emission maximum λ_{em} ; full width at half maximum (FWHM) of the emission peak; room temperature PL QY; fitting parameters of the PL decay curves^a; and color coordinates of solid-state QDs-based luminophores according to CIE 1931.

Sample	λ_{abs} (nm)	λ_{em} (nm)	FWHM (nm)	PL QY (%)	τ (ns)	β	CIE (x, y)
Solution							
1	490 ± 2	541 ± 2	53 ± 2	8.3 ± 0.4	13.1 ± 0.5	0.62 ± 0.02	
2	527 ± 2	573 ± 2	69 ± 2	11.1 ± 0.6	14.4 ± 0.5	0.65 ± 0.02	
3	547 ± 2	597 ± 2	74 ± 2	14.3 ± 0.7	18.3 ± 0.5	0.71 ± 0.02	
4	560 ± 2	617 ± 2	76 ± 2	20.5 ± 1.0	21.8 ± 0.5	0.73 ± 0.02	
5	572 ± 2	637 ± 2	79 ± 2	19.2 ± 1.0	24.8 ± 0.5	0.72 ± 0.02	
Powder							
1	492 ± 2	553 ± 2	55 ± 2	12.7 ± 0.6	16.1 ± 0.5	0.66 ± 0.02	(0.380, 0.603)
2	528 ± 2	588 ± 2	65 ± 2	14.9 ± 0.7	17.2 ± 0.5	0.71 ± 0.02	(0.517, 0.479)
3	547 ± 2	613 ± 2	68 ± 2	18.8 ± 0.9	18.9 ± 0.5	0.74 ± 0.02	(0.586, 0.412)
4	561 ± 2	635 ± 2	75 ± 2	17.9 ± 0.9	20.8 ± 0.5	0.73 ± 0.02	(0.627, 0.372)
5	573 ± 2	652 ± 2	82 ± 2	14.9 ± 0.7	22.0 ± 0.5	0.74 ± 0.02	(0.632, 0.367)

^aObtained from the decay analysis of traces in Figure 3 using the stretched exponential function $I(t) = I_0 \cdot e^{-(t/\tau)^\beta}$, where β is a stretch parameter and τ is the decay time.

spectra of CdTe QD colloidal solutions (Fig. 1(a)). Moderate (~ 15 nm) red-shift of the PL peaks of CdTe QDs-based powders (Fig. 1(b)) compared to the starting colloidal QD solutions (Fig. 1(a)) can be due to the reabsorption of the high-energy photons by CdTe QDs incorporated into the salt matrix.

We have compared PL QYs of starting colloidal solutions of CdTe QDs with the PL QYs of the corresponding CdTe QDs@NaCl powders. The latter were determined by absolute method using an integrating sphere with its inner face coated with BENFLEC[®] (Edinburgh Instrument). A non-fluorescent sample consisting of NaCl powder having the same morphological characteristics has been used for correction of scattering. For smaller QDs (PL QYs ranging from 8% for 2.3 nm QDs to 14% for 2.8 nm QDs, as summarized in Table I), the CdTe QDs@NaCl powders showed no

sign of PL quenching, but rather improved PL QYs (up to 13%–19%, Table I). The enhancement of the PL QY in the solid-state powders as compared to starting colloidal solution of QDs is a very encouraging result. It can be ascribed to the surface passivation of QDs by Cl^- ions when they become incorporated into the NaCl salt, which are able to bind surface atoms of QDs while resplasing a fraction of the ligands, as demonstrated recently.²¹

For larger (3.0–3.1 nm) QD sizes, PL QYs of the powdered samples were only slightly reduced, from 19%–20% in colloidal solutions to 15%–18% in the corresponding powdered samples (Table I). We have followed these trends by the time-resolved PL measurements, as the emission lifetime of semiconductor QDs depends both on particle size and surface quality.²² Generally, less than perfect crystallinity or surface passivation of colloidal QDs is accompanied by strong non-radiative emission leading to shorter PL lifetimes.²³ PL decays measured for both sets of samples—the starting colloidal solutions of CdTe QDs and the corresponding CdTe QDs@NaCl powders—all monitored at the respective emission peaks with an excitation at 405 nm, are shown in Fig. 3. The obtained PL decay curves could be well-fitted by the stretched exponential decay function characterised by a lifetime, τ , and a stretch parameter, β , with the reduced $\chi^2 \leq 1.2$. The fitted values of these parameters are given in the insets of Figs. 3(a) and 3(b) for different QDs sizes and are summarized in Table I. The change of both parameters upon the transfer of QDs from colloidal solutions to the NaCl powders reflects the previously described trends of their PL QYs: while smaller CdTe QDs with sizes of 2.3–2.8 nm exhibit longer PL lifetimes in the powdered form, larger CdTe QDs with sizes of 3.0–3.1 nm possess slightly longer PL lifetimes in solutions. The increase of the PL lifetime for CdTe QDs incorporated into NaCl indicates passivation of surface traps during this process.

The high colors quality of five CdTe QDs@NaCl powders are illustrated in the CIE (international commission on illumination) chromaticity diagram (Fig. 2(d)), which maps colors visible to the human eye in terms of hue and saturation. The CIE color coordinates of these samples are also listed in Table I. Fig. 2(d) further shows that CIE coordinates of the CdTe QDs@NaCl powders provide color gamut which is larger than that required by the International Telecommunication Union high-definition television (HDTV) standard.

NaCl crystals containing CdTe QDs were previously shown to be compatible with a silicone matrix, allowing their deposition on high-power blue InGaN light emitting diode (LED) to fabricate white light-emitting device.¹⁹ Multicolored hybrid LEDs based on CdTe QDs@NaCl powders have not been demonstrated so far. We have processed powdered samples into the transparent polymer host matrix of PMMA (10 mg of powders mixed with 30 ml of PMMA/tetrahydrofuran solution, 15% by weight) and have found that they do retain their favourable characteristics in terms of the color purity and PL QYs. We have then fabricated five differently colored down-converting QDs-based hybrid LEDs by the deposition of CdTe QDs@NaCl powders dispersed in PMMA matrix on the top of the commercial 385 nm UV LED (Figs. 4(a) and 4(b)). True-color photographs of CdTe QDs@NaCl based LEDs of five different

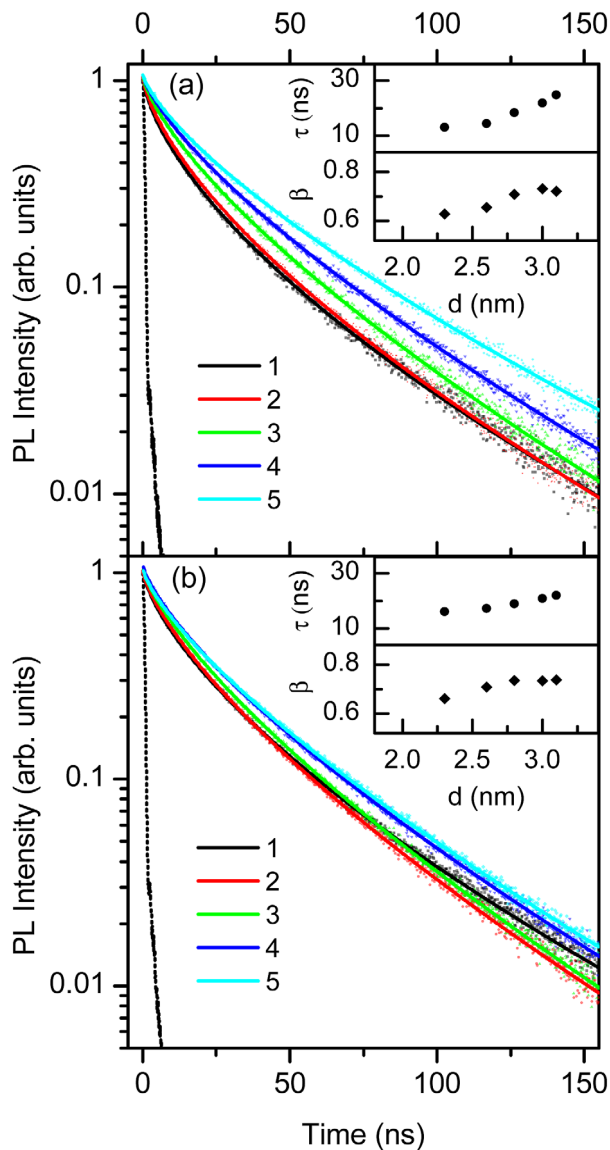


FIG. 3. Normalized time-resolved PL decay curves of (a) starting colloidal solutions CdTe QDs and (b) the corresponding solid-state CdTe QDs@NaCl powders. All measurements were performed at PL peak wavelengths with an excitation wavelength $\lambda_{\text{ex}} = 405$ nm. The curves were fitted to a stretched exponential form (solid lines): $I(t) = I_0 \times e^{-(t/\tau)^\beta}$, where β is a stretch parameter and τ is the decay time, with the reduced $\chi^2 \leq 1.2$. The instrument response function is shown as a black dashed line in both panels. The insets show size-dependent PL decays lifetime of QDs, with the corresponding stretching exponents.

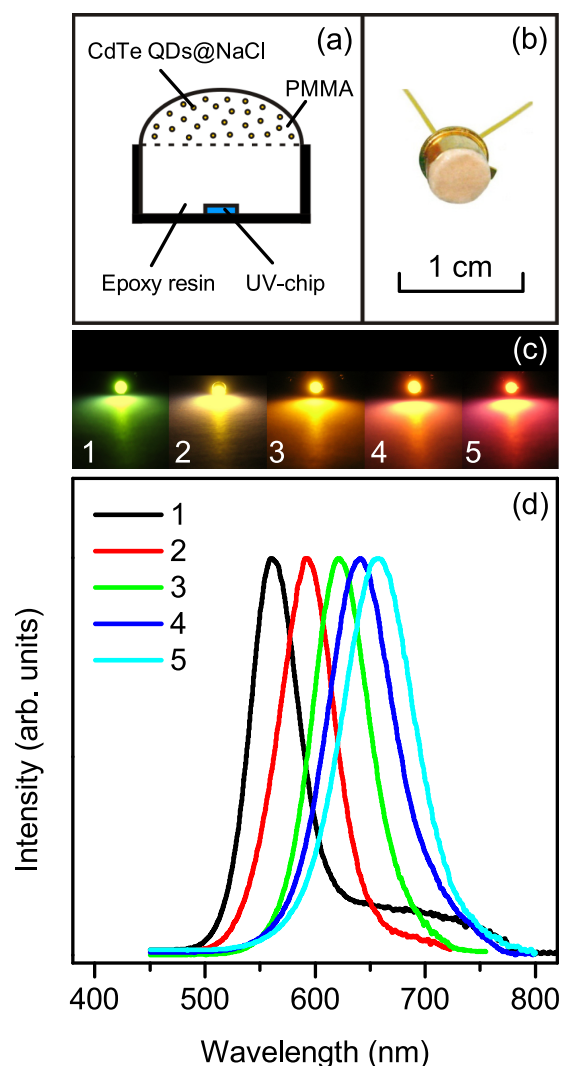


FIG. 4. (a) Schematics and (b) a photograph of a hybrid QDs-based LED with solid-state CdTe QDs@NaCl powders embedded in PMMA matrix on top of a UV-chip. (c) True-color photographs of operating hybrid QDs-based LEDs (applied voltage 3.1 V) of five different colors determined by the sizes of CdTe QDs, with (d) corresponding normalized emission spectra.

colors determined by the sizes of CdTe QDs, operating under applied voltage 3.1 V, are presented in Fig. 4(c), with the corresponding normalized emission spectra shown in Fig. 4(d). Subsequent measurements of the emission spectra and PL QY showed no evidence of deterioration. PL QY of CdTe QDs@NaCl dispersed in PMMA matrix was maintained at about 95% of the initial intensity without any change of the emission wavelength for more than one month of storage at ambient conditions.

In conclusion, we have demonstrated that powders of CdTe QDs embedded into NaCl crystals retain favourable optical characteristics of the starting colloidal solution of QDs, including emission color tunability by QD size, high color purity in terms of CIE coordinates, and finally enhanced PL QY. The latter effect has been attributed to

passivation of surface traps of QDs by Cl^- ions of NaCl matrix. Consequently, prototypes of five differently colored hybrid LEDs of high color quality utilizing CdTe QDs@NaCl powders embedded in a PMMA matrix as a down-converting layer have been demonstrated. Our results suggest that CdTe QDs@NaCl powders are promising lumiphores for use in solid state lighting and displays.

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