One-Step Synthesis of High-Quality Gradient CdHgTe Nanocrystals: A Prerequisite to Prepare CdHgTe−Polymer Bulk Composites with Intense Near-Infrared Photoluminescence

Haizhu Sun,[†,‡] Hao Zhang,[†] Jie Ju,[†] Junhu Zhang,[†] Gang Qian,[§] Chunlei Wang,[†] Bai Yang,*[,†] and Zhi Yuan Wang*[,⊥]

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China, College of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China, State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Changchun 130022, People's Republic of China, and Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

We have demonstrated an efficient method to prepare high-quality CdHgTe alloyed nanocrystals (NCs) by making use of a large difference in the solubility between CdTe and HgTe in aqueous medium. The resultant NCs show a gradient quasi "core/shell" structure in which the "core" is rich in HgTe and the "shell" is rich in CdTe. This unique structure makes the photoluminescence (PL) quantum yield (QY) of CdHgTe NCs up to 45% and remarkably improves their stability. The excellent stability of CdHgTe NCs allows for the successful preparation of NC-polymer bulk composites with intense PL in the near-infrared spectral region (tunable from 1100 to 1400 nm) upon excitation at 550 nm. Not only is the difficulty of preparing the CdHgTe NC−polymer bulk composites overcome, but also the composites show excellent thermal and luminescent stabilities, which is of importance for their future applications.

1. Introduction

Semiconductor nanocrystals (NCs) have attracted much interest during the past decades because of their unique quantum confinement effect and various potential applications.[1] The NCs with emission in the near-infrared (NIR) spectral region (e.g., 800−1500 nm) are particularly needed and potentially useful for the applications such as bio- and tissue-imaging and telecommunication.[2] For example, the fluorescence imaging of deep organs (e.g., liver and spleen in mice) using visible fluorescent tags is hampered because of the limited penetration depth of visible light. One possible solution to this problem is to use NIR fluorescent NCs, because the NIR light can penetrate the tissues deeper in depth.[3] Another advantage associated with the use of NIR fluorescent NCs in biological imaging and detection is the fact that there is little signal interference coming from the autofluorescence and absorbance of the tissues within the spectral window of 900−1300 nm.[4] Other potential applications of NIR fluorescent NCs involve their uses in new waveguide devices for up-conversion and optical amplification in telecommunication systems at wavelengths of 1.3 and 1.55 μm.[5]

Much effort has been devoted to preparation of high-quality Hg-based NCs.[6] In general, semiconductor NCs can be prepared either in an organic medium at elevated temperatures or aqueous medium at ambient temperature. Usually, NCs grown in an organic medium at high temperatures, which facilitates the crystallization process, can exhibit a high degree of crystallinity. However, it is quite difficult to obtain Hg-based NCs with stable photolumines-

* To whom correspondence should be addressed. E-mail: byangchem@jlu.edu.cn (B.Y.); wayne_wang@carleton.ca (Y.W.). Tel: 86-431-85168478. Fax: 86-431-85193423.
† Jilin University.
‡ Northeast Normal University.
§ Changchun Institute of Applied Chemistry.
⊥ Carleton University.

(1) (a) Jr, M. B.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013. (b) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016. (c) Tang, Z.; Kotov, N. A.; Giersig, M. *Science* **2002**, *297*, 237. (d) Li, Y.; Zhong, H.; Li, R.; Zhou, Y.; Yang, C.; Li, Y. *Adv. Funct. Mater.* **2006**, *16*, 1705. (e) Guo, S.; Konopny, L.; Popovitz-Biro, R.; Cohen, H.; Sirota, M.; Lifshitz, E.; Lahav, M. *Adv. Mater.* **2000**, *12*, 302. (f) Wei, G.; Forrest, S. R. *Nano Lett.* **2007**, *7*, 218. (g) Zhang, Q.; Gupta, S.; Emrick, T.; Russell, T. P. *J. Am. Chem. Soc.* **2006**, *128*, 3898. (h) Neiner, D.; Chiu, H. W.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 11016. (i) Li, L.; Qian, H.; Ren, J. *Chem. Commun.* **2005**, 528.

(2) (a) Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S.; Banin, U. *Science* **2002**, *295*, 1506. (b) Sargent, E. H. *Adv. Mater.* **2005**, *17*, 515. (c) Rogach, A. L.; Eychmüller, A.; Hickey, S. G.; Kershaw, S. V. *Small* **2007**, *3*, 536. (d) Murphy, J. E.; Beard, M. C.; Norman, A. G.; Ahrenkiel, S. P.; Johnson, J. C.; Yu, P.; Miæiæ, O. I.; Ellingson, R. J.; Nozik, A. J. *J. Am. Chem. Soc.* **2006**, *128*, 3241. (e) Yu, H.; Li, J.; Loomis, R. A.; Gibbons, P. C.; Wang, L. W.; Buhro, W. E. *J. Am. Chem. Soc.* **2003**, *125*, 16168.

(3) Cai, W.; Shin, D. W.; Chen, K.; Gheysens, O.; Cao, Q.; Wang, S. X.; Gambhir, S. S.; Chen, X. *Nano Lett.* **2006**, *6*, 669.

(4) (a) Gaponik, N.; Radtchenko, I. L.; Gerstenberger, M. R.; Fedutik, Y. A.; Sukhorukov, G. B.; Rogach, A. L. *Nano Lett.* **2003**, *3*, 369. (b) Tsay, J. M.; Pflughoefft, M.; Bentolila, L. A.; Weiss, S. *J. Am. Chem. Soc.* **2004**, *126*, 1926.

(5) (a) Stouwdam, J. W.; van Veggel, F. C. J. M. *Nano Lett.* **2002**, *2*, 733. (b) Oh, J. B.; Nah, M. K.; Kim, Y. H.; Kang, M. S.; Ka, J. W.; Kim, H. K. *Adv. Funct. Mater.* **2007**, *17*, 413. (c) Steckel, J. S.; Coe-Sullivan, S.; Buloviæ, V.; Bawendi, M. G. *Adv. Mater.* **2003**, *15*, 1862.

(6) (a) Tang, B.; Yang, F.; Lin, Y.; Zhuo, L.; Ge, J.; Cao, L. *Chem. Mater.* **2007**, *19*, 1212. (b) Kuno, M.; Higginson, K. A.; Qadri, S. B.; Yousuf, M.; Lee, S. H.; Davis, B. L.; Mattoussi, H. *J. Phys. Chem. B* **2003**, *107*, 5758. (c) Gaponik, N.; Talapin, D. V.; Rogach, A. L.; Eychmüller, A.; Weller, H. *Nano Lett.* **2002**, *2*, 803. (d) Kershaw, S. V.; Burt, M.; Harrison, M.; Rogach, A.; Weller, H.; Eychmüller, A. *Appl. Phys. Lett.* **1999**, *75*, 1694.

cence (PL) from the aforementioned method because of the instability of Hg-based NCs at high temperatures. Therefore, Piepenbrock et al. reported the low-temperature (−78 °C) preparation of HgTe NCs in organic solvents with a narrow size distribution and high PL quantum yield (QY). [7] HgTe NCs are often prepared in aqueous media, because aqueous synthesis is generally simple and less expensive, and can be easily scaled up. Weller, Gaponik, Rogach et al. reported the synthesis of thiol-capped HgTe NCs with the PL QYs up to 50% and demonstrated the electroluminescence of these NCs as well. [8] Kovalenko et al. obtained HgTe NCs with the PL QY up to 40% and demonstrated their use in solar cells. [9] Qian et al. synthesized water-soluble CdHgTe/CdS NCs with PL emission at 600−830 nm and used these NCs for imaging in living animals. [10]

Despite of all the progresses made in the preparations and applications of Hg-based NCs, the stability of these NCs is one of the most major problems. Hg-based NCs show a poor stability even at the ambient temperature, as indicated by the changes in the intensity, position, and shape of their PL spectra. The instability of Hg-based NCs makes it difficult to incorporate them, without phase separation, into polymers with the goal to develop processable bulk composite materials for further application. As we have known, several advantages can be envisaged with the use of NC−polymer composites, such as a good processability of NCs brought by the polymer, the improved long-term stability of NCs in a polymer matrix and the very limited Förster resonance energy transfer between NCs due to site isolation by polymer chains. [11] Recently, NC−polymer bulk composites with the PL in the visible spectra region have been successfully prepared by solving the problem of compatibility between NCs and polymer. [12] However, the preparation of NC−polymer bulk composites with NIR emission is still a challenge. In this case, one must ensure the chemical and thermal stability of NCs under the polymerization conditions, such as radical initiators and elevated temperatures (e.g., 100 °C), in addition to a good compatibility with polymer matrix. Several methods have been developed to incorporate Hg-based NCs into the polymers, but they are limited to producing thin film materials. [13] Passivation by forming a core/shell structure with the inorganic compounds, such as CdHgTe/CdS [10] and CdTe/HgTe/CdTe, [8] can effectively stabilize the NCs. However, the interface strain dramatically accumulates with the increase in the shell thickness, because of the mismatched core/shell structures, and can eventually be released only through the formation of misfit dislocations. [14−16] Therefore, it remains a challenge to develop new methods for the preparation of stable, highly fluorescent NCs that are suitable for incorporating into the polymers.

With the aim of solving the problems mentioned above, herein, we report an efficient one-step synthetic process for producing gradient CdHgTe alloyed NCs. Such a special structure imparts excellent PL properties and stabilities to NCs, which allows for the successful preparation of transparent bulk composites in various shapes with intense NIR emission around 1300 nm.

2. Experimental Section

Materials. Tellurium powder (200 mesh, 99.8%) was purchased from Aldrich Chemical Corporation. *N,N*-Dimethyloctadecylamine, 4-vinylbenzyl chloride, 3-mercaptopropionic acid (MPA), and IR125 were purchased from Acros Chemical Corporation. $CdCl_2$ (99+ %), $HgCl_2$ (99+ %), and $NaBH_4$ (99%) were all commercially available. The synthesis of polymerizable surfactant, octadecyl-4-vinylbenzyldimethylammonium chloride (OVDAC) and NaHTe, was reported in the literature. [11] All of the solvents were analytical grade and used as received. Azodiisobutyronitrile (AIBN) was recrystallized from ethanol prior to use. Styrene and methyl methacrylate were distilled before polymerization.

Synthesis of CdHgTe NCs. To a N_2-saturated aqueous solution of $CdCl_2$ and $HgCl_2$ at pH 9 in the presence of MPA as a stabilizing agent, was added the freshly prepared NaHTe solution. The ratio of metal ion: MPA: HTe^{2-} was 1:2.9:0.5 and the concentration of metal ion was 3.75×10^{-3} M. The solution was then placed in an oven at 40 °C for 30 min. The resulting CdHgTe NCs in aqueous medium were either used directly for the preparation of CdHgTe−polymer bulk composites or precipitated by addition of i-propanol and isolated by centrifugation for analysis by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS), and inductively coupled plasma atomic emission (ICP) measurement.

Preparation of CdHgTe NC−Polymer Bulk Composites. Twelve milligrams of OVDAC was mixed with 4 mL of styrene. The OVDAC−styrene solution was added to 8 mL of CdHgTe

(7) Piepenbrock, M. M.; Stirner, T.; Kelly, S. M.; O'Neill, M. *J. Am. Chem. Soc.* **2006**, *128*, 7087.

(8) (a) Harrison, M. T.; Kershaw, S. V.; Burt, M. G.; Eychmüller, A.; Weller, H.; Rogach, A. L. *Mater. Sci. Eng.* **2000**, *355*, B69–70. (b) Rogach, A.; Kershaw, S.; Burt, M.; Harrison, M.; Kornowski, A.; Eychmüller, A.; Weller, H. *Adv. Mater.* **1999**, *11*, 552. (c) Koktysh, D. S.; Gaponik, N.; Reufer, M.; Crewett, J.; Scherf, U.; Eychmüller, A.; Lupton, J. M.; Rogach, A. L. *ChemPhysChem* **2004**, *5*, 1435.

(9) (a) Kovalenko, M. V.; Kaufmann, E.; Pachinger, D.; Roither, J.; Huber, M.; Stangl, J.; Hesser, G.; Schäffler, F.; Heiss, W. *J. Am. Chem. Soc.* **2006**, *128*, 3516. (b) Günes, S.; Neugebauer, H.; Sariciftci, N. S.; Roither, J.; Kovalenko, M.; Pillwein, G.; Heiss, W. *Adv. Funct. Mater.* **2006**, *16*, 1095.

(10) Qian, H.; Dong, C.; Peng, J.; Qiu, X.; Xu, Y.; Ren, J. *J. Phys.Chem. C* **2007**, *111*, 16852.

(11) (a) Sun, H.; Zhang, H.; Zhang, J.; Ning, Y.; Yao, T.; Bao, X.; Wang, C.; Li, M.; Yang, B. *J. Phys. Chem. C* **2008**, *112*, 2317. (b) Sun, H.; Zhang, J.; Zhang, H.; Xuan, Y.; Wang, C.; Li, M.; Tian, Y.; Ning, Y.; Ma, D.; Yang, B.; Wang, Z. Y. *ChemPhysChem* **2006**, *7*, 2492. (c) Sun, H.; Zhang, J.; Tian, Y.; Ning, Y.; Zhang, H.; Ju, J.; Li, D.; Xiang, S.; Yang, B. *J. Nanomater.* **2007**, doi:10.1155/2007/38589, Article ID 38589.

(12) (a) Zhang, H.; Cui, Z.; Wang, Y.; Zhang, K.; Ji, X.; Lü, C.; Yang, B.; Gao, M. *Adv. Mater.* **2003**, *15*, 777. (b) Yang, Y.; Tu, C.; Gao, M. *J. Mater. Chem.* **2007**, *17*, 2930. (c) Yang, Y.; Wen, Z.; Dong, Y.; Gao, M. *Small* **2006**, *2*, 898.

(13) (a) Jang, J.; Cho, K.; Lee, S. H.; Kim, S. *Nanotechnology* **2008**, *19*, 015204. (b) Choudhury, K. R.; Sahoo, Y.; Prasad, P. N. *Adv. Mater.* **2005**, *17*, 2877.

(14) (a) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468. (b) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463. (c) Reiss, P.; Bleuse, J.; Pron, A. *Nano Lett.* **2002**, *2*, 781. (d) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *Nano Lett.* **2001**, *1*, 207.

(15) (a) Bailey, R. E.; Nie, S. *J. Am. Chem. Soc.* **2003**, *125*, 7100. (b) Ouyang, J.; Ratcliffe, C. I.; Kingston, D.; Wilkinson, B.; Kuijper, J.; Wu, X.; Ripmeester, J. A.; Yu, K. *J. Phys. Chem. C* **2008**, *112*, 4908.

(16) (a) Zhong, X.; Han, M.; Dong, Z.; White, T. J.; Knoll, W. *J. Am. Chem. Soc.* **2003**, *125*, 8589. (b) Sung, Y. M.; Lee, Y. J.; Park, K. S. *J. Am. Chem. Soc.* **2006**, *128*, 9002. (c) Zheng, Y.; Yang, Z.; Ying, J. Y. *Adv. Mater.* **2007**, *19*, 1475. (d) Swafford, L. A.; Weigand, L. A.; Bowers II, M. J.; McBride, J. R.; Rapaport, J. L.; Watt, T. L.; Dixit, S. K.; Feldman, L. C.; Rosenthal, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 12299. (e) Pradhan, N.; Goorskey, D.; Thessing, J.; Peng, X. *J. Am. Chem. Soc.* **2005**, *127*, 17586. (f) Wang, S.; Jarrett, B. R.; Kauzlarich, S. M.; Louie, A. Y. *J. Am. Chem. Soc.* **2007**, *129*, 3848.

Table 1. Composition, PL Peak Position, and QY of CdHgTe NCs with Different Cd/Hg Feed Ratios

Cd/Hg feed ratio	resultant composition[a]	PL peak position (nm)	QY (%)
2.5	$Cd_{0.46}Hg_{0.54}Te$	940	19
1.25	$Cd_{0.29}Hg_{0.71}Te$	1085	43
1	$Cd_{0.23}Hg_{0.77}Te$	1125	45
0.8	$Cd_{0.14}Hg_{0.86}Te$	1135	39
0	HgTe	1135	20

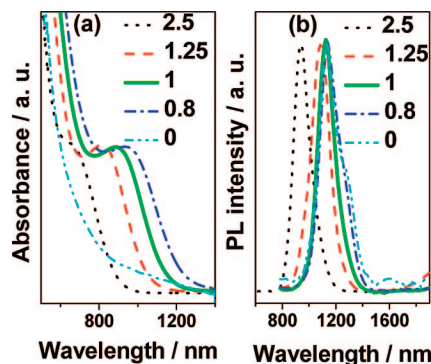[a] Refer to the molar ratio determined by ICP test.

Figure 1. (a) UV−vis absorption and (b) PL spectra of CdHgTe NCs with different Cd/Hg feed ratios of 2.5, 1.25, 1, 0.8, and 0, corresponding to $Cd_{0.46}Hg_{0.54}Te$, $Cd_{0.29}Hg_{0.71}Te$, $Cd_{0.23}Hg_{0.77}Te$, $Cd_{0.14}Hg_{0.86}Te$, and HgTe NCs, respectively. The CdHgTe NCs with the highest QYs are the bold traces.
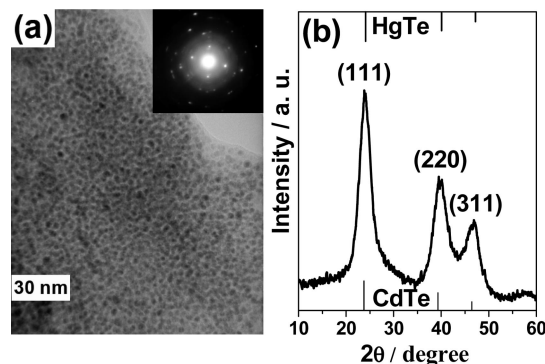

Figure 2. (a) TEM image (inset: the SAED pattern) and (b) XRD pattern of $Cd_{0.23}Hg_{0.77}Te$ NCs.

aqueous solution with vigorous stirring. After being left on standing for 2 h, the organic phase was separated and diluted with methyl methacrylate with a specific ratio of 1: 9. After adding 0.2 wt % AIBN, we heated the mixture of NC−containing styrene and methyl methacrylate at 93 °C for 10 min. The resulting viscous liquid was transferred into a mold and left in an oven at 60 °C for 15 h. The temperature was then further increased to 80 °C for 15 h and 100 °C for 1 h. After cooling and demolding, transparent CdHgTe NC−polymer composites were obtained.

Characterizations. UV−vis spectra were acquired on a Shimadzu 3600 UV−vis-NIR spectrophotometer. Fluorescence experiments were performed on a PTI Fluorescence Master System. The QYs of CdHgTe NCs were estimated using IR125 as a reference. The absorbance of the samples and IR125 at the excitation wavelength (765 nm) was below 0.1 in order to avoid any significant reabsorption. TEM on the selected areas of the samples was performed on a JEOL-2010 electron microscope operating at 200 kV. XRD was carried out using a Siemens D5005 diffractometer. XPS was done on a VG ESCALAB MK II spectrometer with Mg K excitation (1253.6 eV). ICP was carried out with PERKIN ELMER OPTIMA 3300DV analyzer. Thermogravimetric analysis (TGA) was carried out with an NETZSCH STA 449C analyzer with a heating rate of 10 °C/min in N_2 and scanned up to 800 °C.

3. Results and Discussions

3.1. Synthesis and Characterization of CdHgTe NCs. CdHgTe NCs are usually synthesized in two steps.[8] CdTe NCs are prepared first, and then mercury salt solution is added to the CdTe solution. The HgTe shell is formed by the substituting Cd^{2+} with Hg^{2+} at the surface of CdTe core. Although this process can produce CdHgTe NCs with high QY (40−50%), the size distribution is quite broad (e.g., 400−500 nm width at half-maximum). A post-treatment by size-selective precipitation is necessary to obtain CdHgTe NCs with a narrower distribution. Above all, the resultant NCs fail to preserve their PL after being incorporated into polymers because of poor stability. In our case, CdHgTe NCs were synthesized in one step. The reaction is straightforward, simply by adding the freshly prepared NaHTe solution to an aqueous solution of $CdCl_2$ and $HgCl_2$ in the presence of MPA as a stabilizing agent. After standing at 40 °C for 30 min, the resulting CdHgTe NCs could be either used directly for the preparation of CdHgTe NC−polymer bulk composites or precipitated by addition of i-propanol and isolated by centrifugation for further analyses and other uses. Table 1 lists the Cd/Hg feed ratio, resultant composition, PL peak position, and the QY of obtained NCs. The factual components determined by ICP are $Cd_{0.46}Hg_{0.54}Te$, $Cd_{0.29}Hg_{0.71}Te$, $Cd_{0.23}Hg_{0.77}Te$, $Cd_{0.14}Hg_{0.86}Te$, and HgTe, corresponding to the Cd/Hg feed ratios of 2.5, 1.25, 1, 0.8, and 0, respectively.

Figure 1 shows the absorption and PL spectra of CdHgTe NCs with the same sizes prepared using different feed ratios of Cd to Hg. Only one peak can be seen in the absorption and PL spectra, which excludes the possibility to form HgTe and CdTe NCs separately (Figure S1 in the Supporting Information). A systematic red-shift in both the absorption and PL spectra with an increase in the Hg content in NCs is clearly evident. Interestingly, when the feed ratio of Cd to Hg is close to 1, the PL peak position is almost identical, but the peak shape is different to that of pure HgTe NC (Figure 1b). Such a change in peak shapes indicates a strong influence that Cd has brought on the PL properties of NCs. In comparison with HgTe NCs, $Cd_{0.23}Hg_{0.77}Te$ NCs show much more clearly 1s−1s electron transition (bold traces in Figure 1a). The $Cd_{0.46}Hg_{0.54}Te$ NCs have the QY of 19%, whereas the QY for $Cd_{0.23}Hg_{0.77}Te$ NCs reaches 45% and pure HgTe NCs have the QY of 20%.

To better understand the reason of the excellent PL property of $Cd_{0.23}Hg_{0.77}Te$ NCs obtained in this one-step process, the NCs were characterized by TEM, XRD, and XPS measurement. The TEM image of the MPA-capped $Cd_{0.23}Hg_{0.77}Te$ NCs indicates that the sizes of NCs are uniform and about 3 nm in diameter (Figure 2a), which is consistent with the calculated diameter from the XRD patterns (Figure 2b). Selected-area electron diffraction (SAED) and XRD patterns indicate that $Cd_{0.23}Hg_{0.77}Te$ NCs are highly crystalline and regular in shape. The crystal has a cubic zinc blende structure, as reported in the literature.[9]
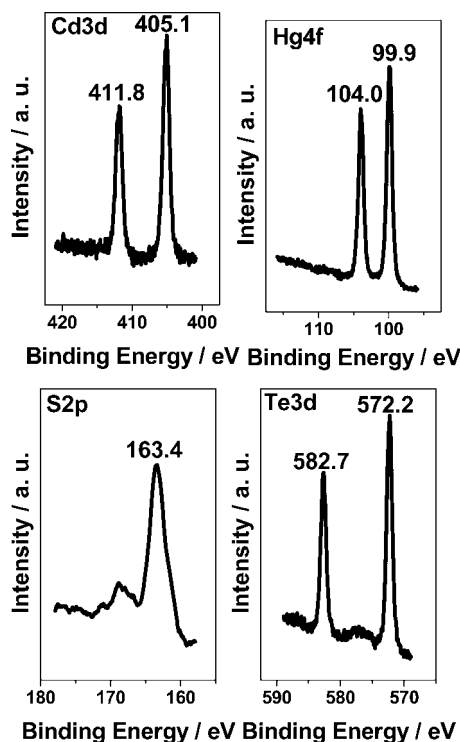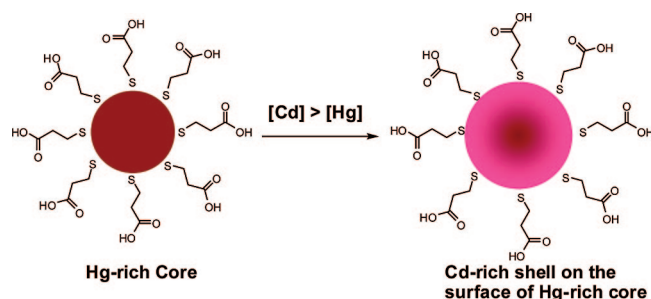
Figure 3. XPS spectra of Cd3d, Hg4f, S2p, and Te3d for the $Cd_{0.23}Hg_{0.77}Te$ NCs.

Scheme 1. Formation of CdHgTe NCs with the Gradient Alloyed Structure

The presence of cadmium, mercury, sulfur, and tellurium species in CdHgTe NCs is confirmed by XPS analyses (Figure 3), showing characteristic Cd3d peak at 405.1 eV, Hg4f at 99.9 eV, S2p at 163.4 eV, and Te3d at 572.2 eV. Only two peaks in the XPS spectrum of element Te show the NCs have not been photooxidated, indicating a good passivation of these NCs.

3.2. Structure and Stability of CdHgTe NCs. The reactivity difference is apparently brought by the different solubility of HgTe and CdTe in water. Because the solubility (K_{sp}) of HgTe in water is approximately 20 times lower than that of CdTe,[6a,8a] the speed of nucleation for HgTe should be much faster than that of CdTe when the concentration of Hg^{2+} and Cd^{2+} is comparable. Therefore, the initial core should be rich in Hg because of its more rapid reaction rate for Hg (Scheme 1). As the free Hg ion is being depleted from the reaction mixture, CdTe deposition becomes dominant in the subsequent crystal growth. Consequently, the shell rich in Cd is formed on the core surface, without much mismatch owing to the similar crystallographic constants of CdTe and HgTe,[8a] yielding the alloyed NCs with Cd
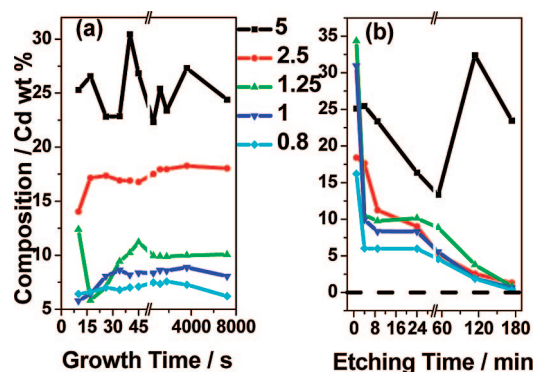

Figure 4. Plot of the Cd (wt %) content vs (a) growth time and (b) etching time with acid for CdHgTe NCs with the Cd/Hg feed ratios of 5, 2.5, 1.25, 1, and 0.8. The dashed line refers to the zero Cd (wt %) content.

concentration increasing from the core to the surface. Because the outer layer is largely made of CdTe, it can act as an encapsulating shell for the HgTe-rich core. Therefore, it is believed that the NCs possess a quasi "core/shell" structure.[15] Another important factor for the formation of this gradient structure is the ratios of Cd to Hg. A high ratio results in the structure that Cd randomly distributes in the NCs, whereas a low ratio leads to the incomplete formation of CdTe-rich shell. Therefore, both the cases can not form quasi "core/shell" structure and the QY as well as the stability of their PL is poor.

To further confirm the quasi "core/shell" structure of these NCs, changes in the Cd content during the growth of NCs with different feed Cd/Hg ratios were analyzed by ICP. As shown in Figure 4a, when the Cd/Hg ratio is higher than 2.5, the Cd content varies randomly, indicating a random distribution of Cd in the NCs. This leads to the structural defects and low QY of these NCs. When the Cd/Hg ratio is lower than 2.5, the gradient alloyed structure begins to form, indicated by the gradual increase in the Cd content during the NC growth. Specifically, with an equal amount of Cd and Hg, the gradient quasi "core/shell" structure is readily formed. The ICP data indicate that the Cd content increases gradually from 5.79 wt % at the beginning of the reaction to 8.05 wt % after two hours. These NCs were also etched with acid and then analyzed for their breakdown products as a function of time by ICP. As shown in Figure 4b, within a short etching time, the Cd wt % decreases abruptly for the NCs with Cd/Hg ratios of 2.5, 1.25, 1, and 0.8, indicating that the shell of the NCs is rich in Cd. With increasing the etching time, the Cd content decreases gradually. Especially for the Cd/Hg feed ratios of 1.25, 1.0, and 0.8, after 174-min etching, the Cd wt % are found to be only 0.82, 0.65, and 0.38 wt %, respectively, indicating that the core of these NCs is rich in Hg. Thus, the results strongly suggest that these ternary NCs have a gradient alloyed structure.

Unlike HgTe/CdTe core/shell NCs synthesized in two sequential steps, our gradient alloyed NCs are prepared in a single step and do not have a sharp boundary between the Hg-rich core and the Cd-rich shell. Because of this gradient alloyed structure, CdHgTe NCs exhibit the excellent photophysical properties (e.g., NIR PL and high QY), compared to the core/shell NCs having a fairly sharp boundary. In addition, this gradient alloyed structure provides a structural

Scheme 2. Preparation of CdHgTe NC−polymer Bulk Composites

OVDAC capped CdHgTe NCs   **Styrene**   **Methyl methacrylate**
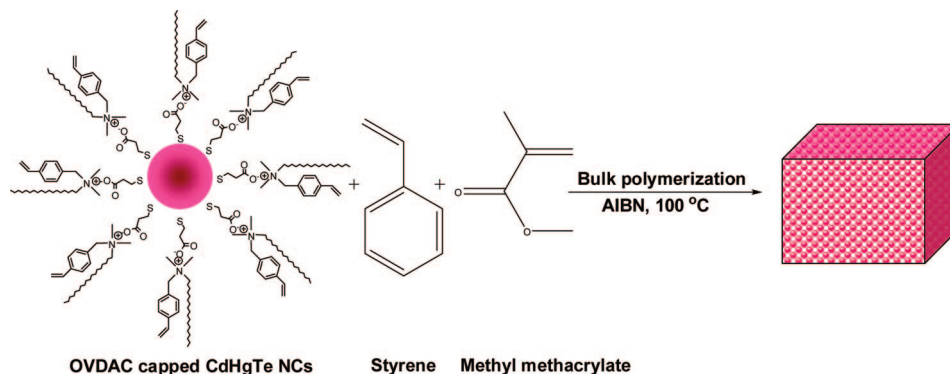
stability, free of surface stress, to the NCs, which can in turn impart the desirable chemical and thermal stability to CdHgTe NCs. Through monitoring the PL of $Cd_{0.23}Hg_{0.77}Te$ NCs, there is no change in peak intensity, position and shape in its PL spectrum after two months storage (Figure S2 in the Supporting Information). The highly luminescent stability of CdHgTe NCs is necessary for these NCs to be incorporated into polymer matrix under the free-radical polymerization conditions at elevated temperatures.

3.3. Preparation of CdHgTe NC−Polymer Bulk Composites. To incorporate CdHgTe NCs into polymer, a good compatibility between NCs and monomer/polymer is necessary. Consequently, aqueous CdHgTe NCs were first transferred to styrene by extraction method using OVDAC as a polymerizable surfactant. The NC-containing styrene phase was then separated and mixed with another monomer, methyl methacrylate. The bulk polymerization was initiated using AIBN at 93 °C, proceeded at 60 °C for about 15 h, 80 °C for about 15 h, and 100 °C for 1 h. After cooling and demolding, transparent CdHgTe−polymer bulk composites were obtained (Scheme 2).

Figure 5 displays the PL spectra of bulk composites **1−5** preparing from the NCs with the Cd/Hg feed ratios of 2.5, 1.25, 1, 0.8, and 0, respectively, which correspond to $Cd_{0.46}Hg_{0.54}Te$, $Cd_{0.29}Hg_{0.71}Te$, $Cd_{0.23}Hg_{0.77}Te$, $Cd_{0.14}Hg_{0.86}Te$, and HgTe. The emission falls in the NIR spectral region ranging from 1100 to 1400 nm. However, the PL intensity varies significantly depending on the NC incorporated, which
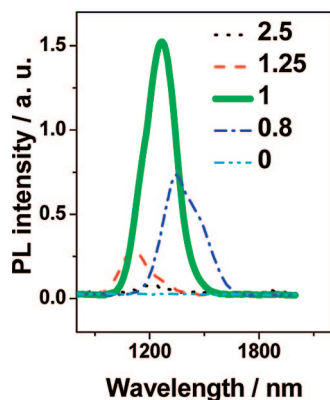
implies the NC structure has an important influence on the properties of composites. When the Cd/Hg ratio is higher than 2.5, the random distribution of Cd ion results in the structural defects in NCs, making the NCs unstable during the polymerization, as evident by the red-shifted and largely quenched PL of composite **1**. When the Cd/Hg ratio is lower than 2.5, the gradient alloyed structure begins to evolve. At the Cd/Hg ratio of 1, the gradient quasi "core/shell" structure of NCs makes composite **3** have the best PL properties in terms of the intensity and peak shape (bold trace in Figure 5). This implies that the gradient alloyed structure can effectively protect the NCs from being damaged by heat or free radicals during the polymerization. When the Cd/Hg ratio is below 1, the incomplete CdTe-rich shell makes composite **4** have a lower PL intensity than composite **3**. For HgTe NCs without a protective shell, however, the PL is quenched completely under the same measurement conditions. Therefore, it can be concluded that one of the important requirements for successful preparation of the CdHgTe NC−polymer composites is the chemical and thermal stability of the NCs, which is governed by their structures and compositions.

3.4. Properties of CdHgTe NC−Polymer Bulk Composites. The CdHgTe NC-polymer composites have a cross-linked network structure with each of NCs as a cross-linking point. Thus, CdHgTe NCs are locked in place within the three-dimensional network, making them thermally and optically stable.[17] TGA showed the onset temperature for thermal decomposition above 340 °C, being higher than that of the host polymer (280 °C) and almost equal to that of pure NCs (Figure S3 in the Supporting Information). Although the composites possess cross-linked network, it does not mean the materials lost their processiblity. CdHgTe NC-polymer bulk composites in various shapes such as a tube were obtained by varying the content of NCs in the polymer as well as changing the ratios of copolymerization monomers (Figure 6a). The covalent bonding between NCs and polymer matrix through the OVDAC group also ensures a good transparency of the composites. The distribution of NCs in a polymer matrix is homogeneous, as indicated by the TEM image (Figure 6b). The polymer coating on the surface of the NCs further stabilize the NCs during the polymerization, resulting in the improvement of their optical

Figure 5. PL spectra of composites **1−5** prepared by using CdHgTe NCs with Cd/Hg feed ratios of 2.5, 1.25, 1, 0.8, and 0, corresponding to $Cd_{0.46}Hg_{0.54}Te$, $Cd_{0.29}Hg_{0.71}Te$, $Cd_{0.23}Hg_{0.77}Te$, $Cd_{0.14}Hg_{0.86}Te$, and HgTe NCs, respectively.

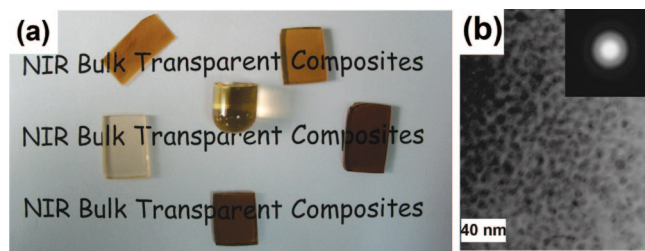(17) Demir, M. M.; Castignolles, P.; Akbey, Ü.; Wegner, G. *Macromolecules* **2007**, *40*, 4190.

Figure 6. (a) Optical photographs of CdHgTe NC-polymer bulk composites in various shapes. (b) TEM image of $Cd_{0.23}Hg_{0.77}Te$ NC−polymer composite based on the microtome method. Inset is the SAED pattern.
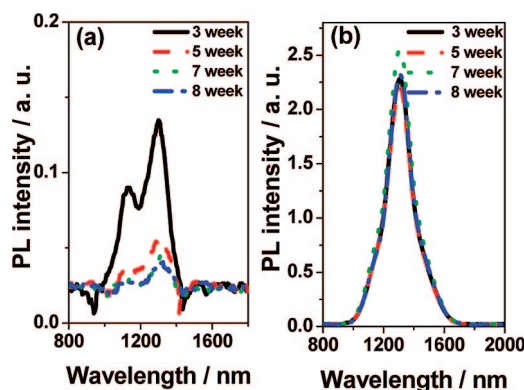

Figure 7. PL spectra after heat treatment at 100 °C of (a) CdHgTe NCs in aqueous solution and (b) the NC−polymer composites.

stability. The PL properties of both CdHgTe NC−polymer composites and pure CdHgTe NCs were monitored over weeks after being treated at 100 °C for 1 h. For the aqueous CdHgTe NCs, a noticeable decrease in the PL intensity is seen over time (Figure 7a). Neither the peak position nor its shape could remain stable. These results indicate that the unique fine structures of NCs are readily destroyed by the high-temperature treatment without the polymer protection. For the composites, in contrast, it was found that the peak position and shape did not change as being monitored for 8

weeks (Figure 7b), which indicates the composite is very stable. Clearly, the polymer chains can protect and stabilize the fine structures and thus the luminescent properties of these NCs, allowing their further uses in various applications.

4. Conclusion

By taking the advantage of a large difference in the solubility between CdTe and HgTe in aqueous medium, stable CdHgTe NCs, having a unique structure of HgTe-rich core and CdTe-rich shell, were prepared by a one-step process. The good stability of NCs, compatibility of polymerizable surfactant OVDAC with monomer, and covalent bonding between NCs and polymers allow for successful incorporation of CdHgTe NCs into polymer matrix. Realization and availability of bulk composites with intense and stable NIR emission at the telecommunication wavelength of 1300 nm offer ample opportunities for further materials innovation in optical communications, such as NC−polymer composite-based waveguide devices for optical amplification and up-conversion.

Supporting Information Available: PL spectra of $Cd_{0.23}Hg_{0.77}Te$ NCs in visible spectra region and $Cd_{0.23}Hg_{0.77}Te$ NCs over time after preparation. TGA traces of the $Cd_{0.23}Hg_{0.77}Te$ NCs, $Cd_{0.23}Hg_{0.77}Te$ NC−polymer composites and polymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM8018296