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Bright White Light Emission from Ultrasmall Cadmium Selenide Nanocrystals

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Supporting Information

ABSTRACT: A simple treatment method using formic acid has been found to increase the fluorescence quantum yield of ultrasmall white light-emitting CdSe nanocrystals from 8% to 45%. Brighter white-light emission occurs with other carboxylic acids as well, and the magnitude of the quantum yield enhancement is shown to be dependent on the alkyl chain length. Additionally, the nanocrystal luminescence remains enhanced relative to the untreated nanocrystals over several days. This brightened emission opens the possibility for even further quantum yield improvement and potential for use of these white-light nanocrystals in solid-state lighting applications.

The discovery of ultrasmall white light-emitting CdSe nanocrystals in 2005 has given rise to their possible use as a white-light source in efficient solid-state lighting.[1−3] The nanocrystals are smaller than 2 nm in diameter and have the majority of their atoms on the surface, giving rise to their characteristic emission from surface trap states.[4,5] White light-emitting nanocrystals offer a solution to the drawbacks of current light-emitting diodes (LEDs) because they are synthesized as a single component system that emits pure white light,[5−7] as opposed to a combination of monochromatic materials which together emit white light.[8] These nanocrystals have been incorporated into prototypical frequency down-converting devices (LEDs) and in electroluminescent devices.[9−11] However, this application is currently limited by the nanocrystal emission efficiency, since the fluorescence quantum yield is only 8−9%, which is too low for commercial use.[5,12] The efficiency must be greatly improved if these nanocrystals are to be used widely as a single source broad spectrum solid-state lighting device.[9]

Various methods have been attempted in the past to brighten CdSe nanocrystals, the most common of which is to synthesize core−shells, such as CdSe/ZnS.[13] The problem with shelling the white-light nanocrystals is that the shell passivates surface trap states on the nanocrystal, which are likely responsible for their white-light emission.[4,14] As a result, the nanocrystals are brightened at the expense of the broad emission spectrum, collapsing to narrow (near monochromatic) fluorescence.[14] Thus, a different approach must be taken that involves altering the surface chemistry of the nanocrystal without eliminating the trap states. Changing the organic ligands surrounding the nanocrystals or treatment with different chemical substances is another effective way of brightening nanocrystals.[15] Here we treated ultrasmall CdSe nanocrystals with carboxylic acids in an attempt to enhance the quantum yield of the white-light emission.

Ultrasmall CdSe nanocrystals were synthesized and purified as previously reported[14] with slight modifications (Supporting Information). The white-light nanocrystals were then treated with various carboxylic acids in the following manner. A 0.3−1 mM solution of nanocrystals in toluene (about 3−5 mL) was added to a 50 mL three-neck round-bottom flask. The flask was fitted with a heating mantle and temperature probe and placed onto a stirplate, while leaving two necks of the flask open to air. This reaction was set up as to have no direct light on the flask. The formic acid was added to the nanocrystals in a 30 000 molar excess via syringe injection to the flask at the same time that the heating was started. The solution was heated from 24 to 60 °C in 5 to 6 min. Upon reaching 60 °C, the flask was immediately removed from heat and cooled with compressed air to 28 °C while stirring. If the yellow nanocrystal solution was cloudy (as in the case of formic acid treatment), it was transferred to a glass vial and centrifuged at 2500 rpm for 15 min to separate the excess formic acid from the treated nanocrystals in toluene. The top nanocrystal layer was then transferred to 2-mL microtubes and centrifuged at 15 500 rpm for 15 min (or until layers are completely separated) to further remove any excess acid. The quantum yield of both the original nanocrystals and the acid-treated nanocrystals were taken within a few hours of the treatment in reference to either Coumarin 152A or Coumarin 153 as the standard (Supporting Information). This method was used to successfully treat nanocrystals with the following carboxylic acids: formic, acetic, hexanoic, octanoic, and oleic (see Supporting Information for emission data). Other carboxylic acid treatments were examined to test if they had a similar effect on brightness; no quantitative conclusion or trend has been made, as some acids brightened the nanocrystals to different extents, and some quenched the emission. Both liquid and solid acids can be used

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in this procedure, and the solid additives were simply added through the top of the flask.

This formic acid treatment demonstrated the highest reported quantum yield increase for white-light CdSe nanocrystals, with an example emission spectrum and sample photo shown in Figure 1. The average quantum yield is 31 ± 6.4%, with a maximum recorded yield of 45%. Comparing the absorption spectra before and after formic acid treatment, it is clear that the size and monodisperse characteristic of the nanocrystals have not significantly changed. The band edge absorption consistently tends to shift to a lower wavelength by 1 or 2 nm, but the features in the spectrum remain the same (Figure 1).

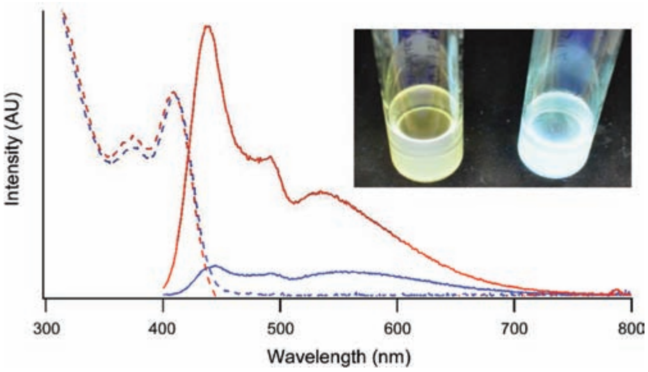

Figure 1. The comparison of the emission spectra of original (solid blue) and formic acid-treated (solid red) CdSe nanocrystals show a significant increase in the quantum yield from 9% to 43%, while the CIE (*Commission Internationale de L'Eclairage*, 1931) coordinates changed to a bluer emission (0.311, 0.333 to 0.238, 0.243). The absorption spectra before (dashed blue) and after treatment (dashed red) show that the nanocrystals stay monodisperse with an almost identical size, with the band edge absorption maximum only shifting from 410 to 407 nm. (Spectral intensities are normalized.) Inset: Vials containing concentrated white-light CdSe nanocrystal solutions before (left) and after (right) a sample formic acid treatment.

A single formic acid treatment was tested over time. Immediately after treatment, the quantum yield increased from 7% to 30%. Over the course of 41 h, it only degraded to 23%, keeping the same emission features. This result is promising because it demonstrates that the increase in the quantum yield is not a temporary effect and that the nanocrystals do not decrease to their original brightness over a 2 day period. This increases the chance to stabilize the higher quantum yields for lighting applications by encapsulation.[9] To further examine this possibility, three separate batches were treated with formic acid and their quantum yield was measured over an 18 day period. After day one, the average quantum yield reached a maximum of around 41%, which slowly decayed to 30% by day 15 (see Supporting Information). The mechanism behind the reduction over time is likely a result of an equilibrium effect between the surface states and the free formic acid in solution, as a portion of the formic acid phase separates from the nanocrystal−toluene solution. This is supported the by the appearance of formic acid droplets at the bottom of the vials after day 1 and by the fact there is very little change in the nanocrystal absorption spectrum. Other conventional quenching mechanisms are also likely in play, including photobleaching and oxidation.

Several explanations are possible for the increase in quantum yield. One explanation is a ligand exchange process. In this study, after synthesis and cleaning, the nanocrystal surface is mostly covered with phosphonic acid ligands,[4,16] with trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) likely present to a lesser degree. Upon treatment with formic acid, a ligand exchange model would dictate that the acid molecules replace most or all of the original ligands, changing the ligand coverage of the nanocrystal. Ligand exchanges are commonly used to change the solubility or functionality of nanoparticles.[17] The process relies on adding either a more strongly binding molecule or a large molar excess of a weakly binding molecule to displace some or all of the native surface ligands. In the case of replacing a phosphonic acid, TOPO, or HDA ligand with a carboxylic acid, the carboxylic acid interaction is actually less favorable.[18] Thus, an exchange would have to occur as a result of the large molar excess of the added acid.[19] Also, during the cleaning process after synthesis, some ligands from the nanocrystal will also be lost, creating vacant surface sites for the formic acid to easily attach. A complete ligand exchange is doubtful because exchanges on nanocrystal surfaces have been shown to be a partial process.[20,21] Also, phosphonic acid and formic acid are different in their solubility, which would suggest that nanocrystals with only formic acid ligands would likely precipitate out of the original toluene solution.

A more plausible explanation for the increased quantum yield could be that there are nonradiative surface trap sites that already exist on the surface of the nanocrystal, which can be passivated with the carboxylic acid ligands. Passivation of a competitive nonradiative surface site is a more likely possibility, as opposed to improving the efficiency of the radiative process, since the latter would require surface ligand to interact with at least three processes that produce the white light. A pure exchange with the original ligands would not have to occur if the smaller formic acid molecules simply passivated some of the existing trap states in between the phosphonic acid ligands. In the work of Schreuder et al. concerning the effect of phosphonic acid surface ligands on ultrasmall CdSe nanocrystals, changing the ligand affected the wavelength and intensity of the first blue emission peak, as well as the overall quantum yield of the nanocrystals, which ranged from 0.2% to 9% depending on the phosphonic acid variant.[22] Tuning the wavelength of that first emission feature was concluded to be caused by the electronegativity (inversely proportional to chain length) of the surface ligand, while the quantum yield increase was probably a result of the sterics and physical structure of the ligand.[22] (As chain length increased, quantum yield increased, suggesting that a long chain might guard the surface of the nanocrystal against quenching agents by bending around, covering surface traps.) In this study with formic acid, the first emission peak blueshifts an average of 7 nm from the original nanocrystals. This result corresponds with the finding of Schreuder et al. because a ligand of a shorter chain length (higher electronegativity) blueshifted the emission peak, ranging up to 20 nm difference between varying chain lengths.[22] Thus, an explanation involving partial ligand exchange or the addition of formic acid ligands to the surface is supported.

Formic acid caused the greatest overall increase in quantum yield compared to the other straight-chain carboxylic acids. The average post-treatment quantum yields from original nanocrystals (∼8%) were as follows: formic 31 ± 6.4% (n = 31), acetic 19 ± 2.5% (n = 19), hexanoic 15 ± 3.0% (n = 5), octanoic 16 ± 1.8% ($n = 5$), and oleic 13 ± 1.9% ($n = 5$). For each 'n', a separate batch of white light nanocrystals was treated and its optical properties measured. This effect may be due to the shorter carbon chain length. Longer chain lengths may hinder the ability of the acid to reach the nanocrystal surface past the long-chain phosphonic acid and bulky TOPO and HDA ligands that are associated with the nanocrystal. The acid chain length also affects the pK_a of the acid, increasing acidity with shorter alkyl chain lengths. Consequently, formic acid is the most acidic of these four acids, implying that there may be a correlation between a more acidic ligand and a higher increase in quantum yield. The close proximity of quantum yields for the longer chain acids and nearly insignificant quantum yield increase for oleic acid suggest that the chain-length effect becomes minimal after hexanoic acid.

One effect of using formic acid is that after the nanocrystals are treated, their emission spectrum deviates from pure white, relative to the emission of the original nanocrystals. The CIE coordinates become more "blue" relative to the white 0.333, 0.333 center, as shown visually in Figure 1.[23] This is an interesting consequence of the treatment with all the acids and is most pronounced with the formic acid. The mechanism for this result is not evident. Upon examination of the brightened spectra, it is apparent that all three emission peaks are retained and enhanced, with the first blue peak simply brightened to a greater degree than the other two. The disproportionate increase thus cannot be explained by differentiating the reasons for the existence of each peak. The blue peak is a direct result of the surface-passivating phosphonic acid ligands on the nanocrystal, and it is absent when a different ligand is used in place of the phosphonic acid or is shifted depending on the alkyl chain length of the phosphonic acid.[4,22] The broad red peak is from conventional deep trap emission, confirmed with ultrafast fluorescence upconversion spectroscopy.[4,14] The middle feature is still a mystery, though it is hypothesized to be related to the surface state at the Se atoms on the nanocrystal.[4] In this treatment, the middle peak may be enhanced due to the overlapping spectral features of the first and last peak. Because of the different origins of emission, it would seem that formic acid would only affect one mechanism, especially the surface ligand cause, which would explain the disproportionate increase of the blue peak. Nonetheless, the data suggests that more than one mechanism is affected.

While the "blueing" effect is currently unexplained, it can be compensated for by modulating the color of the original nanocrystals after synthesis to exhibit a warmer white emission prior to the addition of formic acid. After the acid treatment to enhance the blue peak, the resultant nanocrystals should then ideally achieve a more balanced white emission. A recent aspect of this work has also demonstrated that adding dodecanethiol to the nanocrystals significantly decreases the first two emission peaks down to negligible emission, which changed the CIE coordinates from 0.30, 0.32 to 0.47, 0.44. Thiols like dodecanethiol coordinate strongly to the cadmium surface sites, likely displacing the phosphonic acid. Since the blue peak is associated with the cadmium–phosphonic acid bond, the substitution with a thiol should quench the blue peak. A normal formic acid treatment was then able to restore those peaks, resulting in a spectrum that is close to balanced white-light again at 0.34, 0.36, as shown in Figure 2. (See Supporting Information for corresponding absorption spectra and CIE plot.) These twice-treated nanocrystals have a quantum yield between that of original nanocrystals and formic acid-treated samples, since the dodecanethiol somewhat quenches CdSe emission.[24] Modulating the amount of excess dodecanethiol that is added to the nanocrystals should make it possible to tune the CIE coordinates for a desired white light.

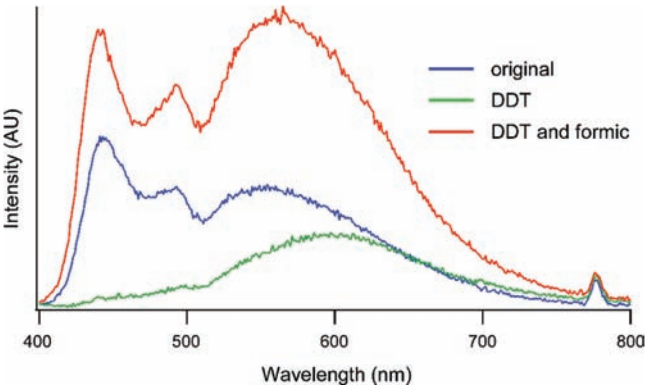

Figure 2. Emission spectra of original CdSe with quantum yield 10.2%, after DDT treatment with quantum yield 4.2%, and after final formic treatment with quantum yield 20.5%.

In conclusion, this work demonstrates that enhancement of the complex trap state emission exhibited by white light-emitting CdSe nanocrystals can be achieved. Postpreparative treatments with formic acid improved the fluorescent quantum yield up to 45%. A likely explanation for the brightening is that of a partial ligand exchange or a greater passivation of some nonradiative surface traps, suggested by the bluer emission of the treated nanocrystals. This bluish emission may be compensated for by incorporating a preliminary treatment after synthesis that first warms the emission of the nanocrystals with a chemical such as dodecanethiol before cooling it with the acid. In testing various acids, it was apparent that acids with shorter alkyl chain lengths cause a greater increase in quantum yield, indicating a possible correlation with acidity and steric effects. With nanocrystals that have a 40% quantum yield, LEDs could be coated with a higher luminous efficiency than previously calculated with 8% efficient nanocrystal emission.[11] This efficiency in lumens per watt is calculated using the following equations:[25]

$$\text{Efficiency} = \eta_{\text{LED}}\eta_{\text{NC}}\eta_{\text{extrac}} \times 250$$

with

$$\eta_{\text{NC}} = \eta_{\text{abs}} \times \text{QY} \times S$$

where η_{LED} and η_{NC} are the efficiencies of the LED source and nanocrystal encapsulant, and η_{extrac} is the extraction efficiency. The constant 250 lm/W changes with the color characteristics of the white light emission. The purpose of this constant is to convert the radiant flux to luminous flux. The nanocrystal efficiency is dependent on η_{abs} (the absorption efficiency), QY (the quantum yield of the nanocrystals), and S (the Stokes loss efficiency). The only variable in the luminous efficiency calculation that is variable within the nanocrystal chemistry is the quantum yield of the nanocrystals. A predicted value for 40% efficient quantum dots, using a standard commercial UV-LED, is 3.8 lm/W, which is 4 times more efficient than with the 8% nanocrystals. Specific values used for this calculation can be found in the Supporting Information. Improvements in the efficiency of the UV-LED and extraction efficiency could further increase the device efficiency upward to 100 lm/W. This work demonstrates progress toward the desired efficiency of a commercially viable solid-state lighting device.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

White-light CdSe nanocrystal synthesis description and spectral analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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