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White-Light Emitters

Solution-Processable White-Light-Emitting Hybrid Semiconductor Bulk Materials with High Photoluminescence Quantum Efficiency**

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As an alternative lighting source, solid-state lighting (SSL) technologies (primarily light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs)) have received considerable attention in recent years owing to their enormous potential for use in lighting and displays. The major advantages of SSL are lower energy consumption, higher efficiency, and longer lifetime.[1] White-light-emitting diodes (WLEDs) are of particular interest because of the great need in general illumination applications. Common approaches to produce WLEDs include blending of three primary colored LEDs, namely red, green, and blue (RGB) diodes, or combination of a blue (or UV) LED with a yellow phosphor (or multi-phosphors).[2–5] Either process requires complex doping/mixing and delicate control of multiple materials and colors, which proves both challenging and costly.[2–4] At the present time, commercially available WLEDs are predominantly phosphor based (e.g. a yellow-emitting phosphor, yttrium aluminum garnet or (YAG):Ce^{3+}, coupled with a blue-emitting InGaN/GaN diode).[2] While less expensive than the RGB diodes, the (YAG):Ce^{3+} type phosphors and WLEDs have issues such as unsuitability for solution process, poor color rendering index (CRI), and high correlated color temperature (CCT) which limit their widespread commercialization in general lighting market[2,3c] Semiconductor quantum dots (QDs) or nanocrystals (NCs) with broad and strong absorption and tunable emission are promising alternative phosphors because they are solution processable.[6–13] However, their emission bands are often too narrow.[9] White light obtained by combining blue-, green-, and red-emitting QDs of various sizes, on the other hand, often suffers from low efficiency caused by self-absorption, scattering and related energy-transfer issues.[3] In addition, it is of great difficulty and complexity to control the size of QDs and maintain an appropriate amount of each component to balance the color. WLEDs based on QDs/NCs typically have relatively low quantum efficiency (QE), that is, 2 % for Mn-doped CdS NCs[14] and 2–3 % for magic-sized CdSe NCs.[7a]

These problems may be reduced or eliminated by developing a) more complex QDs/NCs composites[6] or b) single-phased white-light emitters in bulk form.[4,5] For (a), significantly improved quantum efficiency of 30 % for onion-like CdSe/ZnS/CdSe/ZnS,[6] 17 % for trap-rich CdS,[6] 17 % for Cu:Mn-ZnSe,[13] and 12 % for alloyed $[Zn_xCd_{1-x}Se]$,[8] have been achieved. However, in most cases, multiple steps are involved in the synthesis, and precise control of NC core and/or shell size remains highly challenging. In addition, surface modification is often required which adds further complexity to the synthesis process. For (b), on the other hand, there are only very few known examples of single-phase white-light emitters in bulk form.[4,5,8] One of them is $[\{AgL\}_n{\cdot}n\,H_2O]$ (L = 4-cyanobenzoate), for which a quantum yield (QY) of 10.9 % is attained.[4c] Additionally, several single-phase organic white-light-emitting materials have been developed.[4] Herein we report a unique family of solution-processable, low-cost, and high-efficiency hybrid semiconductor bulk materials as single-phase white-light-emitting phosphors. These crystalline structures are built on periodically arranged two-dimensional (2D) nano-modules of ZnS and organic amines. Having a white light emission QY as high as 37 %, the new phosphors are approaching the performance of (YAG):Ce^{3+}.

Over the past several years we have developed a unprecedented class of inorganic–organic hybrid semiconductor bulk materials.[15] With a general formula of $[M_nQ_n(L)_x]$ (M = Mn, Zn, Cd; Q = S, Se, Te; L = mono- or di-amine; $n = 1$ and 2; $x = 0.5$ and 1), these crystalline compounds are extended networks of one-, two- and three-dimensions and are composed of alternating II–VI binary semiconductor (inorganic) modules and amine molecules (organic) at nano- or sub-nanometer scale and in periodic arrangement by coordinate bonds (Figure 1). They exhibit a number of enhanced properties over their parent II–VI semiconductors, as well as important new phenomena as a result of blending of the two distinctively different components in a single crystal lattice. These include strong structure-induced quantum confinement effect (QCE), high absorption power, systematic and broad band-gap tunability.[15] In addition, the low-cost and very simple one-pot synthesis, the solution processability and ease for scale-up, the well-defined and precisely-controlled crystal structures and composition, and high thermal stability (up to 200 °C), are all attractive features that make them promising candidates for various optoelectronic applications.

Previously we have demonstrated that some of these materials may have potential for use as single-phase white-light emitters.[16] Both $[Cd_2S_2(ba)]$ and $[Cd_2Se_2(ba)]$ (ba = butylamine) are capable of generating white light upon

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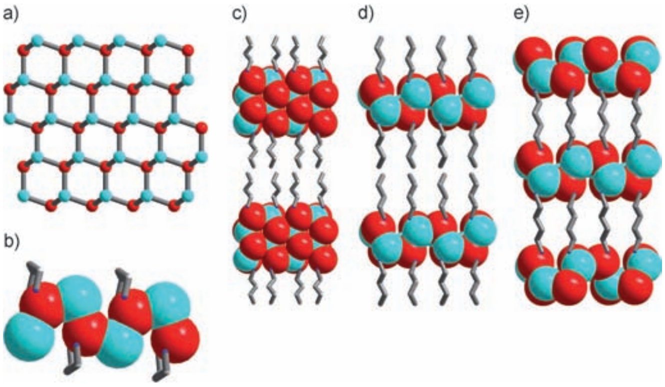

Figure 1. View of a) single layer of honeycomb-like net of ZnS in the $[M_nQ_n(L)_x]$-type hybrid structure (M = Zn, Cd; Q = S, Se, Te; L = mono- or diamine), b) single-chain 1D-[MQ(L)] structure, c) double-layer 2D-$[M_2Q_2(L)]$ structure, d) single-layer 2D-[MQ(L)] structure, and e) single-layer 3D-$[MQ(L)_{0.5}]$ structure. Blue M, red Q, in (b)–(d) the stick model corresponds to L.

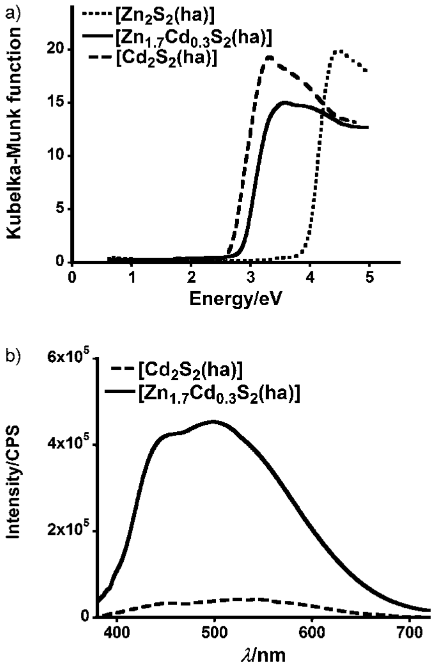

Figure 2. a) Room-temperature absorption and b) emission spectra of double-layer $[Zn_{1.7}Cd_{0.3}S_2(ha)]$ and $[Cd_2S_2(ha)]$ excited at a wavelength of 365 nm. The adsorption spectrum of $[Zn_2S_2(ha)]$ is also included as a reference.

excitation with UV light and their emission properties can be tuned. However, these systems only serve as a concept proving case because their quantum efficiencies are very low (QY ≈ 4–5 %). In an effort to enhance the performance of this type of materials we have further developed a series of ZnS based $[Zn_2S_2(L)]$ compounds that are built on 2D nanomodules of ZnS of a uniform layer thickness. Investigation of their emission properties reveals drastically improved quantum efficiencies over the CdQ (Q = S, Se) based hybrid structures.

The $[Zn_2S_2(L)]$ (L = propylamine (pa), butylamine (ba), hexylamine (ha), and octylamine (oa)) compounds crystallize in orthorhombic space groups.[15a,16a] They feature a double-layer structure made of 2D ZnS semiconductor motifs (ca. 8 Å in thickness) that are bonded to amine (L) molecules (Figure 1 c).[15a] One-pot solvothermal synthesis under mild conditions (e.g. 120 °C) offers pure phased product in high yield. All samples used in LED aggregates are solution processed in DMSO at room temperature (see Supporting Information, Figure S1). $[Zn_2S_2(ha)]$ shows a sharp optical absorption edge and its optical band gap is 3.9 eV, approximately 1.2 eV higher than that of its Cd analogue, $[Cd_2S_2(ha)]$ (ca. 2.7 eV; Figure 2 a). $[Zn_2S_2(ha)]$ emits strongly in the green–blue region with its emission peak centered at approximately 420 nm (Supporting Information, Figure S2), giving an order of magnitude increase in the emission intensity compared to that of the $[Cd_2S_2(ha)]$ analogue. An optimized composition of $[Zn_{1.7}Cd_{0.3}S_2(ha)]$ gives rise to a well-balanced white light emission, as shown in Figure 2 b. The International Commission on Illumination (CIE) coordinates of $[Zn_{1.7}Cd_{0.3}S_2(ha)]$ are calculated to be (0.31, 0.29), well within the white region of the color space chromaticity diagram (Supporting Information, Figure S3).

$[Zn_{1.7}Cd_{0.3}S_2(ha)]$ illustrates a single and sharp band edge absorption peak (Figure 2 a), from which a band gap of approximately 2.9 eV is estimated. Phase purity is confirmed by powder X-ray diffraction (PXRD, see Figure S4), elemental analysis (EA), thermogravimetric analysis (TGA; Supporting Information, Tables S3 and S4), and optical absorption experiments. The very broad emission peak of $[Zn_{1.7}Cd_{0.3}S_2$ (ha)] is most likely a combined result of band edge emission, Cd substitution (Supporting Information, Figure S2),[17] and also possibly contributions from the ligand modulated trap-state[7d,9] and surface state emission related to its 2D nanostructures.[7,18,19]

The fluorescence QY of the $[Zn_{1.7}Cd_{0.3}S_2(ha)]$, obtained by both relative/comparative and absolute methods on solution and solid samples (see Supporting Information, Figure S5 and Table S5), is in the range of 17–18 %, significantly higher than the values for $[Cd_2Q_2(ba)]$ (Q = S, Se, 4–5 %),[16] and CdSe QDs (2–3 %).[7a] To further improve the emission efficiency, we have examined the effect of Mn on the luminescence properties of the compounds. Previous studies have shown that Mn doping leads to both enhancement of photoluminescence (PL) intensity[20–24] and tunable emission range.[14] However, the position of the emission peak depends on the strength of the crystal field and the coordination environment of Mn^{2+}.[2a] In the case of $[Zn_{1.7}Cd_{0.3}S_2(ha)]$, we find that the maximum enhancement occurs at a very small amount of Mn (ca. 0.08 mole percent). Higher or lower concentrations all give rise to reduced PL intensity (Figure 3 a,b). The same trend was reported for Mn doped CdS quantum dots.[25] Efficient energy transfer from the ZnS host to the Mn^{2+} ions facilitated by mixed electronic states is responsible for the enhancement in the luminescence.[24] The very strong confinement in the 2D layers of the hybrid systems further promotes such energy transfer. Subsequent decrease of PL intensity as the amount of Mn^{2+} reaches a threshold level is due to the concentration quenching.[26] Increase in the Mn^{2+} concentration leads to the energy

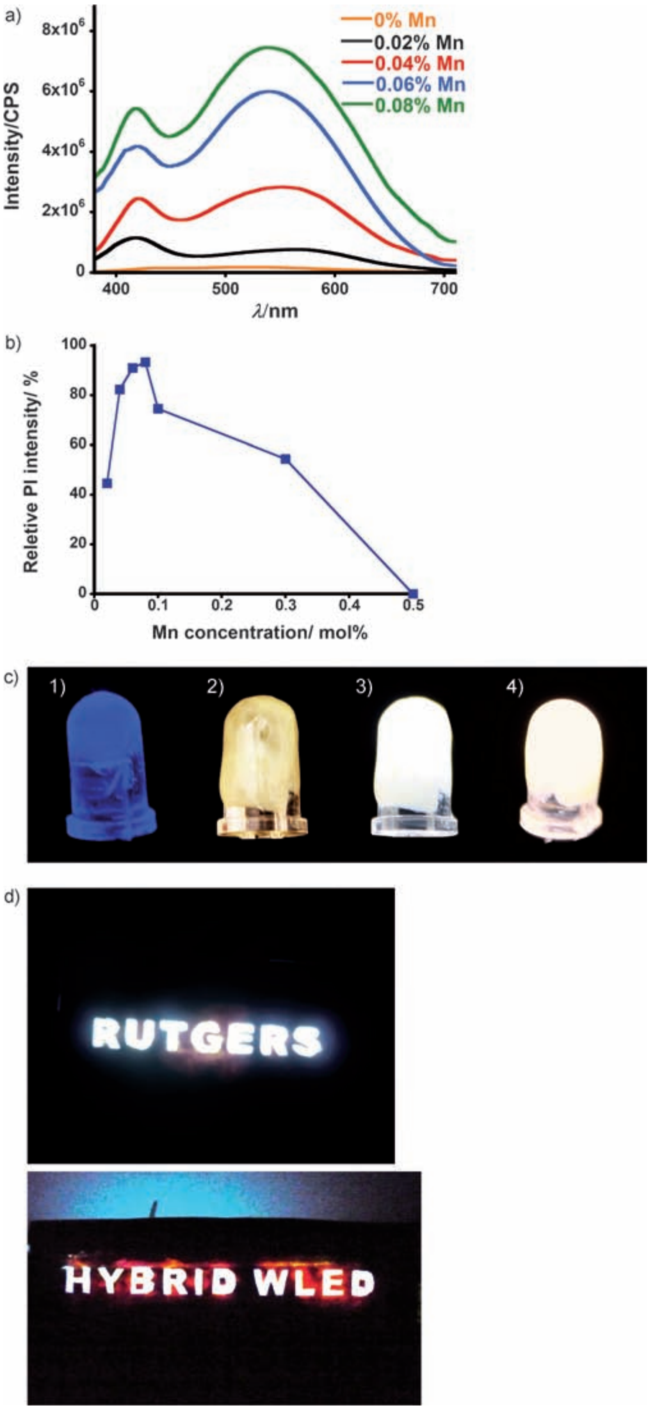

Figure 3. a) White-light emission spectra of [$Zn_{1.7}Cd_{0.3}S_2$(ha):Mn] at various Mn concentrations ($\lambda_{ex}=365$ nm); b) integrated emission intensity of [$Zn_{1.7}Cd_{0.3}S_2$(ha):Mn] as a function of the amount of Mn dopant (0.02–0.5 mol%); c) white-light LED aggregates made by coating a thin layer of sample on the surface of a 5 mm reference UV LED (360 nm emission, commercially available from Le Group Fox, Inc.): 1) illuminating reference UV LED, 2) the LED in (1) coated with a thin layer of [$Zn_{1.7}Cd_{0.3}S_2$(ha)] prepared in a DMSO solution (before illumination), 3) the LED in (2) illuminating, and 4) [$Zn_{1.7}Cd_{0.3}S_2$(ha)]:0.08%Mn]-coated LED illuminating; and d) bright white light from a [$Zn_{1.7}Cd_{0.3}S_2$(ha):0.08%Mn] (top) and a [$Zn_{1.7}Cd_{0.3}S_2$(ha)] (bottom) sample deposited on glass excited at 365 nm with a UV lamp.

migration among the ions and as a result some energy will be lost in defect sites by nonradiative decays.[26]

The manganese substitution leads to appreciable change in the relative peak intensities (Figure 3a) but does not impose any noticeable effect on the band gap (Supporting Information, Figure S6). This change in the intensity distributions results in a warmer color (lower correlated color temperature, CCT) of the emitted light which gives a more yellowish appearance (Figure 3c,d).[2i] The fluorescence quantum yield for the [$Zn_{1.7}Cd_{0.3}S_2$(ha): 0.08% Mn] is calculated to be of 26–29%, a remarkable increase of 51–69% with respect to the undoped compound.

To examine the effect of organic ligands on the absorption and emission behavior of the hybrid compounds, [$Zn_{1.7}Cd_{0.3}S_2$(L)] samples containing four amines with various chain length (L = pa, ba, ha, oa), were synthesized and structurally characterized. As shown in Figure 4, the PL intensity increases considerably as a function of chain length, showing the same trend observed in a number of other II–VI semiconductor systems.[16,21] This phenomenon may be explained by the extent of quantum confinement (QC) along the packing direction of the II–VI layers. Such a confinement leads to the formation of 2D excitons.[21] As the length of amine molecule increases, the interlayer interactions are reduced, and thus, an enhanced quantum confinement to the 2D inorganic layers. consequently, local carrier density of states close to Fermi energy is increased and more electrons become available, leading to the enhancement of both absorption power and PL intensity.[21] In contrast to their strong effect on the PL emission intensity, changes in amine chain length show negligible effect on the band gap of the hybrid compounds (Figure 4a). Fluorescence QY of 25–28% was obtained for [$Zn_{1.7}Cd_{0.3}S_2$(oa)] (C8 amine), again a

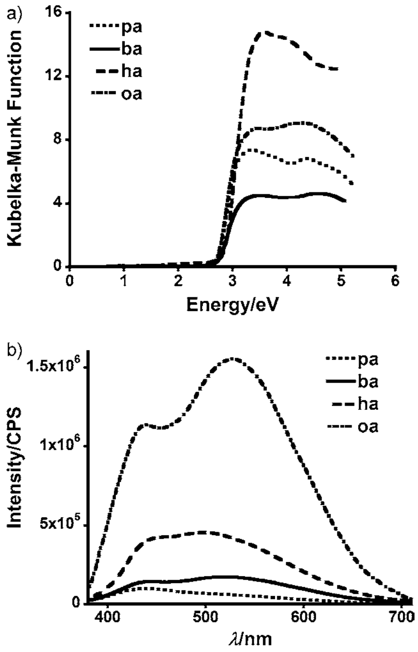

Figure 4. Room-temperature absorption (a) and emission (b) spectra of [$Zn_{1.7}Cd_{0.3}S_2$(L)] (L = pa, ba, ha, oa). Estimated band gap values are 2.89, 2.89, 2.90, and 2.92 eV for pa, ba, ha, and oa, respectively.

significant increase (46–63 %) from that of $[Zn_{1.7}Cd_{0.3}S_2(ha)]$ (C6 amine). Moreover, Mn doped (0.08 mol %) $[Zn_{1.7}Cd_{0.3}S_2(oa)]$ yielded a QY of 31–37 %, a value that is approaching to some of the phosphors currently used in commercial WLED productions.[1,2]

In summary, we have developed a new family of bulk semiconductor materials as single-phase white-light-emitting phosphors with high quantum efficiency. These ZnS-based crystalline inorganic–organic hybrid semiconductors have well-defined and precisely controllable crystal structure and composition. Their optical emission properties, including intensity, quantum yield, and color quality, can be systematically tuned by varying the composition of both inorganic and organic components. Having fluorescence quantum yields as high as 37 %, combined with excellent solution-processability, low-temperature, and cost-effective one-pot synthesis, accurate stoichiometry control, and high yield, the ZnS-based hybrid materials demonstrate a number of advantageous features over quantum-dot-based phosphors and (YAG):Ce^{3+} phosphors that currently dominating the commercial market of WLEDs.

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