Communication

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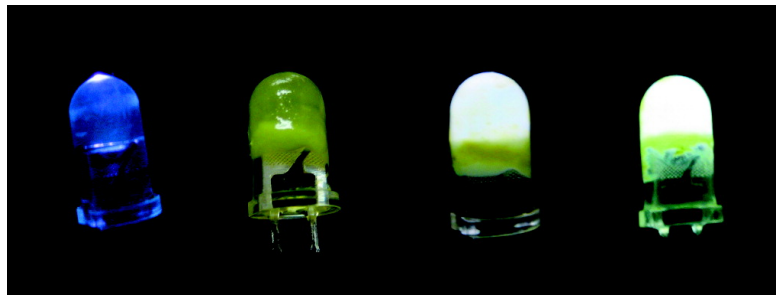

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A Semiconductor Bulk Material That Emits Direct White Light

Wooseok Ki and Jing Li*

Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Road, Piscataway, New Jersey 08854

Received March 6, 2008; E-mail: jingli@rci.rutgers.edu

Solid-state lighting (SSL) is an energy-saving lighting technology. Light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs) are two main branches of SSL technology that are evolving most rapidly in the recent years.[1,2] Utilizing semiconductor materials, SSL devices convert electricity to light much more effectively than conventional lighting sources. Additionally, they contribute to reduction of green house gases and offer a cleaner environment.[3–5] Solar-powered LEDs can make direct use of renewable energy for our society's lighting needs.[6] It has been estimated that a reduction of approximately 29% (50%) of U.S. (global) energy consumption for lighting could be reached by 2020 as a result of solid-state lighting applications.[7,8]

White-light LEDs, which have enormous potential for general lighting applications, are produced by either mixing red, green, and blue (RGB) LEDs or by phosphor conversion, in which white light is generated by coating a blue or near-UV LED with a yellow or multichromatic phosphor.[3] However, both processes are associated with complex mixing or doping schemes and significant reduction of device efficiency due to problems such as self-absorption, relatively low light capture efficiency of phosphors, or nonradiative carrier losses.[9,10] A recent discovery shows that ultrasmall CdSe nanocrystals (NCs) give rise to a broad (white-light) emission covering the entire visible spetrum,[11] as a direct result of very high surface-to-volume ratio and, thus, a significantly larger number of midgap surface sites. These tiny nanocrystals are promising for use as a direct white-light phosphor without involving complicated doping/mixing procedures.

While they may offer some advantages over other phosphors, the weak correlations among the nanocrystals will limit their uses as white-light-emitting diodes, due to the difficulties in achieving high conductivity and mobility required for a LED. Semiconductor bulk materials that have good transport properties and can convert electricity directly to white light are most desirable. In this work, we demonstrate that a unique family of inorganic−organic hybrid semiconductors[12,13] show great promise to be used as a single-material white-light-emitting source directly in a LED configuration. These highly crystalline materials are composed of two-dimensional layers of II−VI semiconductor motifs (inorganic component) that are bonded by amine molecules (organic component) to form perfectly ordered crystal lattices (Figure 1a,b). They not only possess a number of enhanced semiconductor properties with respect to their parent II−VI binary compounds but also exhibit very strong structure-induced quantum confinement effect (QCE),[14,15] to the same (and often higher) extent as those of the smallest colloidal quantum dots (QDs) reported to date.[16,17] We show that a select group of these materials emit over the entire visible region, very much like the magic-sized CdSe NCs. More significantly, they represent the first semiconductor bulk materials that generate direct white light and possess the following advantageous features over the CdSe NCs: (a) their crystal structures are fully characterized; (b) the infinite layers of the II−VI can provide efficient conduction pathways for electrons and holes to achieve better transport properties; (c) the crystal structures and optical properties can be controlled and tailored precisely and systematically; and (d) they can be processed in bulk forms and have no limitations/restrictions on issues related to particle size.

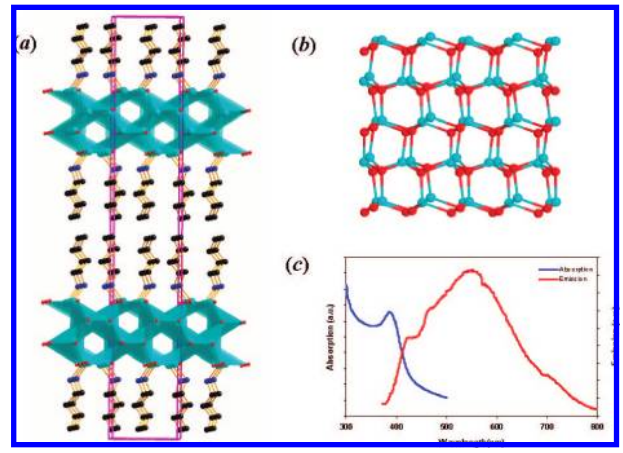

Figure 1. (a) Side view of the double-layer 2D-[Cd_2S_2(*ba*)] based crystal structure, **1**. Cd: teal; S: red; N: blue; C: black spheres. (b) The double layer of CdS in **1**. (c) Room temperature absorption and emission spectra of **1** (λ_{ex} = 360 nm).

Shown in Figure 1a is a 2D-[Cd_2S_2(*ba*)] (*ba* = *n*-butylamine) based double-layer structure, **1**. A view of the double layer is depicted in Figure 1b. The room temperature absorption and emission spectra of the same compound are plotted in Figure 1c.

The broad emission covers the entire visible spectrum, and interestingly, band edge emission is significantly reduced, leading to a well-balanced white-light spectrum. A similar observation was reported for very small CdSe NCs. The phenomenon was ascribed to deep trap emission that takes place when a photogenerated hole is trapped in a midgap state (surface site) and combines with an electron before it relaxes back to the ground state via a nonradiative pathway.[11,18] Because of the very small particle size of CdSe NCs, the surface-to-volume ratio is very large, giving rise to dominating surface states, diminished band edge emission features, and a very broad emission. In the case of the hybrid materials, it is worth noting an interesting relationship between their crystal structures and emission bandwidth. As shown in Figure S1 (Supporting Information), a double-layer 2D-[Cd_2S_2(*ba*)] has a very large number of surface sites within each crystal, due to the nature of its layered structure. A single-layer structure made of the same inorganic elements, 3D-[CdS(hda)$_{0.5}$], however, possesses no surface sites within each crystal. The emission bandwidth of the 3D-[CdS(hda)$_{0.5}$] is significantly narrower (Figure S2b, Supporting Information).

Figure 2 shows the white-light emission from **1** and Mn-doped **1**. A commercial LED (360 nm) illuminates blue light (Figure 2a). A thin layer of yellowish-colored **1** prepared from a DMSO solution

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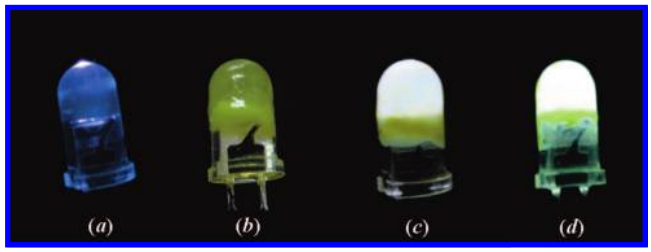

Figure 2. White-light emission from the double-layer 2D-[Cd_2S_2(*ba*)] based structures. (a) A 5 mm reference UV LED (360 nm) illuminating blue light (commercially available from Le Group Fox, Inc.); (b) the same LED coated with a thin layer of sample **1** (before illumination); (c) the same LED illuminating a coated thin layer of sample **1**; and (d) the same LED illuminating a coated thin layer of Mn-doped **1** (0.1 mol %).

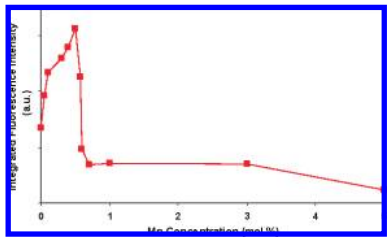

Figure 3. The integrated PL intensity (λ_{ex} = 360 nm) as a function of Mn dopant amount (0−5 mol %). Line is drawn to guide the eyes.

was coated onto the LED (Figure 2b). Upon illumination, it generated white light (Figure 2c). Isolated manganese ion (Mn^{2+}) is known to be a strong luminescent center and has led to photoluminescence (PL) enhancement in numerous II−VI systems as well as in II−VI hybrid materials.[19–23] Figure 2d shows a LED illuminating a coated thin layer of **1** with 0.1 mol % of Mn. The highest PL intensity was achieved at a dopant level of 0.5 mol % of Mn (see Figure 3 and Figure S3). Higher Mn^{2+} concentration results in a decrease in the PL intensity, due to appreciable Mn^{2+}−Mn^{2+} interactions as a consequence of close proximity of these ions.[22,23] The chromaticity coordinates range from 0.31 to 0.34 (*x*) and 0.35 to 0.40 (*y*) for **1** and Mn-doped samples, falling well within the white region of the International Commission on Illumination (CIE) 1931 color space chromaticity diagram (Figure S4, Supporting Information).[24] The fluorescence quantum yield was obtained following a similar procedure reported previously for CdSe[11,21] and is on the order of 4−5%, compared to 2−3 and 1−5% for the CdSe[11] and ZnSe[25] nanocrystals, respectively.

The length of the organic monoamines (*L*) also plays a role in the PL emission. The emission intensities of Mn^{2+}-doped single-layer 3D-[$Zn_{1-x}Mn_xSe(L)_{0.5}$][26] series (L = ethylenediamine or *en*, propyldiamine or *pda*, butyldiamine or *bda*, and hexayldiamine or *hda*) increase monotonically from *en* to *hda* at $x \approx 0.2$.[22] The same effect was observed in the single-layer 3D-[$Cd_{1-x}Mn_xSe(L)_{0.5}$] structures (L = *en*, *hda*).[23] This was attributed to the extent of interlayer Mn^{2+}−Mn^{2+} interactions. As the length of the diamine molecules increases, the interlayer manganese interactions are weakened and the more prominent 2D confinement led to enhanced PL intensities.[22,23] The same trend is found in the double-layer 2D-[$Cd_2S_2(L)$] series. The integrated intensities for L = *n*-propylamine or *pa*, *ba*, *n*-pentylamine or *pta*, and *n*-haxylamine or *ha* are plotted in Figure 4.

In summary, we have developed the first semiconductor bulk materials that are capable of generating direct white light and are

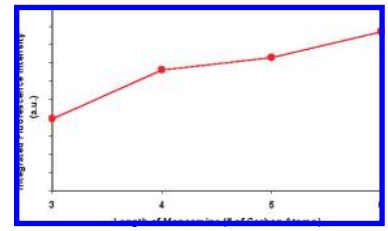

Figure 4. The integrated PL intensity as a function of the amine length (L = *pa*, *ba*, *pta*, and *ha*, λ_{ex} = 360 nm). Line is drawn to guide the eyes.

promising for use as a single-material white-light-emitting source in LEDs. We have shown that their structures and light-emitting properties can be tuned systematically. More importantly, these hybrid semiconductors have distinctive advantages of possessing perfectly ordered and extended (infinite) structures as their parent II−VI semiconductors and, thus, are possible to attain high carrier conductivity and mobility that are necessary for high-efficiency light-emitting diodes.

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Supporting Information Available: Details of structures, absorption, and photoluminescence experiments, CIE coordinates, and other related materials. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) *The Promise of Solid State Lighting for General Illumination*; Optoelectronics Industry Development Association: Washington, DC, 2001.
(2) http://www.netl.doe.gov/ssl/.
(3) Uchida, Y.; Taguchi, T. *Opt. Energy* **2005**, *44*, 124003-1.
(4) Taguchi, T. *Proc. SPIE* **2004**, *5530*, 7.
(5) Taguchi, T. *J. Light Visual Environ.* **2003**, *27*, 131.
(6) Xiao, J. P.; Xie, Y.; Tang, R.; Luo, W. *Inorg. Chem.* **2003**, *42*, 107.
(7) *Energy Savings Potential of Solid State Lighting in General Illumination Applications*; Navigant Consulting Inc.: Washington, DC, 2003, http://lighting.sandia.gov/.
(8) Bergh, A.; Craford, G.; Duggal, A.; Haitz, R. *Phys. Today* **2001**, *54*, 42.
(9) Mueller, A. H.; Petruska, M. A.; Achermann, M.; Werder, D. J.; Akhadov, E. A.; Koleske, D. D.; Hoffbauer, M. A.; Klimov, V. I. *Nano Lett.* **2005**, *5*, 1039.
(10) Yang, W.-J.; Luo, L.; Chen, T.-M.; Wang, N.-S. *Chem. Mater.* **2005**, *17*, 3883.
(11) Bowers, M. J.; McBride, J. R.; Rosenthal, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 15378.
(12) Huang, X.-Y.; Li, J.; Fu, H.-X. *J. Am. Chem. Soc.* **2000**, *122*, 8789.
(13) Huang, X.-Y.; Heulings, H. R., IV; Le, V.; Li, J. *Chem. Mater.* **2001**, *13*, 3754–3759.
(14) Huang, X.-Y.; Li, J.; Zhang, Y.; Mascarenhas, A. *J. Am. Chem. Soc.* **2003**, *125*, 7049.
(15) Huang, X.-Y.; Li, J. *J. Am. Chem. Soc.* **2007**, *129*, 3157.
(16) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.
(17) Nozik, A. J.; Micic, O. I. *Mater. Res. Soc. Bull.* **1998**, *23*, 24.
(18) Underwood, D. F.; Kippeny, T. C.; Rosenthal, S. J. *J. Phys. Chem. B* **2001**, *105*, 436.
(19) Norris, D. J.; Yao, N.; Charnock, F. T.; Kennedy, T. A. *Nano Lett.* **2001**, *1*, 3.
(20) Yang, H.; Santra, S.; Holloway, P. H. *J. Nanosci. Nanotechnol.* **2005**, *5*, 1364.
(21) Nag, A.; Sarma, D. D. *J. Phy. Chem. C* **2007**, *111*, 13641.
(22) Lu, J.; Wei, S.; Peng, Y.-Y.; Yu, W.-C.; Qian, Y.-T. *J. Phys. Chem. B* **2003**, *107*, 3427.
(23) Lu, J.; Wei, S.; Yu, W.-C.; Zhang, H.-B.; Qian, Y.-T. *Chem. Mater.* **2005**, *17*, 1698.
(24) CIE (1932); Commission Internationale de l'Eclairage Proceedings, 1931; Cambridge University Press: Cambridge.
(25) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem. B* **1998**, *102*, 3655.
(26) An example of three-dimensional (3D) single-layer 3D-[$MQ(L)_{0.5}$] (M = Zn, Cd; Q = S, Se, and Te) type structure, 3D-[$CdS(bda)_{0.5}$], is shown in Supporting Information (Figure S1).

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