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Semiconductor-Nanocrystals-Based White Light-Emitting Diodes

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Abstract: *In response to the demands for energy and the concerns of global warming and climate change, energy efficient and environmentally friendly solid-state lighting, such as white light-emitting diodes (WLEDs), is considered to be the most promising and suitable light source. Because of their small size, high efficiency, and long lifetime, WLEDs based on colloidal semiconductor nanocrystals (or quantum dots) are emerging as a completely new technology platform for the development of flat-panel displays and solid-state lighting, exhibiting the potential to replace the conventionally used incandescent and fluorescent lamps. This replacement can cut the ever-increasing level of energy consumption, solve the problem of rapidly depleting fossil fuel reserves, and improve the quality of the global environment. In this review, the recent progress in semiconductor-nanocrystals-based WLEDs is highlighted, the different approaches for generating white light are compared, and the benefits and challenges of the solid-state lighting technology are discussed.*

Keywords – Light-emitting diodes, Nanocrystals, Quantum dots, Solid-state lighting, White light.

1. Introduction.

Illumination, the second largest energy use in buildings,[1] globally consumes 20% of the electrical energy.[2] The ever-increasing energy demands along with the concerns of global warming and climate change place an enormous emphasis on the exploration of high-efficiency light sources to reduce energy consumption.[3–6] Switching from conventional to solid-state lighting is of significant importance, not only for reducing the consumption of electricity and fossil fuels, but also for decreasing the growing dependence on foreign sources of energy. This switch is estimated to cut power use by 760 GW over a period of 20 years and reduce carbon emission by 42 megatons per year in the United States alone,[7–10] thus enabling an energy-efficient future as well as the deployment of ''the cheapest, cleanest, fastest energy source.''[11–12] Therefore, solid-state lighting in the form of light-emitting diodes (LEDs) shows overwhelming promise in meeting the challenge of saving energy. The market for LEDs is predicted to expand to $11 billion in 2010,[13] with the majority of growth coming from highly bright and efficient white-light LEDs (WLEDs).[14] Currently, WLEDs can be found in a wide variety of applications,[15–18] such as displays, architectural lighting, and flashlights. The use of WLEDs could also be extended to vehicle headlamps, which are reported to consume billions of liters of gasoline and diesel globally each year.[19] The high efficiency of WLED technology could also reduce the impact that vehicles have on the environment, as well as increase the distances currently popular electric vehicles can go.

In order to achieve the full potential of WLEDs, advanced technologies must be developed to produce a high quality of white light that is highly efficient, has a long lifetime, and is cost competitive. The ideal WLEDs should emit a broad spectrum of white light that is similar to natural sunlight and most appealing to the human eyes. Most of the current WLEDs, however, emit a harsh cool light with a slightly blue tint that resembles fluorescent lighting. To evaluate the quality of the white light emitted from WLEDs, several parameters, such as Commission Internationale de l'Eclairage (CIE) chromaticity coordinates, color rendering index (CRI), correlated color temperature (CCT), and luminous efficacy (LE), have been introduced.[20–23] Each of these parameters is important in the characterization of WLEDs. The CIE chromaticity coordinates (x, y) can be measured to specify the accurate emission color, as perceived by human eyes. For example, (0.33, 0.33) is the ideal CIE coordinate value for white light. The CRI, presented on a scale of 0 to 100, is a quantitative measure of the ability of a light source to reproduce the colors of a variety of objects in contrast to an ideal or natural light source. The desirable light source in color-critical applications should have a high CRI. The CCT is a specification of the color appearance of a light source, determined by comparing the chromaticity of this light source with that of an ideal black-body radiator. The temperature in Kelvin (K) at which the heated black-body radiator matches the color of a tested light source is the color temperature of that source. Low CCT indicates warmer (more yellow/red) lights, while high CCT implies cooler (more blue) lights. Ideal CCT values for WLEDs have a range from warm white (2500 to 4500 K) to cold white (4500 to 6500 K).[24] LE, expressed in lumens per watt, is the quotient of the total luminous flux divided by the total lamp power input or radiant power emitted. Comparatively, luminous efficiency is the dimensionless ratio of LE for a given wavelength to the value of maximum LE. The distinction between efficacy and efficiency in the published sources is not always carefully maintained, and thus it is not uncommon to see efficacy expressed as a percentage, or efficiency expressed in lumens per watt.[25]

To provide the guidance for the transition from traditional light sources [incandescent, fluorescent, and high-intensity discharge (HID)] to solid-state lighting, the U.S. Department of Energy has recommended the following targets for WLEDs to be implemented for general use: a CIE chromaticity coordinate of pure white light (0.33, 0.33), a high CRI (>80), and a luminous efficiency of 200 lm W ^{1}.[10] Also, high-quality WLEDs are strongly advocated by the Light Up The World Foundation to supply safe, efficient, affordable, and healthy light sources around the world.[26] Such a strong worldwide demand for high-quality illumination motivates the develop-ment of WLEDs. Although all aspects of conventional light sources are being investigated to improve their efficiency, the opportunities for improvement are limited. Focus has cons-equently switched to the actively developing organic and inorganic WLED technology, which has the potential to double the efficiency of current white-light sources.[11]

Organic technology for generating white light provides the major advantage of low-cost fabrication for large-area light-emitting panels, but these panels produce a poor quality of color emission and typically have a limited device lifespan.[27–29] Such problems may be overcome by the integration of semiconductor nanocrystals, which are also referred to as quantum dots (QDs), into inorganic LEDs because semiconductor nanocrystals are known to have a very narrow band emission and high quantum yield. Nanocrystals also show strong absorption as well as high resistance to photo-oxidation,[30] in contrast to the common emissive materials, such as organic dyes. Another important aspect of colloidal nanocrystals that should be mentioned is their post-synthetic solution processability,[31] making their surface easily functionalized with a variety of organic molecules/inorganic shells. Therefore, semiconductor nanocrystal-based WLEDs are currently in the spotlight of research, triggering many related publications and inventions.[32–34] Based on the recent reports released by U.S. Department of Energy,[11–12] we classify the WLEDs associated with semiconductor nanocrystals into three categories (Figure 1):
a) discrete color mixing, b) color conversion, and c) direct white-light generation. On the basis of these three categories, this review will address the recent development of nanocrystals-based WLEDs. It is accompanied by detailed discussion of issues associated with the quality of WLED-generated white light. We also conclude with future challenges and expectations for the further development of nanocrystal-related solid-state lighting.

2. Semiconductor-Nanocrystals-Based WLEDs.

2.1. WLEDs Based on Discrete Color Mixing.

Phosphors, substances that exhibit the phenomenon of phosphorescence,[35] are commonly used in fluorescent lamps. Unlike conventional phosphors, such as $Y_3Al_5O_{12}:Ce^{3þ}$ (YAG:Ce), semiconductor nanocrystals have their emission colors tuned by simply altering the nanocrystal size or com-position, making them attractive candidates for applications in solid-state lighting. Based on CdSe semiconductor nanocrystals, Alivisatos's group pioneered the electroluminescent LEDs.[4] Such type of LEDs was re-structured by Bulovic's group,[3] who observed a significant improvement in the luminous efficiency. One intuitive approach for achieving white light is to optically mix several colors of electrolumines-cent emissions (e.g., red, green, and blue) of semiconductor nanocrystals in an appropriate ratio. For example, blue-, green-, and red-emitting CdSe/ZnS (core/shell) nanocrystals were blended to generate WLEDs, potentially providing a general approach to prepare long-lifetime electroluminescent devices.[36–37] WLEDs were also designed by mixing blue (CdZnS alloy), green (ZnSe/CdSe/ZnS core/shell/shell), and red (CdSe/ ZnS core/shell) emitting colloidal nanocrystals into a monolayer.[38] This monolayer and the charge transport layers could be independently processed, thus allowing the precise tuning of emission spectra by simply altering the quantity ratio of different-color nanocrystals in the monolayer.

Moreover, the prevalent CdSe-related nanocrystals were hybridized with organic polymers to fabricate hybrid WLEDs.[39] Park et al. obtained white-light emission from polymer/nanocrystal ternary nanocomposites, where red emis-sion from the 7.0-nm CdSe nanocrystals, green emission from the 3.0-nm CdSe nanocrystals, and blue emission from poly(9,9^{0}-dihexylfluorene-2,7-divinylene-m-phenylenevinylene-stat-p-phenylenevinylene) (PDHFPPV) jointly contribute to the emission of white light.[40] In the study by Li et al., red-emitting CdSe/ZnS (core/shell) nanocrystals were combined with a blue-emitting polymer, poly[(9,9-dihexyloxyfluoren-2,7-diyl)-alt-co-(2-methoxy-5-{2-ethylhexyloxy}phenylen-1,4-diyl)] (PFH-MEH), and a green-emitting metal chelate complex Alq_3 to fabricate WLEDs with a CIE coordinate of (0.30, 0.33).[41] Subsequently, this type of hybrid WLEDs based on CdSe/ZnS (core/shell) nanocrystals also appeared in the publications of (PVK) and CdSe/ CdS core/shell semiconductor nanocrystals to construct hybrid WLEDs with a quite pure white light; Chou et al. reported the fabrication of WLEDs by integrating yellow-emitting CdSe/ ZnS core/shell nanocrystals and blue-emitting polyfluorenes; Ahn et al. used red-emitting CdSe/ZnS (core/shell) nanocrystals and a blue-green fluorescent organic dye, 2,7-bis[2-(4-diphenyl-aminophenyl)-1,3,4-oxadiazol-5-yl]-9,9-dihexylfluorene, to fab-ricate hybrid organic/inorganic WLEDs. This device, however, had some disadvantages, such as low efficiencies, high drive voltages, and color instability. Such problems could potentially be avoided by fabricating separate layer structures with the nanocrystal layer on the opposite side of the substrate to the organic material.

A large fraction of the emitted energy from semiconductor nanocrystals is likely to be absorbed by either the nanocrystals themselves or the neighboring nanocrystals due to the small Stokes shift between the absorption and band-edge emission energies. For instance, the emissions from the blue-emitting nanocrystals would be significantly absorbed by the green- and red-emitting ones nearby. One more additional disadvantageous requirement of this color mixing approach is to maintain the particle size of

each type of nanocrystals within a very narrow range.[49] That is because the emission wavelength (color) of nanocrystals is extremely dependent on their particle size. If any type of the component nano-crystals in the color mixing was of broad size distribution, the corresponding emission should have a poor color purity. It may increase the complexity of maintaining appropriate proportions of the individual component in the mixing.

2.2. Color-Conversion WLEDs

In comparison to the WLEDs based on discrete color mixing, the color-conversion technique employing phosphors has been relatively successful and commercia-lized.[50–51] Color mixing to generate white light, as presented above, is based on an appropriate blend of various electroluminescence colors (e.g., red, green, and blue) of nanocrystals. Comparatively, in color-conversion WLEDs, blue/UV LED chips are usually employed as the primary light source. This relatively high-energy light, generated as electro-luminescence, passes through a wavelength conversion layer, where the phosphors or nanocrystals are caused to enter an excited state. As the phosphor/nanocrystal layer relaxes, lower-energy and longer-wavelength light is emitted (via photo-luminescence), converting the original wavelength of light into various colors. Such color-conversion layers do not damage package materials and illuminated bodies. Based on this concept, Xie and co-workers have demonstrated that a combination of green-emitting *a*-sialon:$Yb^{2þ}$ and red-emitting $Sr_2Si_5N_8$:$Eu^{2þ}$ with a blue LED die could produce WLEDs with good optical properties (e.g., tunable CCT and acceptable CRI).[52] Similarly, Wu et al. obtained a three-band WLED by coating a mixture of green phosphors ($SrGa_2S_4$:$Eu^{2þ}$ powder) and red phosphors (Ca_{1-x} Sr_xS:$Eu^{2þ}$ powder) on a blue InGaN-based LED chip.[53] However, it is difficult to control the composition of phosphor layers and subsequently deposit uniform films, thus causing the undesired visible color variations.[54] Additionally, it is not simple to adjust the photoluminescence properties of phosphors, which makes it difficult to tune the color parameters of the corresponding white light.

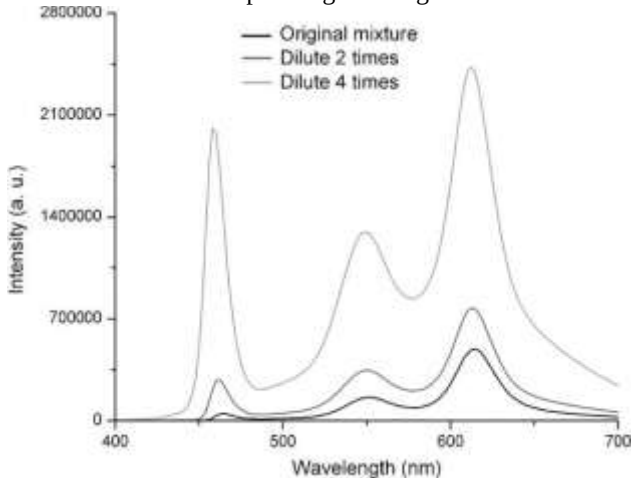


Figure 1. Photoluminescence of the mixture of 460-nm CdS/ZnS core/ shell nanocrystals, 550-nm CdSe/ZnS core/shell nanocrystals, and 615-nm core/shell CdSe/CdS nanocrystals. With the increasing dilution of the mixed solutions, the blue-emitting CdS/ZnS core/shell nanocrystals exhibited the increasing intensity of photoluminescence, altering the white-light chromaticity.

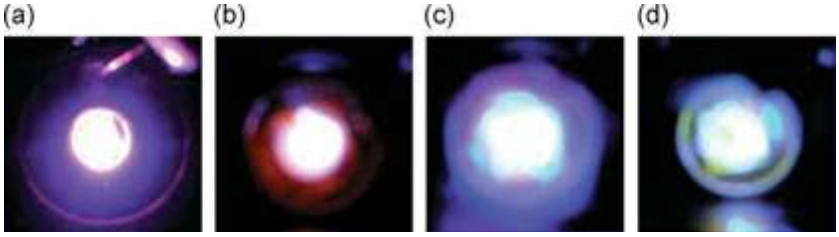
As an alternative to phosphors, semiconductor nanocrystals that exhibit size-dependent properties have recently been considered for the color-conversion layers in WLEDs to overcome the disadvantages mentioned above.[55] Chen et al. coated CdSe/ZnS (core/shell) nanocrystals on a blue/green InGaN/GaN LED to convert some blue photons into red light, generating white light.[56] Also, Chen and co-workers fabri-cated WLEDs based on the blue-emitting InGaN chips and green- and red-emitting CdSe/ZnSe (core/shell) nanocrystals.[57] Such nanocrystal-conversion WLEDs were reported to have flexible selected color and emit white light with a CIE chromaticity coordinate of (0.33, 0.33). On the basis of the similar blue/UV-emitting InGaN/GaN LEDs, Demir's group and others later employed CdSe/ZnS (core/shell) nanocrystals as a color convertor to produce WLEDs with the convenient adjustment of white light parameters.[54,58–62] The CIE chromaticity coordinates, CCT, and CRI could be adjusted from CIE ¼ (0.37, 0.25), CCT ¼ 2692 K, and CRI ¼ 14.69 to CIE ¼ (0.24, 0.33), CCT ¼ 11171 K, and CRI ¼ 71.07, while InGaN/GaN LEDs were coated with CdSe/ZnS (core/shell) nanocrystals of single (yellow), dual (cyan and red), triple (green, yellow, and red), and quadruple (cyan, green, yellow, and red) combinations, respectively (Figure 4).[58] It should be mentioned that the color para-meters could be also adjusted by varying the device parameters, such as the size/compo-sitions,[58] concentration and numbers of the integrated nanocrystals,[59] and the thickness and microstructure/ordering of the nanocrystal films.[60] The nanocrystal density and the related film thickness contributed to the conversion from the incident photon to the emitted/transmitted photons in each nanocrystal layer. Therefore, the capability of adjusting the above device para-meters could make the generation of intended white light possible. Such CdSe/ZnS-based WLEDs that could provide warm white light were further improved to reach a decent CRI of 82.4 and a high LE of 300 lm/W.[63] Additionally, hybridization of CdSe-related nanocrystals and highly

fluor-escent polymers (such as 9,9-bis(2-ethylhexyl)polyfluorene, 2,3-dibutoxy-1,4-poly(phenylene vinylene) (DBPPV), and Poly {(9,9-dioctyl-2,7-divinylenefluorenylene)-alto-co-(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene)}) on a InGaN-based LED pump source was developed to control the generation of white light with a high CRI value (>75).[64–66] In comparison, a lower CRI of 62 and 61.4 was obtained in the WLEDs fabricated with Mn-doped CdS/ZnS core/shell nanocrystals and blue LED chips,[67] and with dual CdSe nanocrystals and blue LED chips,[68] respectively.

Although the nanocrystals-based WLEDs presented above have decent CRI values, it is difficult to achieve a CRI over 85. Some recent reports have demonstrated that excellent CRI values could be achieved by combining conventional phosphors and semiconductor nanocrystals.[69–72] By integrating both the organically capped red-emitting CdSe nanocrystals and green-ish-yellow-emitting $Sr_3SiO_5:Ce^{3þ},Li^{þ}$ phosphors into the blue InGaN LEDs-pumped WLEDs, Jang et al. reported a CRI of 90.1.[69] Replacing these CdSe nanocrystals with CdSe/ZnSe core/shell nanocrystals, Jang and colleagues later fabricated WLEDs with a high CRI of 85.[70] An alternative to toxic CdSe nanocrystals, red-emitting silica-coated InP/ZnS nanocrystals together with green-emitting $Sr_{0.94}Al_2O_4:Eu_{0.06}$ converters and yellow $Y_{2.94}Al_5O_{12}Ce_{0.06}$ were dispersed in silicone and then coated on top of a blue LED chip to generate white light with a CRI of 86.[71] These results indicate that the combination of both semiconductor nanocrystals and phosphors with the commercial LEDs provides a wonderful solution to create white light with extremely high CRI properties.

2.3. WLEDs Based on Direct White-Light Generation

Color mixing involves the optical blending of several colors of electroluminescent emissions. Color conversion includes electroluminescence to generate blue/UV light, photolumines-cence of phosphor/nanocrystal layers, and the combination of the two.



Recently, there emerges great interest in the development of direct white-light emitters for solid-state lighting. Direct white-light generation is photoluminescence of only one type of nanocrystal layers that emit white light. In the device design, such white-light emission can be excited by the light source of UV LEDs. Chen and co-workers have synthesized direct white light-emitting ZnSe nanocrystals,[73] where the production of white light was attributed to the mixture of both the energy band blue emission and the broad surface-trapped green/red emission. Based on these white-light ZnSe nano-crystals, they have successfully fabricated WLEDs with a CIE chromaticity coordinate of (0.38, 0.41). In another study, Li et al. first synthesized the fluorescent $ZnO–SiO_2$ composite nanopowders and dispersed them into a transparent epoxy, where the epoxy super-nanocomposites displayed broad emission spectra and were successfully applied to fabricate highly bright WLEDs.[74]

Rosenthal's group used a similar approach to achieve direct white light by integrating the broad surface-state emissions and band-edge emission from 1.5-nm magic-sized CdSe nanocrystals (which were most recently termed as ''ultrasmall nanocrystals'') with an emission efficiency of 2%.[48] This relatively low efficiency at the early and exploratory stage may not be considered as an intrinsic disadvantage, because the utility of directly white light-emitting nanocrystals as the emitter eliminates the need for complex color mixing or conversion techniques. The modified approaches have the potential to enhance the lighting efficiency. One proposed modification was to increase the chain length of surface ligands, phosphonic acid, to enhance the nanocrystal quantum yield to 10%.[75] Also, utilizing the modulation of the phosphonic acid ligand could control the nanocrystal surface-state emission, indicating that the surface ligand played the dominant role in tuning the emission properties of these nanocrystals. Another improvement by Rosenthal's group was to increase the loading level of these white-light nanocrystals into the encapsulating polymer,[76–78] such as biphenyl perfluorocyclobutyl polymer. In this polymer, the nanocrystal loading level could reach up to 18%, where the encapsulated ultrasmall CdSe nanocrystals created white light with CIE coordinates of (0.324, 0.322) and a high CRI of 93. It should be noted that the loading level of nanocrystals could not be unlimitedly increased, because the overload would lead to the aggregation of nanocrystals. Most recently, Rosenthal's group reported direct white-light generation based on the electroluminescence of ultrasmall white-light CdSe nanocrystals.[79] Previously, the electroluminescence from nanocrystals with a particle size less than 2.0 nm was thought to be unattainable. The fabricated WLEDs had excellent parameters, defined by pure white-light CIE coordinates of (0.333, 0.333), CCT of 5461-6007 K, and CRI of 96.6. Additionally, Dai and his co-workers reported that the combination of the emissions from magic- and regular-sized nanocrystal colloids could also achieve the goal of white-light generation.[80] Although recent progress shows the strategies associated with ultrasmall nanocrystals are able to tailor the white-light shades through surface chemistry and synthetic modulation,[75,81] the related WLEDs have very low luminous efficiency (1.0 lm/W), and the stability of optical properties needs further improvement.[77]

It is worth noting a paper, reporting two additional routes to generating white light.[82] The first one is to fabricate the multi shell structures on a nanocrystal core (e.g., core/shell/ shell/shell), emissions from which have different wavelengths and thus can mix to generate white light. This route is somewhat similar to the one based on color mixing. The other route resembles the one reported by Rosenthal's group,[48] combining surface-state emissions with the band-edge emission in plain nanocrystals to emit white light. This strategy was also employed by Ozel et al.,[83] who carefully integrated the silver nano-island film with CdS nanocrystals in a poly(methyl methacrylate) matrix. Such careful integration could enhance the broad surface-state emission and simultaneously suppress the band-edge transition of CdS nanocrystals through matching their surface-state emissions with the localized plasmon resonance of silver films. This resonance engineering approach provided an alternative for the nanocrystals-based solid-state lighting. Also, broad and white emission from CdS nanocrystals was realized by either of Nizamoglu et al. and Shea-Rohwer et al.[84–86] Via the surface modification and ligand displacement, the fluorescence quantum yield for these CdS nanocrys-tals could be increased to 37%.

Additionally, metal ion-doped nanocrystals, such as ZnS: $Pb^{2þ}$,[87] ZnS-doped silicon,[88] $Mn^{2þ}$-doped ZnS,[89] and $Mn^{2þ}$-doped CdS,[49] have the potential to serve as a new class of direct white light-emitting materials. In contrast to the undoped counterparts, these nanomaterials have the potential to overcome some intrinsic disadvantages, such as self-absorption and sensitivity to thermal, chemical, and photochemical disturbances.[90] One such doped nanomaterial, $Mn^{2þ}$-doped CdS nanocrystals, helped explain the generation mechanism of white light, involving the combination of broad surface-state emissions from the nanocrystal host with inner-core transitions from dopant centers.[49] In other words, the nanocrystal host has broad surface-state emission, but this emission is not broad enough to cover the entire white-light range. The addition of $Mn^{2þ}$ as a dopant into the host nanocrystals can extend emissions to a broader wavelength range of visible emission, covering the whole white-light region. For example, doping a certain amount of $Mn^{2þ}$ ions can introduce red light (630 nm) derived from the $^4T_1$-$^6A_1$ transition of $Mn^{2þ}$ d electrons. The inner-core transition at the dopant sites as well as the surface-state emissions of the host nanocrystals are relatively less sensitive to the variation of nanocrystal sizes, compared with the size-dependent bandgap emission for semiconductor nanocrystals. Therefore, the chromaticity of the emitting light does not closely depend on the nanocrystal size distribution, making it possible to use a nanocrystal specimen with large size distributions to generate white light. In order to demonstrate that the direct generation of white light did not require a narrow size distribution of nanocrystals, Nag et al. synthesized $Mn^{2þ}$-doped CdS nanocrystals with a size distribution as large as 17%.[49] This sample emitted white light with a chromaticity coordinate of (0.33, 0.38), similar to that of the sample with narrow size distributions. This is unlike the color mixing app-roach that requires a high degree of control on the nanocrystal size distribution, as discussed in Section 2.1. Furthermore, the different white-light shades can be achieved by simply altering the relative proportion of the surface-state emission from inspiring and was extensively employed in the synthesis of highly monodisperse CdE (E ¼ S, Se, Te) nanocrystals with different sizes and shapes, the starting materials, such as $Cd(CH_3)_2$, are extremely toxic, pyrophoric, explosive, and expensive.

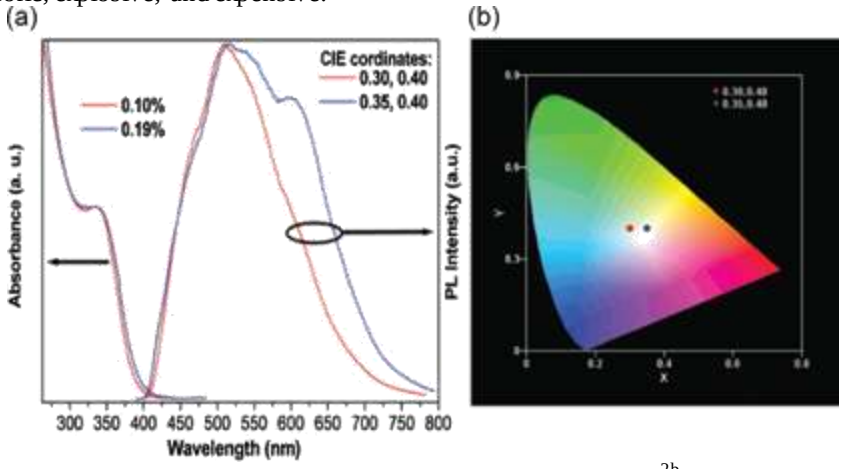


Figure 3. a) Absorption and photoluminescence (PL) spectra of 0.10% and 0.19% $Mn^{2þ}$-doped CdS nanocrystals. b) CIE diagram of the corresponding two nanocrystal samples in Panel a, showing the chromaticity coordinates of the produced white light with different shades. Reproduced with permission from Reference [49].

Therefore, researchers explored greener approaches to synthesize high-quality semi-conductor nanocrystals. For example, the $Cd(CH_3)_2$-related method was replac-ed by the relatively stable CdO-related scheme,[95] and the solvent trioctyl-phosphine oxide was replaced by 1-octade-cene (less expensive and much less toxic than toluene).[96] More recent reports showed that other nontoxic reagents, such as edible olive oil,[97–98] could be used as the sole solvent to synthesize high-quality semiconductor nanocrystals.

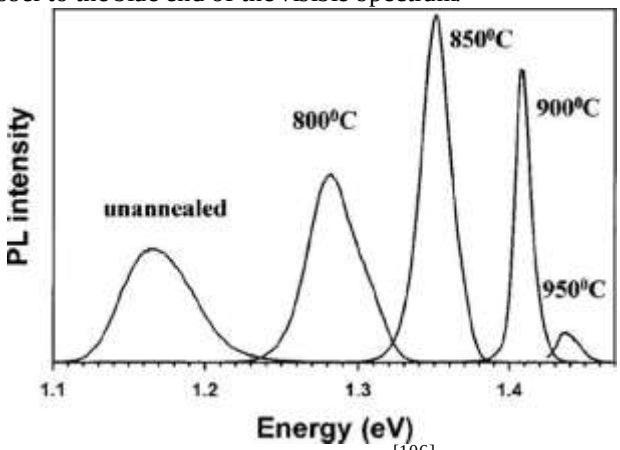
To fulfill the practical application, it is indeed important for a green strategy to have the capability of producing large-scale quantities of high-quality nanocrystals. In contrast to the historical development of quantum dot nanocrystals for medical or biological applications, solid-state lighting demands engineering-scale production of nanocrystals to manufacture large-dimension

devices. In this sense, the prevalent injection-based approaches described above might not meet this requirement because the rates of both reagent injection and mass transfer are limited by the apparatus for large-scale industrial syntheses. Instead, a recent approach called non-injection syntheses was reported to have the potential to scale up the production of high-quality semiconductor nanocrystals.[99–102]

3. Research and Development Needs in the Synthesis and Processing of Semiconductor Nanocrystals

By their very nature, nanocrystals have a very high surface-to-volume ratio. Regardless of the manufacturing technique, nanocrystal structures contain numerous defects, both within the nanocrystal and at the interface with the matrix material.[104] The point defects act as nonradiative recombination sites. In these sites electron-hole pairs recombine without generating a photon, thus decreasing the quantum efficiency of the device.[105] Colloidal nanocrystal structures typically contain 10^9 to 10^{10} defects cm^2, the range over which the efficiency of standard semiconducting materials is dramatically reduced.[16] The traditional approaches for reducing the number of defects in a material have focused on the crystal growth process, which favors a slow and highly ordered crystal growth. Other techniques have focused on reducing the number of defects through thermal annealing.

Thermal annealing can relieve strain on the as-deposited nanocrystal structure and reduce the number of defects by several orders of magnitude.[106] Since this reduces the number of non-radiative recombination sites, it also increases the quantum efficiency.[107–109] Figure 7 shows that the photo-luminescent intensity of InAs/GaAs nanocrystal structures increases significantly after thermal annealing for 30 s at temp-eratures up to 850 8C. Although this is a promising result, a few disadvantages associated with traditional thermal annealing are also evident. At temperatures above 850 8C, the 30-s time interval is sufficient to allow inter-diffusion of dopants across the nanocrystal interface. This changes the composition of the nanocrystal and effectively ''smears'' the nanocrystal boundaries, causing damage to the structure, and reducing the photo luminescent intensity.[110] Also, notice that the peak intensity in Figure 7 shifts to higher energies as the annealing temperature increases. This is commonly referred to as ''blue shift'' because as the composition of the nanocrystals changes, the effective bandgap increases, and the wavelength of emitted light shifts closer to the blue end of the visible spectrum.



The long time interval at high temperatures also allows for grain growth,[106] which alters one of the primary functional parameters of a nanocrystal structure—its size.

A technique called rapid thermal annealing (RTA) has been used to address the issues of diffusion and grain growth. RTA exposes the sample to extremely high levels of radiant energy for a short amount of time, resulting in a steep thermal gradient through the thickness of the sample. On a time-averaged basis, the amount of energy delivered to the bulk of the sample does not result in a significant temperature rise. Not only does this permit the use of temperature-sensitive substrates such as LEDs, but it also preserves the integrity of the nanocrystal structure by discouraging diffusion and crystal growth. As shown in Figure 8, using a pulsed excimer laser for RTA increases the integrated photo luminescent intensity of a nanocrystal structure by more than a factor of 5 without any appreciable shift in the peak emission wavelength.[111] The increased intensity was attributed to a decrease in the defect density of the nanocrystal structure. Unfortunately, laser annealing is restricted to an extremely small processing area and generates significant thermal gradients across the surface of the material. Large area and cost-effective forms of thermal annealing are needed to apply this technology to a manufactur-ing environment.

4. Summary and Outlook

In this review, we have highlighted the recent developments in semiconductor nanocrystals-based solid-state lighting (i.e., WLEDs) in terms of the different approaches to generating white light, including discrete color mixing, color conversion, and direct white-light generation. The widespread use of CdSe nanocrystals is a testament to their excellent size-dependent optical

properties in the visible range. For fundamental studies, CdSe nanocrystals have served as an excellent model system. However, cadmium, an extremely toxic component, makes future use of this type of nanoscaled candidate uncertain in practical applications. It is well known that cadmium is a highly

toxic element, any potential release of which is considerably harmful to the environment and mankind.[98,112–113] Cadmium

can build up in the kidney and liver and cause chronic diseases. Eventually, the inherent toxicity of cadmium-related

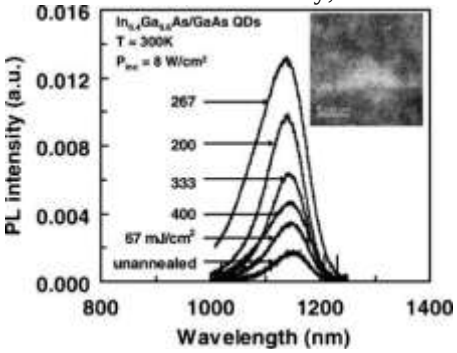
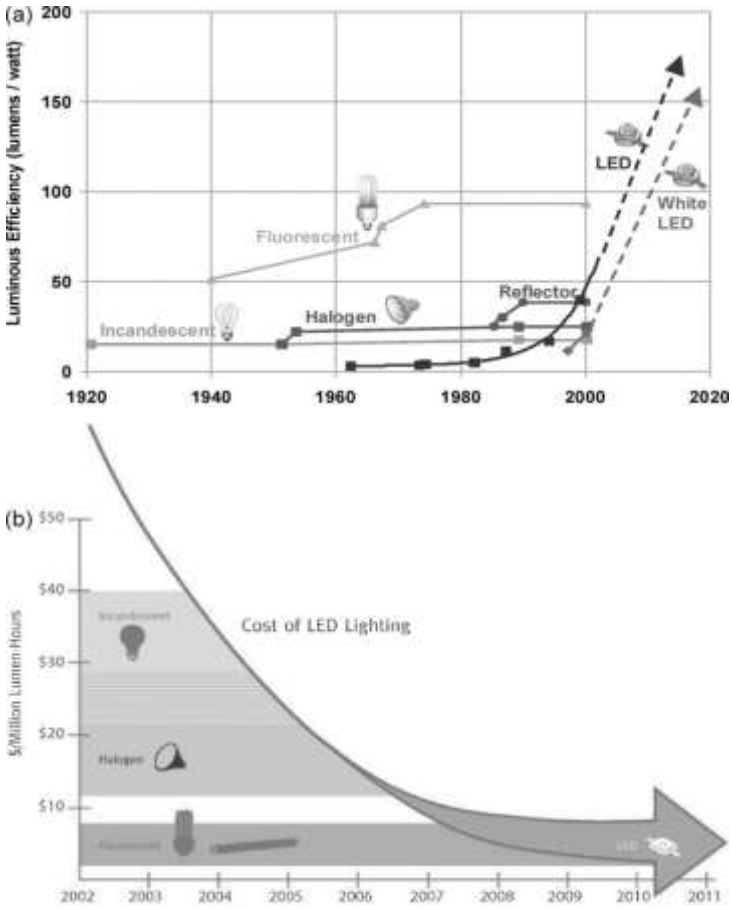


Figure 5. Increase in photoluminescence of quantum dot structures due to rapid thermal annealing. Reproduced with permission from Reference [108]. Copyright American Institute of Physics, 1997.

nanomaterials will prevent their applications to the ever-increasing WLED market and other related fields. Therefore, the engineering development for large-scale production of nontoxic, user-friendly, and environmentally benign nanomaterials is needed, where non-cadmium nanocrystal-based WLEDs will be the priority. In response to this requirement,

Figure 6. Increase in photoluminescence of quantum dot structures via laser annealing. Reproduced with permission from



Reference [111]. Copyright Springer, 2004.

For example, the red InP/ZnS nanocrystals were combined with green-emitting $Sr_{0.94}Al_2O_4:Eu_{0.06}$ and yellow $Y_{2.94}Al_5O_{12}Ce_{0.06}$ converters to generate high-quality white light.[71] Additionally, ion-doped ZnSe nanocrystals[118–120] (such as Mn- or Cu-doped ZnSe), nano-scaled ZnO,[121–126] and ternary semicon-ductor nanocrystals[127–129] (e.g., $CuInS_2$ and $AgInS_2$) also have the potential to exhibit the comparable optical properties to CdSe nanocrystals, and thus might be acceptable for real-world applications because of their nontoxicity and environ-mental benignity.

Despite the great improvement in light quality of WLEDs, the primary focus for the future development of nanocrystals-based WLEDs will be increasing the efficiency and reducing the cost associated with large-area lighting production. Table 1 compares the typical performance of the nanocrystals-based WLEDs to commercial WLEDs and conventional lighting technologies. WLEDs are expected to be 2–3 times more efficient than fluorescent lighting and estimated to be up to 200 lm W^{-1} efficient by 2020 (Figure 9a),[10–12,17] but they currently have lower light output and higher lamp cost when compared with the conventional light sources. Until these issues can be resolved, WLEDs will not be an effective alternative to current lighting technology. However, the development of WLED technology is relatively new, and there is much opportu-nity for improvement. For example, the proof-of-concept WLEDs developed by Demir's group are able to emit white light with LE >300 lm W^{-1}.[63,130] This may be achieved by involving the improvement of the material quality and the design of novel structures with increasing light-extraction efficacy. With the advancement of solid-state lighting technology, the cost of WLEDs is expected to become competitive with the fluorescent lamps (Figure 7).[12,16,131]

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