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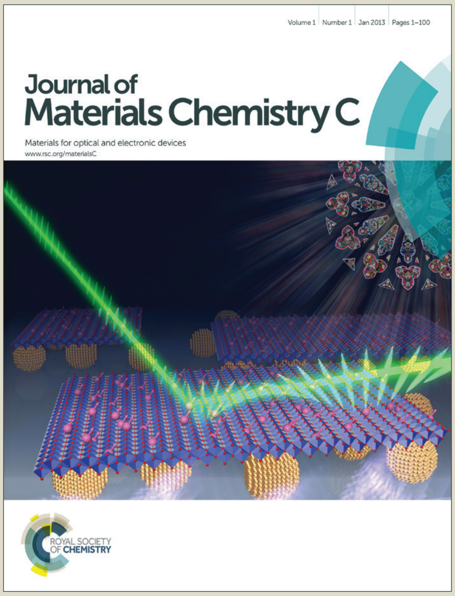

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Preparation of highly luminescent $BaSO_4$ protected CdTe quantum dots as conversion materials for excellent color-rendering white LEDs

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Abstract

The incorporation of colloidal CdTe quantum dots into inorganic matrix ---- $BaSO_4$ through a handy and rapid co-precipitation method is demonstrated for the first time. Owing to the protection of $BaSO_4$ matrix, the resulting composites show strong luminescence, long fluorescent lifetime, high photo- and thermal stability as well as anti-acid compared to the parental CdTe QDs. Moreover, the composites hold several advantages for industrial applications. White light-emitting diodes (WLEDs) utilizing the composites as red color conversion layer are fabricated, which produce bright white light with high color rendering properties including a CIE coordinate of (0.34, 0.33), an Ra of 88, and a Tc of 5112K at 20 mA, suggesting their great potential application in solid-state lighting system with high color-rendering properties.

Keywords: CdTe quantum dots; Co-precipitation; CdTe@$BaSO_4$ composite; White light-emitting diodes; Color-rendering properties

Introduction

White light-emitting diodes (WLEDs) have attracted more and more attentions because of their numerous merits, for example, high efficiency in converting electrical energy into light, fast response, long operating lifetime and high mechanical stability and so on.[1-3] Nowadays, they have almost replaced conventional incandescent bulbs, halogen lamps, the excitation sources of cathode ray tubes and cold cathode fluorescent lamps, and have already become the most promising illumination source, which are popular in a wide variety of applications, such as home lighting, traffic signal lamps and liquid crystal display (LCD) backlights, among others.[4, 5] Currently, most commercially available WLEDs usually utilize a blue-emitting InGaN-based LED chip with $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) yellow phosphors as color conversion layer.[6, 7] However, this kind of WLEDs show color rendering index (Ra), usually below 85, which is mainly due to the lack of red emission part of the spectrum of YAG:Ce yellow phosphors.[7-9] In an attempt to solve this problem, many approaches have been applied, among which semiconductor nanocrystals, also known as colloidal quantum dots (QDs), have been considered to be the most promising color conversion materials to fabricate excellent color rendering WLEDs, due to their unique properties, such as tunability of the emission wavelength, narrow emission bandwidths, broad excitation spectrum, high color purity and high photo luminescent quantum yield (PLQY).[10-13]

Nowadays, many kinds of colloidal quantum dots are almost synthesized in organic-phase or water-phase, such as CdSe,[12, 14] CdSe/CdS,[15] CdSe/ZnS,[16-18] $CdSe_xS_{1-x}/ZnS$,[19] CdS:Cu/ZnS[20] and CdTe.[21, 22] CdTe QDs, usually synthesized via an aqueous method, are less expensive, lower toxic and more ecofriendly.[23] However, most of the optical devices require QDs-based solid state materials isolated from solution where they have been initially synthesized.[24, 25] For example, CdTe QDs incorporated in SiO_2 particles and in polymer beads are both effective measures.[26, 27] There are still several challenges to obtain high luminescent solid state QDs since PLQY is significantly reduced when they are transferred from solution to solid state. PLQY of QDs is sensitive to heat, light and oxygen in a solid state, unlike in the colloidal solution phase where there typically exist an excess of surface ligands passivating the QDs surface.[28] Therefore it is of great importance to find suitable matrices which could control interparticle spacing, prevention of QDs aggregation and saturation of QDs surface defects, remaining the PLQY of the starting colloidal QDs. Recently introduced fabrication of mixed crystals of CdTe QDs and NaCl provided an efficient approach to protect the QDs from the surrounding environment and prevent the reduction of QDs PLQY.[29, 30] In this situation, the incorporation of CdTe QDs into NaCl matrix needs long time (several weeks) and the loading value of the QDs into the crystals is very low (below 1%). Moreover, the resulting composites are soluble in water due to the solubility of NaCl in water, which could limit their application. Therefore, for the utilizations of solid state LED, the challenges are still kept to find rapid and effective routes to fabrication of QDs incorporating with solid state inorganic materials, which hold efficient waterproof and anti oxygen without quantum yield reducing.

In this paper, we prepared colloidal CdTe QDs embedded in $BaSO_4$ matrix through a fast, green and efficient approach which is suitable for industrial application. The resulting composites exhibit excellent performance, such as high photoluminescence, low toxicity, long fluorescent lifetime, high photo- and thermal stability as well as anti-acid, due to the protection of tight $BaSO_4$ matrix. Based on these excellent properties, we applied the as-prepared composites as well as YAG:Ce yellow phosphors as color conversion layers to fabricate a WLED which showed high color rendering properties, including a CIE coordinate of (0.34, 0.33), an Ra of 88, and a Tc of 5112K at 20 mA.

Experimental

Chemicals

The raw materials used in the experiment were as follows: Tellurium powder (99.999%), sodium borohydride ($NaBH_4$, 99.5%), ethanol (99.7%), sodium hydroxide (NaOH, ≥85%), sodium sulfate (Na_2SO_4, 98%) and barium chloride ($BaCl_2$, 99.5%) were purchased from Sinopharm Chemical Reagents Co. Ltd. Cadmium acetate dehydrate ($CdCl_2{\cdot}2.5H_2O$, 99%) and 3-Mercaptopropionic acid (MPA, 99%) were products of Tianjin Chemical Reagents Co. Ltd. The ultrapure water with 18.2 MΩ/cm (Millipore Simplicity, USA) was used in all syntheses. Transparent epoxy (JH-6800MA and JH-6800MB) used for LED packaging was obtained from Sinopharm Chemical Reagents Co. Ltd. All reagents were used directly without further purification. 460 nm InGaN LED chips with a power of 0.1 W were purchased from APT Electronics Ltd.

Preparation of sodium hydrogen telluride

The method of preparation of NaHTe was described elsewhere, and we made little modifications.[31-33] Briefly, NaHTe was prepared by adding 0.04 g $NaBH_4$ to a flask containing 0.046 g tellurium powder and 2 ml of water under a N_2 atmosphere. The reaction was continued for several hours to ensure that all of the tellurium powder was dissolved and the solution was slightly pink. Then the flask containing the resulting clear aqueous solution was stored in ice bath before transferring into 100 ml of degassed water.

Preparation of CdTe QDs

$CdCl_2 \cdot 2.5H_2O$ (0.114 g) and MPA (0.133 g) were dissolved in 100 ml of water, followed by adjustment of the pH to 8.0 by dropwise addition of 1.0 M NaOH solution during which the solution firstly became turbid and then turned clear. The flask was deaerated by N_2 bubbling for 30 min and was then stayed in ice bath. Then, freshly prepared NaHTe solution (400 μL) was quickly injected into the flask under vigorous stirring, followed by heating to 99-100℃ under open air conditions upon refluxing with a condenser attached. Aliquots of the reaction solution were taken out at regular intervals for further PL characterization. The reaction was stopped when the emission of QDs reached to the desired wavelength. CdTe QDs were precipitated by the addition of absolute ethanol, separated by centrifugation and redispersed in water with the concentration unchanged.

Construction of CdTe @ $BaSO_4$ composites

0.426 g of Na_2SO_4 was dissolved in 30 ml of CdTe QDs solution. Then 5 ml of 0.728 g $BaCl_2$ solution was added quickly. Precipitation produced immediately. Under stirring, the mixture was kept at ambient condition for 5 min. When the stirring stopped, it could be seen that after a few minutes the parental solution was colorless and transparent while the precipitation exhibited strong luminescence under UV light. Then the resultant composites were filtered, rinsed with water, dried in an oven and grinded into fine powders.

Fabrication of WLED

Typically, equal weight of transparent epoxy JH-6800MA and JH-6800MB were mixed together. Then desired amount of YAG: Ce^{3+} phosphors and the as-prepared CdTe@$BaSO_4$ powders were added. The mixture was stirred sufficiently to get homogenous and then dispersed on a blue LED chip, and the coated LED chip was solidified in a vacuum oven at 40℃ for 60 min and thermally cured at 150℃ for 1 h.

Characterization

All measurements were performed at room temperature. The TEM and HRTEM images were acquired on a JEM-2100 field emission source transmission electron microscope operating at 200 kV. X-Ray diffraction patterns were recorded with a Rigaku D/MaxrB diffraction using Cu Kα radiation with a wavelength of 0.1540 nm. Fluorescence spectra were obtained by Hitachi F-4600 fluorescence spectrophotometer. Time-correlated single-photon counting (TCSPC) data were performed on an Edinburgh FL 900 photo-counting system. The optical properties of as-fabricated white LEDs were obtained using an integrating sphere (Everfine Photo-E-Info Co., LTD).

Results and discussion

The synthesis pathway of CdTe@$BaSO_4$ powders is shown in Figure 1. Firstly, MPA-capped CdTe QDs was prepared in aqueous solution, in which Na_2SO_4 and $BaCl_2$ was added in order. $BaSO_4$ precipitation with pink color immediately appeared and a few minutes later, the parental solution was colorless and transparent while the precipitation showed strong photoluminescence under UV light, indicating that CdTe QDs was completely embedded in $BaSO_4$ matrix. Since the surface of CdTe QDs was capped by MPA, in which S^- was connected to Cd^{2+} while COO^- was bare in the solution, leading to the colloidal nanocrystals with negative charge, thus ensuring the CdTe QDs dispersed in the solution and not aggregated. When $BaCl_2$ was added into the solution, Ba^{2+} would connect to COO^- so that the mechanical equilibrium between CdTe nanocrystals was broken, resulting in coagulation of colloidal CdTe nanocrystals. At the same time, Ba^{2+} and SO_4^{2-} would react to form $BaSO_4$ so that CdTe QDs was incorporated into the $BaSO_4$ matrix, as shown in figure 2(c). To prove the composition of the as-prepared powder, XRD pattern and HRTEM figure are exhibited in figure 2, in which XRD pattern shows the composition of the as-prepared powder is $BaSO_4$. Since the percent of CdTe QDs in the $BaSO_4$ matrix was less than 0.1%, the diffraction peak of CdTe was covered by that of $BaSO_4$ and could not be seen in the XRD pattern. While in figure 2(b), the interplanar space was measured at 0.192 nm, which was approximate with that of (311) face of CdTe QDs (0.195 nm), indicating that CdTe QDs existed in $BaSO_4$ crystals.

The photographs and PL spectra of the as-prepared CdTe QDs solution and their corresponding CdTe@$BaSO_4$ powders are exhibited in figure 3. In the true color photographs of the CdTe@$BaSO_4$ powders under UV lamp in figure 3(a), pure color and strong photoluminescence can be observed. As seen from figure 3(b), moderate red shift in the PL peaks could be observed for CdTe@$BaSO_4$ powders compared to their starting CdTe QDs solution, which could be explained by changes of the dielectric constant[29, 34] of the surrounding media as well as by reabsorption of the emission from small nanocrystals by larger ones.

The calculated average PL decay lifetime for the CdTe QDs solution is between 110 ns and 160 ns. Owing to the reduction of nonradiative channels by the efficient surface passivation of $BaSO_4$ matrix, in which SO_4^{2-} is connected to the bonding Cd^{2+} on the CdTe QDs surface, as shown in figure 2(c), the average lifetime for

CdTe@BaSO_4 powders greatly prolongs to the range of 470 ns to 550 ns, which is much longer than all the reported lifetimes of CdTe QDs.[35, 36]

For the practical application of the CdTe@BaSO_4 powders, photo stability was tested under irradiation of 365 nm UV lamp in the air. As comparison in figure 5(a), both PL intensity and emission wavelength of CdTe QDs solution were increased at the initial 10 h while decreased dramatically in the later hours. It could be explained that photo degradation of MPA passivated the surface of CdTe QDs at the first 10 h irradiation, while MPA was completely degraded 10 h later so that the surface of CdTe QDs was capped with no ligands, leading to aggregation and precipitation of CdTe QDs from the solution. As shown in figure 5(b), there is no significance in both of PL intensity and emission wavelength of CdTe@BaSO_4 powders, indicating excellent photo stability of CdTe@BaSO_4 powders.

In the anti-acid test as shown in figure 5(c) and (d), it could be observed that fluorescence quenching happened when the pH value decreased in CdTe QDs solution while CdTe@BaSO_4 powders showed stable fluorescence properties as the pH value changed. Owing to the protection of tight BaSO_4 matrix, CdTe@BaSO_4 powders were more anti-acid than the starting CdTe QDs solution.

After 150 ℃ thermal treatments for 1 h, which is just the condition LED packaging process usually involved, a dramatic decrease in PL intensity and a significant red-shift of PL peak for the CdTe QDs solution could be observed in figure 5(e). While there is no significant change in both PL intensity and emission for

CdTe@$BaSO_4$ powders as shown in figure 5 (f). Due to the protection of tight $BaSO_4$ matrix ensuring CdTe QDs isolated from the surrounding environment, CdTe@$BaSO_4$ powders show excellent photo- and thermal stability, as well as anti-acid, suggesting their great potential application in the solid-state lighting systems.

A white LED employing the as-prepared CdTe@$BaSO_4$ powders and YAG:Ce yellow phosphors as light conversion materials was fabricated, in which blue-emitting LED chip together with yellow emission from YAG:Ce phosphors, as well as red emission from CdTe@$BaSO_4$ powders produce high quality white light with excellent color rendering properties. As shown in figure 6, the WLED shows bright white light for illuminating a paper in the dark, with a CIE color coordinate of (0.34, 0.33), a high Ra of 88, a color temperature (Tc) of 5112K and a luminous efficiency (LE) of 59 lm/W at 20 mA, which are comparable to the reported literature for many WLEDs,[36, 37] fully indicating the CdTe@$BaSO_4$ powders with excellent optical properties are promising conversion materials in optoelectronic applications.

Conclusion

In summary, we have successfully prepared highly photoluminescent CdTe@$BaSO_4$ powders in aqueous phase through a co-precipitation approach for the first time, which is green, efficient and suitable for industry. Moreover, $BaSO_4$ matrix ensures the protection of CdTe QDs from the surrounding environment and as a result providing the CdTe@$BaSO_4$ powders with excellent optical properties, including strong photoluminescence, long fluorescent lifetime, high photo- and thermal stability as well as anti-acid. Meanwhile, WLEDs applying CdTe@$BaSO_4$ powders as red color conversion layer were also fabricated, which exhibited bright white light and high color-rendering properties, suggesting their promising application in solid-state lighting system.

Acknowledgements

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References

1 E. F. Schubert and J. K. Kim, *Science*, 2005, **308**, 1274-1278.

2 M. S. Shur and A. Zukauskas, *Proceedings of the IEEE*, 2005, **93**, 1691-1703.

3 S. Pimputkar, J. S. Speck, S. P. DenBaars and S. Nakamura, *Nat. Photonics*, 2009, **3**, 180-182.

4 S. Landau and J. Erion, *Nat. Photonics*, 2007, **1**, 31-32.

5 M. S. Shur and A. Zukauskas, *Proceedings of the IEEE*, 2005, **93**, 1691-1703.

6 S. Nakamura and G. Fasol, *P216*.

7 A. B. Muñoz-García, Z. Barandiarán and L. Seijo, *J. Mater. Chem.*, 2012, **22**, 19888-19897.

8 H. S. Jang and D. Y. Jeon, *Appl. Phys. Lett.*, 2007, **90**, 041906-041906-041903.

9 J. K. Park, M. Lim, C. H. Kim, H. D. Park, J. T. Park and S. Y. Choi, *Appl. Phys.*

Lett., 2003, **82**, 683-685.

10 Q. Dai, C. E. Duty and M. Z. Hu, *Small*, 2010, **6**, 1577-1588.

11 P. Reiss, M. Protiere and L. Li, *Small*, 2009, **5**, 154-168.

12 X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59-61.

13 X. Wang, W. Li and K. Sun, *J. Mater. Chem.*, 2011, **21**, 8558-8565.

14 Z. A. Peng and X. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 183-184.

15 X. Dai, Z. Zhang, Y. Jin, Y. Niu, H. Cao, X. Liang, L. Chen, J. Wang and X. Peng, *Nature*, 2014, **515**, 96-99.

16 M. A. Hines and P. Guyot-Sionnest, *The Journal of Physical Chemistry*, 1996, **100**, 468-471.

17 B. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. Heine, H. Mattoussi, R. Ober, K. Jensen and M. Bawendi, *J. Phys. Chem. B*, 1997, **101**, 9463-9475.

18 H. Duan, X. Liu, C. Liu, T. Han, X. Lan and Y. Jiang, *J. Nanosci. Nanotechnol.*, 2012, **12**, 2326-2331.

19 H. Duan, Y. Jiang, Y. Zhang, D. Sun, C. Liu, J. Huang, X. Lan, H. Zhou, L. Chen and H. Zhong, *Nanotechnology*, 2013, **24**, 285201.

20 X. Wang, X. Yan, W. Li and K. Sun, *Adv. Mater.*, 2012, **24**, 2742-2747.

21 N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmüller and H. Weller, *J. Phys. Chem. B*, 2002, **106**, 7177-7185.

22 J. Zhou, G. Chen, B. Nie, J. Zuo, J. Song, L. Luo and Q. Yang, *CrystEngComm*,

2013, **15**, 6863.

23 L. Zou, Z. Gu, N. Zhang, Y. Zhang, Z. Fang, W. Zhu and X. Zhong, *J. Mater. Chem.*, 2008, **18**, 2807-2815.

24 X. Wang, X. Yan, W. Li and K. Sun, *Adv. Mater.*, 2012, **24**, 2742-2747.

25 L. Zhu, L. Xu, J. Wang, S. Yang, C.-F. Wang, L. Chen and S. Chen, *Rsc Adv*, 2012, **2**, 9005-9010.

26 C. Wang, Q. Ma, W. Dou, S. Kanwal, G. Wang, P. Yuan and X. Su, *Talanta*, 2009, **77**, 1358-1364.

27 Y. Li, L. Jing, R. Qiao and M. Gao, *Chem. Commun. (Camb.)*, 2011, **47**, 9293-9311.

28 S. Kalytchuk, O. Zhovtiuk and A. L. Rogach, *Appl. Phys. Lett.*, 2013, **103**, 103105.

29 T. Otto, M. Muller, P. Mundra, V. Lesnyak, H. V. Demir, N. Gaponik and A. Eychmuller, *Nano letters*, 2012, **12**, 5348-5354.

30 M. Müller, M. Kaiser, G. M. Stachowski, U. Resch-Genger, N. Gaponik and A. Eychmüller, *Chemistry of Materials*, 2014, **26**, 3231-3237.

31 H. Zhang, Z. Zhou, B. Yang and M. Gao, *J. Phys. Chem. B*, 2003, **107**, 8-13.

32 Z. Tang, N. A. Kotov and M. Giersig, *Science*, 2002, **297**, 237-240.

33 L. Li, H. Qian, N. Fang and J. Ren, *J. Lumin.*, 2006, **116**, 59-66.

34 R. Koole, P. Liljeroth, C. de Mello Donegá, D. Vanmaekelbergh and A. Meijerink, *J. Am. Chem. Soc.*, 2006, **128**, 10436-10441.

35 S. Kim, B. Fisher, H.-J. Eisler and M. Bawendi, *J. Am. Chem. Soc.*, 2003, **125**,

11466-11467.

36 L. Mao, Q.-H. Zhang, C.-F. Wang and S. Chen, *Ind. Eng. Chem. Res.*, 2014, **53**, 16763−16770.

37 X. Wang, W. Li and K. Sun, *J. Mater. Chem.*, 2011, **21**, 8558-8565.

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Figures:

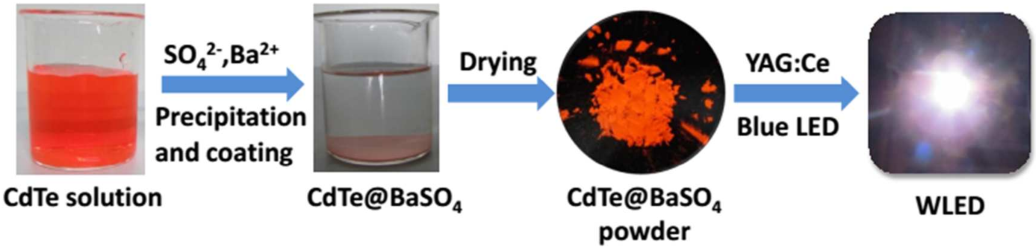


Fig. 1 Synthesis pathway of CdTe@$BaSO_4$ powders and fabrication of WLED.

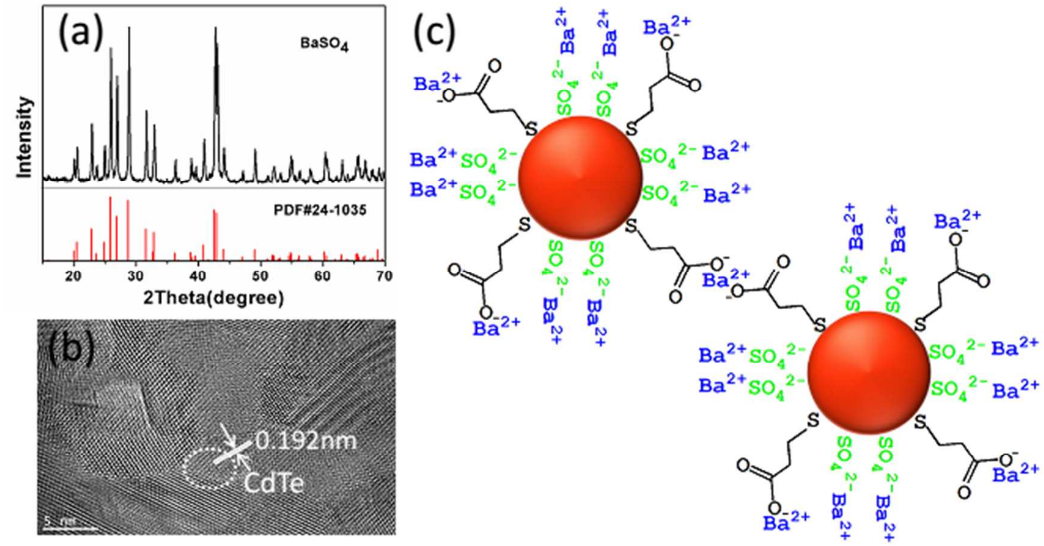


Fig. 2 (a) XRD pattern, (b) HRTEM and (c) schematic of CdTe@BaSO$_4$ composite.

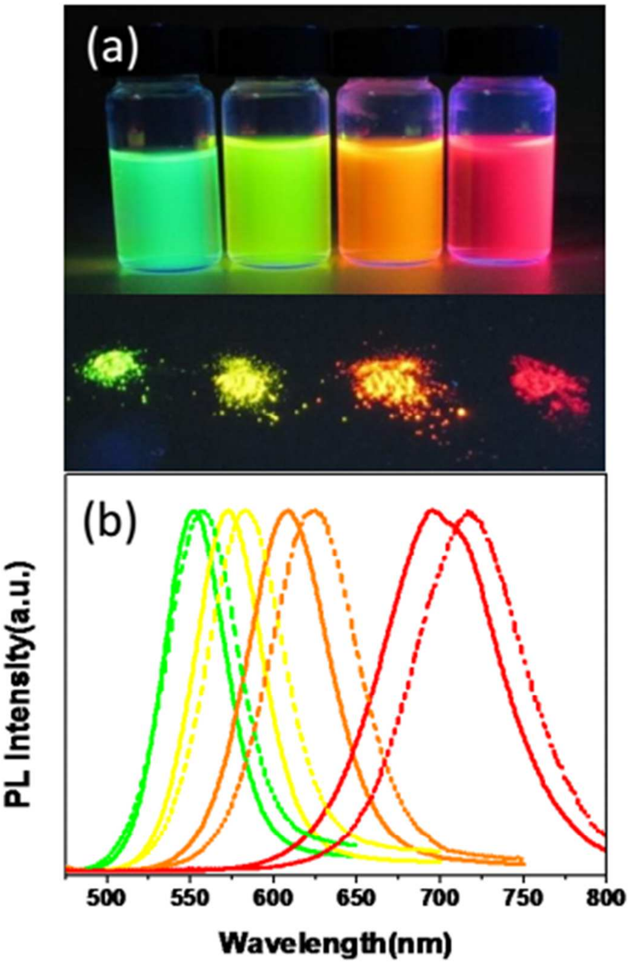


Fig. 3 (a) True-color photographs of starting CdTe QDs solution and CdTe@$BaSO_4$ powders, taken under 365 nm UV light. (b) PL spectra of starting CdTe QDs solution (solid lines) and CdTe@$BaSO_4$ powders (dash lines).

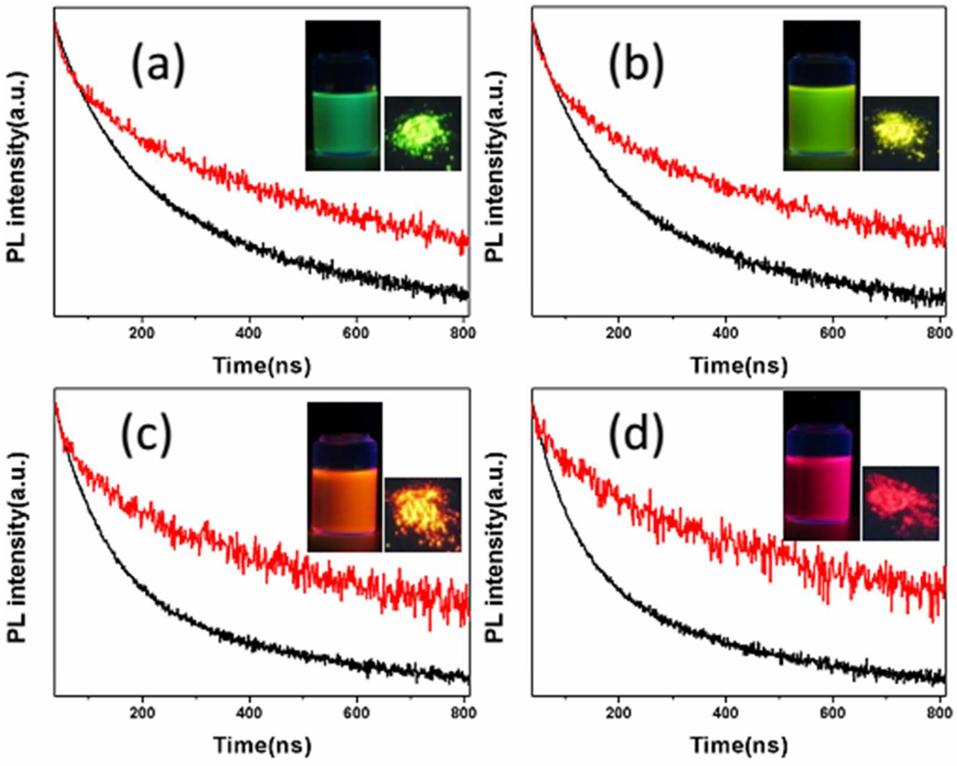


Fig. 4 PL decay lifetime of CdTe QDs solution (black lines) and the corresponding CdTe@$BaSO_4$ powders (red lines) (λ_{ex}=370nm).

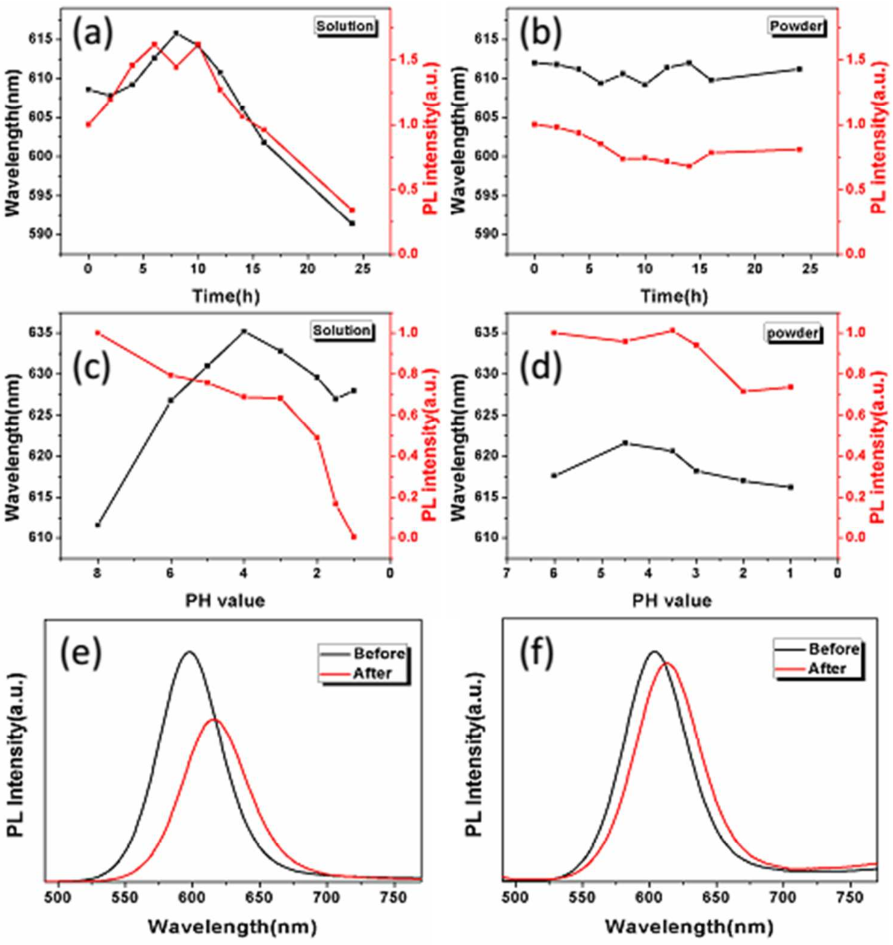


Fig. 5 Dependence of emission wavelength (black lines) and PL intensity (red lines) on radiation time for (a) CdTe QDs solution and (b) CdTe@$BaSO_4$ powders. Evolution of emission wavelength (black lines) and PL intensity (red lines) of (c) CdTe QDs solution and (d) CdTe@$BaSO_4$ powders under different pH value. PL spectra of (e) CdTe QDs solution and (f) CdTe@$BaSO_4$ powders before and after thermal treatment.

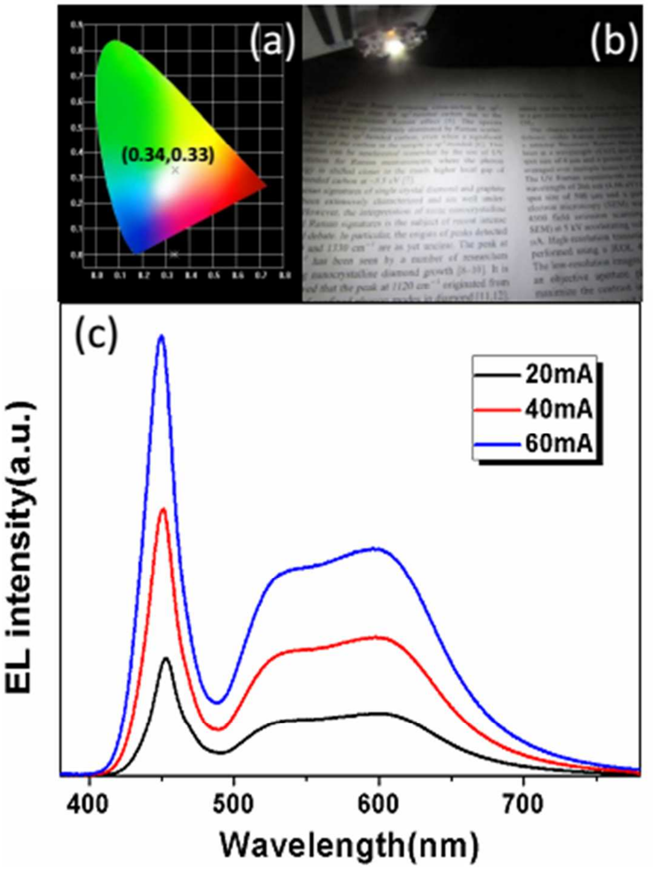
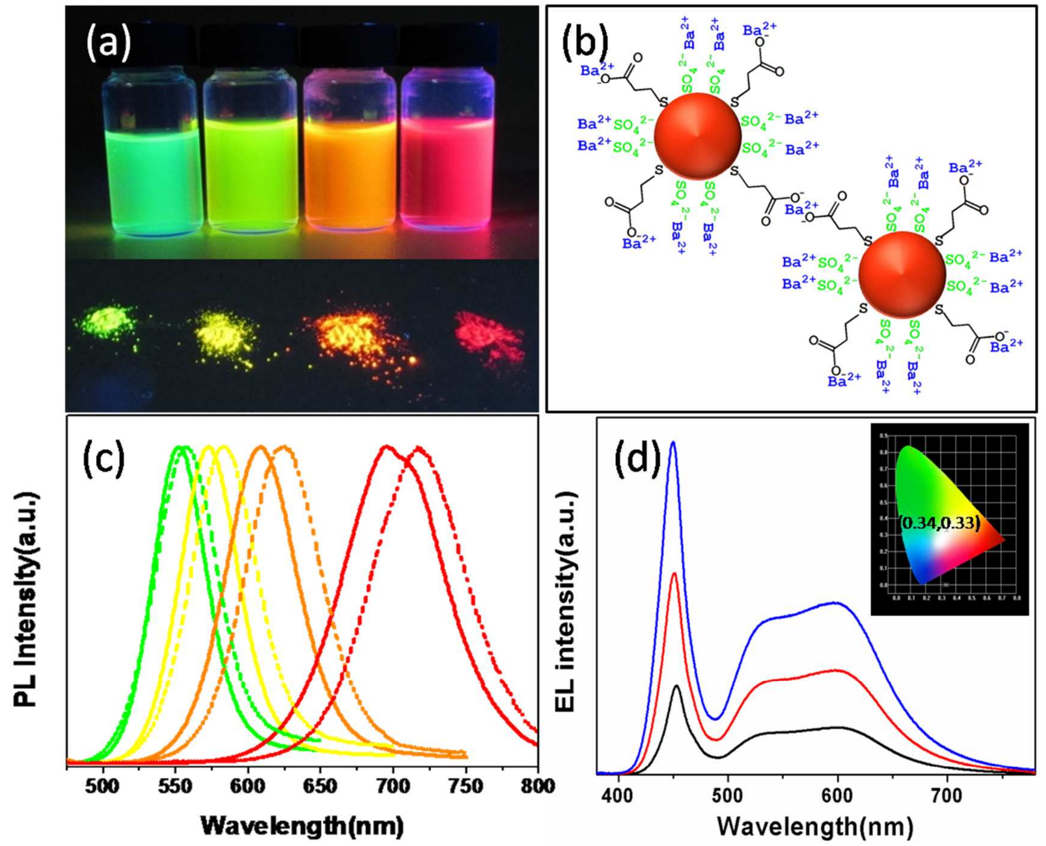


Fig. 6 (a) Color coordinates of the WLED in the CIE 1931diagram. (b) The photograph of a page illuminated by the WLED in the dark. (c) EL spectra of the WLED operated at different forward bias-current.



Colloidal CdTe quantum dots are incorporated into inorganic matrix ---- $BaSO_4$ through a co-precipitation method for the first time.