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Stable and water-soluble CdTe@SiO$_2$ composite nanospheres: Preparation, characterization and application in LED

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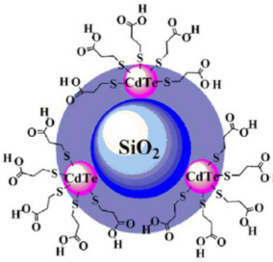
HIGHLIGHTS

- The CdTe formed and attached by Na$_2$SiO$_3$ on the surface of SiO$_2$ nanospheres.
- CdTe grew more slowly at high pH value.
- The spectra of the LED remained almost the same over a range of operation voltages.

GRAPHICAL ABSTRACT



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ABSTRACT

CdTe@SiO$_2$ fluorescent nanospheres were synthesized by heating reflux method. Infrared spectra support the structural formation mechanism of the CdTe@SiO$_2$ composite nanospheres. The CdTe@SiO$_2$ composite nanospheres were characterized by means of SEM, TEM, IR, nitrogen adsorption isotherm, fluorescence spectra and electroluminescence spectra, etc. It was found that both pH value and reflux time played important roles in growth and quantum yield of CdTe@SiO$_2$ fluorescent nanospheres. CdTe@SiO$_2$ fluorescent nanospheres were fabricated to be a single electrode light-emitting diode prototype. The electroluminescence spectra and Commission International de L'Eclairage remained almost the same over a range of operation voltages, and it meant the light-emitting diodes had better color stability. So CdTe@SiO$_2$ fluorescent nanospheres could provide a potential application in light-emitting diode.

1. Introduction

In the last two decades, quantum dots (Q-dots) had been attracting more and more interests because of unique optical and electrical properties such as tuneable size-dependent emission [1], high photoluminescence (PL) quantum yields [2–4], long PL life times [5], large absorption cross sections and narrow and symmetric emission bands [6] which made the Q-dots a new direction of their possible application in life sciences from the molecular and cellular biology, hybrid nanobiosensors and drug delivery systems to the biomedical imaging and diagnostics of cancer [7–12].

Nonetheless, Q-dots materials had to face the following problems in practical applications: ultra-sensitivity of their fluorescence to the surface states [13,14], possible toxicants to living organisms and chemical stabilities in harsh chemical environments [15,16]. Silica coated nanocrystals might solve regarding their end-use in applications. Silica might provide both chemical and physical shielding from the direct environment, thereby improving the stability. At present, the main application of silica coated nanoparticles was their use as biomarkers. However, silica coated nanoparticles might also be used for (opto-) electronic devices, as building blocks for photonic crystals or fundamental single-particle research. In

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these cases, the robustness, (photo) chemical stability, and high control over the particle size were the most important advantages.

The incorporation of Q-dots in silica spheres had been accomplished using two different methods. The first method was the Stöber process-based approaches [17–22], where Q-dots acted as seeds for silica growth in an ethanol/water mixture. This method yielded single or multiple Q-dots per silica sphere, where Q-dots acted as seeds for silica growth in an ethanol/water mixture. The second method used water-in-oil (W/O) reverse microemulsion system which was used for coating inorganic nanocrystals with silica [23–31]. Hydrolysis and condensation of the silica precursor took place at the W/O interface or in the water phase, resulting in highly monodisperse silica particles even at small sizes. This system was previously used for the in situ synthesis of CdTe Q-dots in silica spheres [32,33]. Murase and co-workers recently demonstrated that the maximum size of SiO_2 beads incorporating multiple QDs prepared by the reverse micelle route was several micrometers [34–37]. The incorporated QDs retained their initial PL efficiency because they were coated with a thin SiO_2 shell before the reverse micelle procedure, which prevented removal of the ligands from their surface during incorporation. However, all the samples were prepared in the dark and under oxygen free condition [32]. The reaction was controlled difficultly, and the conditions were severe. The CdTe@SiO_2 composite spheres were used for confocal images of cells [22]. However, no studies had been reported about electrode light-emitting diode so far.

In this work, we reported a heating reflux method which was controlled simple and no need in the dark and under oxygen free compared with previous work. The CdTe were attached by Na_2SiO_3 on the surface of SiO_2 nanospheres to form CdTe@SiO_2 composite nanospheres, so it constituted a novel method. The CdTe@SiO_2 composite nanospheres had better stability in the open air and were water-soluble. Photoluminescence color of CdTe@SiO_2 fluorescent nanospheres could be controlled by reaction time. We provided some experimental results to support the structural formation mechanism for the CdTe@SiO_2 composite nanospheres. CdTe@SiO_2 fluorescent nanospheres were fabricated to be a single electrode light-emitting diode and their electroluminescence spectra, Commission International de L'Eclairage and the current density versus voltage were investigated for the first time.

2. Experimental

2.1. Materials

The 3-mercaptopropionic acid (MPA) was purchased from Alfa Aesar and Triton X-100 was obtained from Fluka. $CdCl_2{\cdot}2.5H_2O$, trisodium citrate dehydrate, aqueous ammonia solution (25 wt.%), sodium tellurite (98%), sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS) and hydrazine hydrate (80%) were analytical grade and commercially available products. GaN chip was purchased from CREE Company.

2.2. Preparation of SiO_2 nanospheres

The SiO_2 nanospheres were prepared according to the literature by reverse microemulsion method at room temperature [38]. The microemulsion was made up of deionized water (3.2 mL), cyclohexane (40 mL), *n*-hexanol (10 mL), and TritonX-100(10.8 g). Typically, TEOS (1 mL) and ammonia aqueous solution (1 mL) were added after the microemulsion system had formed for 30 min. The reaction system was then kept under vigorous magnetic stirring for 24 h. Acetone was used to demulsify the solution and the resultant precipitate were washed with acetone.

2.3. Synthesis of CdTe@SiO_2 fluorescent nanospheres

In a typical synthesis procedure, SiO_2 nanospheres were dispersed in deionized water (48 mL) with the aid of supersonication. Under vigorous agitation, 1.6 mL $CdCl_2$ aqueous solution (0.1 M) and 40 μL MPA was added into the above solution at room temperature. The solution pH value was adjusted with 0.1 M NaOH. Subsequently, 8 mg sodium tellurite was put into the above solution. The mixture was then kept under vigorous magnetic stirring for 6 h. Finally, the solution was heated to reflux and 1.0 mL hydrazine hydrate was injected into the solution. The CdTe size was controlled by refluxing time. Acetone was used to terminate the reaction and the resultant precipitate of CdTe@SiO_2 composite nanospheres were washed with water. The synthesis was conducted in the open air.

2.4. Fabrication of hybrid devices made of CdTe@SiO_2 composite nanospheres and GaN chip

Briefly, a GaN LED chip which was an excitation source and part of a CdTe@SiO_2–GaN hybrid had the following specifications. The blue light radiation from the GaN chip excited CdTe@SiO_2 composite nanospheres and CdTe@SiO_2 transformed the blue light radiation into different color emission. The structure of the hybrid device consisting of the GaN LED and yellow emitting CdTe@SiO_2 composite nanospheres was shown in Scheme 1. A wire bonded bare GaN LED chip was coated with CdTe@SiO_2 composite nanospheres dissolved in water. Then, the water solvent was dried off. Transparent epoxy materials were put over the CdTe@SiO_2–GaN LED chips to harden and formed a dome shape. The home-made hybrid device of CdTe@SiO_2–GaN LED was produced as shown in Scheme 1.

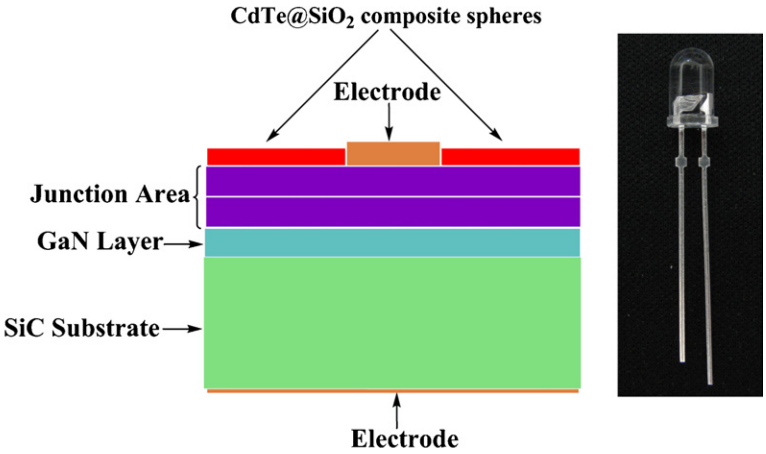
2.5. Characterizations

Infrared (IR) spectra of SiO_2 nanospheres and CdTe@SiO_2 composite nanospheres were measured on a BRUKER IFS 66 v/S. Nitrogen sorption isotherm and textural properties of SiO_2 nanospheres and CdTe@SiO_2 composite nanospheres were determined at −196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP2010 system. Fluorescence spectra were obtained at room temperature using a Cary Eclipse spectrofluorimeter. If not specifically mentioned in the text, an excitation wavelength of 365 nm was used. The quantum efficiency in solution was measured in dilute distilled water, using quinine sulfate in 0.1 M sulfuric acid as standard. The size and morphologies of CdTe@SiO_2 fluorescent nanospheres were characterized by the aid of JEOL JEM-6700F scanning electron microscope (SEM) and JEM-100CXII transmission electron microscope (TEM). EL spectra were measured with a Photoresearch PR650 spectrascan spectrometer and the current–voltage characteristics of Q-dots-LED were measured with a Keithley 2400 programmable voltage-current source.

3. Results and discussion

3.1. Synthesis of CdTe@SiO_2 composite nanospheres

In the reverse microemulsion system, cyclohexane was served as a continue phase and TritonX-100 and *n*-hexanol were used as surfactant and co-surfactant, respectively. The TEOS and ammonia was added into the above solution under magnetic stirring. The SiO_2 nanospheres formed after the reaction system was then kept under vigorous magnetic stirring for 24 h. As shown in Scheme 2, SiO_2 nanospheres were dispersed in water solution (pH 10) which contained $CdCl_2$, MPA, trisodium citrate dehydrate



Scheme 1. Schematic structure of the device consisting of the GaN LED chip and orange emitting CdTe@SiO$_2$ composite nanospheres. The photo image of home-made hybrid device of CdTe@SiO$_2$–GaN LED.

and NaOH under magnetic stirring for 6 h. The MPA coordinated with Cd^{2+}, and the SiO_2 reacted with NaOH and formed Na_2SiO_3 on the surface of SiO_2 nanospheres. After hydrazine hydrate was added into the solution, lots of Te^{2-} ion appeared. The CdTe formed and were attached by Na_2SiO_3 on the surface of SiO_2 nanospheres; lots of MPA molecules which were taken to the surface of SiO_2 nanospheres together with CdTe made CdTe@SiO$_2$ composite nanospheres dissolve in water; the CdTe nanoparticles grew as reflux time continued. Finally, acetone was used to demulsify the solution and the CdTe@SiO$_2$ composite nanospheres were precipitated [33]. The Na_2SiO_3 on the surface of SiO_2 nanospheres reacted with carbon dioxide and formed silicic acid in the open air, and silicic acid deposited on the surface of CdTe Q-dots in order to prevent oxygen from oxidating CdTe. In order to prove that Na_2SiO_3 took an important role in preventing oxygen from oxidating CdTe, in comparison, the solution pH value was adjusted to 10 with aqueous ammonia solution instead of sodium hydroxide. Acetone was used to demulsify the solution and the resultant precipitate was oxidated to be black solid over night.

When the pH value of solution was adjusted with 0.1 M NaOH, the amount of SiO_2 nanospheres also should be adjusted. When the pH value was 9, 10 and 11, the amount of SiO_2 nanospheres was 50 mg, 100 mg and 150 mg, respectively. If the amount was above this, there were SiO_2 nanospheres which did not combine with quantum dots. That the addition amount of SiO_2 nanospheres was different at different pH value could attribute to Na_2SiO_3 on the surface of each silica nanospheres and the adsorption of Cd^{2+} on silica. It had been shown that the adsorption of Cd^{2+} ions on silica increased strongly as pH value increased in the range of pH 4–10 [39]. The more SiO_2 nanospheres which reacted with NaOH and formed Na_2SiO_3 in the surface of SiO_2 nanospheres at high pH value were, the more MPA molecules taken to the surface of SiO_2 nanospheres together with CdTe were.

3.2. Formation mechanism of CdTe@SiO$_2$ composite nanospheres

Infrared (IR) spectra of SiO_2 nanospheres and CdTe@SiO$_2$ composite nanospheres which were synthesized at pH 10 were shown in Fig. 1. IR results of SiO_2 nanospheres showed that the absorption peak at 1629 and 3411 cm^{-1} could attribute to bend vibration and stretching vibration of hydroxyl which came from absorbed water [40], the absorption peak between 1009 and 1251 cm^{-1} was determined by asymmetrical stretching vibration of Si—O—Si [41], absorption peak at 951 cm^{-1} belonged to bend vibration of Si—OH [42], and the absorption peaks at 799 cm^{-1} and 468 cm^{-1} corresponded to bend vibration and bend vibration of Si—O bond [43], respectively.

But IR absorption peaks of Si—O bond became weak in CdTe@SiO$_2$ composite nanospheres, IR absorption peak of Si—OH almost lost especially. The reason was that sodium hydroxide reacted with silicon dioxide on the surface of SiO_2 nanospheres and formed sodium silicate; a part of sodium silicate dissolved in water; the others finally reacted with carbon dioxide and formed silicic acid in the open air after acetone was used to demulsify the solution and the solid was precipitated. So the IR absorption peaks of Si—O were weakened and absorption peak of Si—OH lost. The absorption peak at 1398 cm^{-1} might belong to stretching vibration of C—O, and the absorption peak at 1608 cm^{-1}could attribute to stretching vibration of C=O which was so strong that absorption peak which belonged to bend vibration of hydroxyl was covered. It meant there were many MPA molecules on the surface of CdTe@SiO$_2$ composite nanospheres. That there was no IR absorption peak of sulfhydryl suggested sulfhydryl coordinated with Cd^{2+}. The observed IR bands of CdTe@SiO$_2$ composite spheres between 3110 and 3629 cm^{-1} could attribute to stretching vibration of hydroxyl which was stronger than SiO_2 nanospheres, and the result could be attributed to MPA and water on the surface of CdTe@SiO$_2$ composite nanospheres.

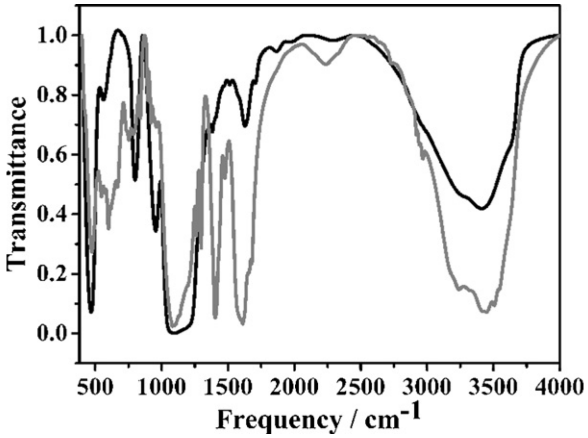
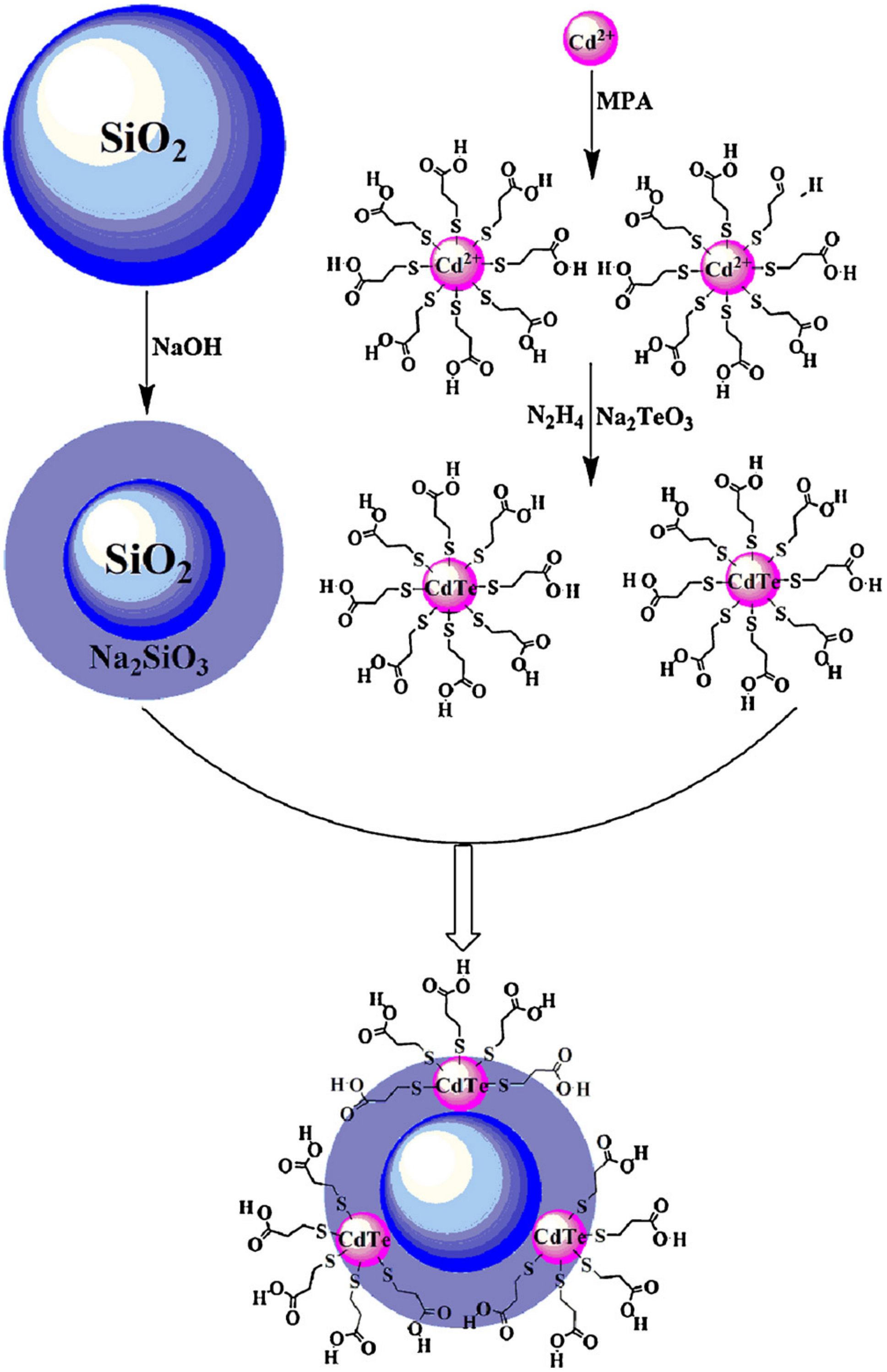


Fig. 1. IR spectra of SiO_2 nanospheres (black line) and CdTe@SiO$_2$ composite nanospheres (gray line).



Scheme 2. Schematic representation of the incorporation mechanism of hydrosoluble CdTe@SiO_2 composite nanosphere.

3.3. *The morphology of CdTe@SiO_2 composite nanospheres*

The microstructures of the as-prepared samples were then investigated with SEM and TEM. Fig. 2a–c, presented the morphology of SiO_2 nanospheres. As figure showed, the size distribution of the SiO_2 nanospheres was narrow, and the surface was smooth. Fig. 2d showed the general morphology of the fluorescent CdTe@SiO_2 composite nanospheres. All composite nanospheres present a universal structure with CdTe Q-dots locating at the surface of each silica nanospheres. But the surface became rough, and CdTe@SiO_2 composite nanospheres were agglomerated together. The reason was that sodium hydroxide reacted with silicon dioxide

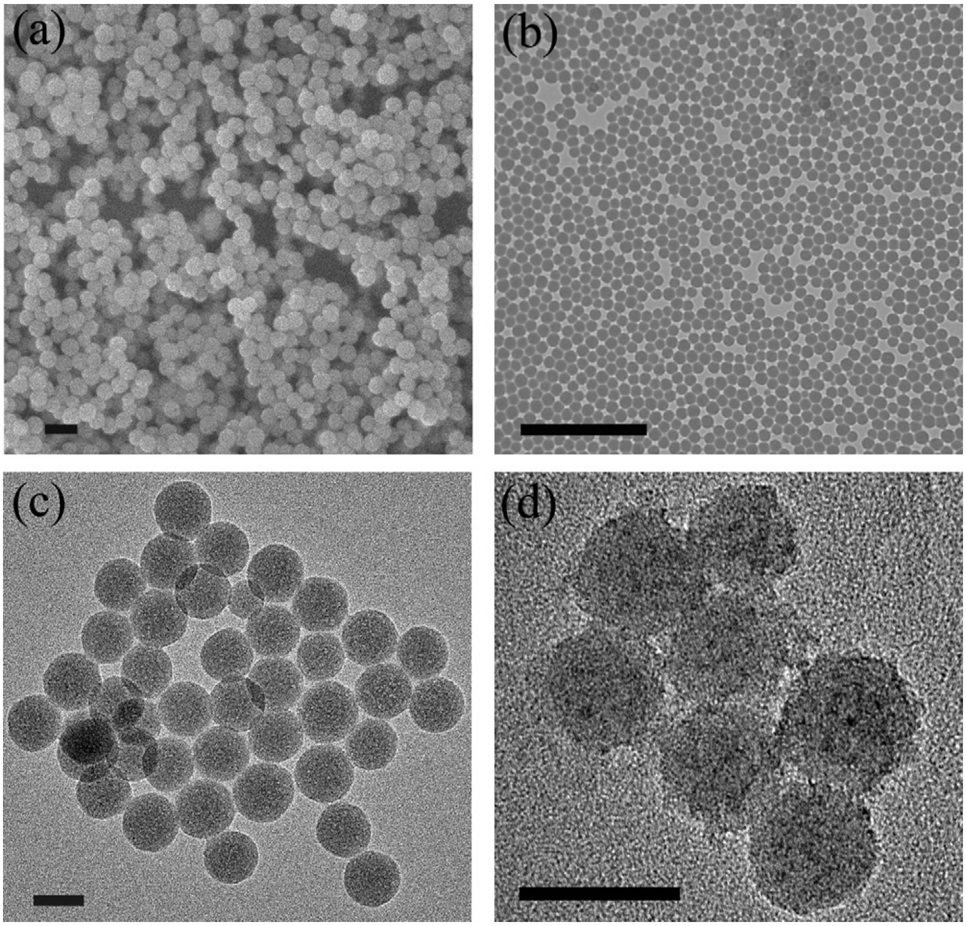


Fig. 2. SEM image of (a) SiO_2 nanospheres, TEM of (b) SiO_2 nanospheres, (c) magnification of the same sample and (d) TEM of CdTe@SiO_2 composite nanospheres. Scale bar is 100 nm in (a), 500 nm in (b) and 50 nm in (c) and (d).

on the surface of SiO_2 nanospheres and formed sodium silicate which made CdTe@SiO_2 composite nanospheres agglomerate together.

3.4. Nitrogen sorption analysis

Nitrogen adsorption isotherm experiments were carried out to analyze surface area. With use of the adsorption data, the apparent specific surface area S_{BET} can be calculated based on the Brunauer–Emmett–Teller (BET) method. BET surface area of SiO_2 nanospheres and CdTe@SiO_2 composite particles was 70.2698 and 2.5783 $m^2\,g^{-1}$ respectively. The reason why BET surface area of CdTe@SiO_2 composite nanospheres became much smaller was that CdTe@SiO_2 composite nanospheres were attached each other by sodium silicate which was on the surface of CdTe@SiO_2 composite nanospheres. The BET surface area of CdTe@SiO_2 composite nanospheres proved that general morphology of the fluorescent CdTe@SiO_2 composite nanospheres investigated by TEM was correct.

3.5. Effect of pH on the luminescence response of CdTe@SiO_2 composite nanospheres

The pH value of solution played a great role in the growth of CdTe. Usually, CdTe grew more quickly at higher pH value. But in our system, CdTe grew more slowly at higher pH value (Fig. 3). We thought it could attribute to the amount of SiO_2 nanospheres. As illustrated in above paragraphs, the amounts of SiO_2 nanospheres which reacted with NaOH and formed Na_2SiO_3 on the surface of SiO_2 nanospheres were fewer at lower pH value. But the amount of Q-dots was invariable at different pH value. There were less CdTe attached by Na_2SiO_3 on the surface of SiO_2 nanospheres at lower pH value. Because of sodium silicate's high viscosity, the Q-dots which were attached on the surface of SiO_2 nanospheres grew slowly. The Q-dots which were not attached on the surface of SiO_2 nanospheres grew quickly. There were more Q-dots which were not attached on the surface of SiO_2 nanospheres at lower pH value, so the fluorescence peak position moved more quickly at lower pH

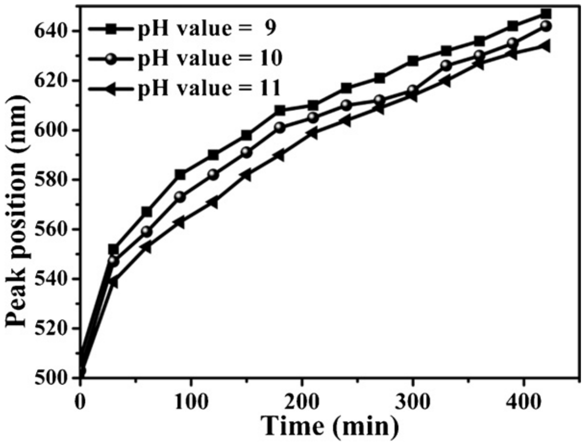


Fig. 3. Fluorescence peak positions of CdTe@SiO_2 composite nanospheres during their growth at different pH value.

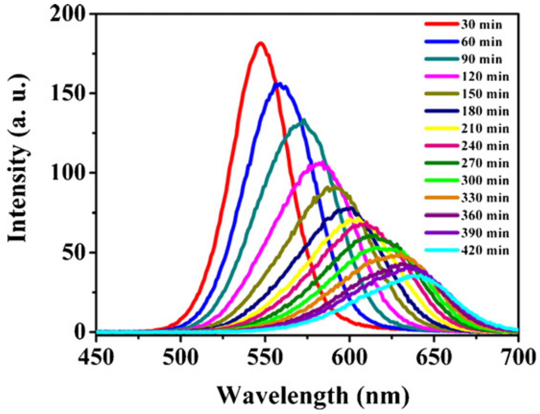


Fig. 4. The fluorescence spectra of CdTe@SiO_2 composite nanospheres during their growth at different time.

value. As shown in Fig. 4, with prolonging the reflux time, the full width at half maximum of the fluorescence peak got wider. The Q-dots which were in the solution and not attached on the surface of SiO_2 nanospheres grew quickly, and the Q-dots which were attached on the surface of SiO_2 nanospheres grew slowly as reflux time continued, so the size distribution of CdTe Q-dots got wider. Correspondently, the full width at half maximum of the fluorescence peak got wider and wider as reflux time continued. All the CdTe Q-dots get larger with prolonging the reflux time, so the main fluorescence peak was red-shifted.

And it also caused change of quantum yield (QY) was got lower as reflux time continued at different pH value (Fig. 5). But the quantum yield of Q-dots was usually low in water solution. The quantum efficiency in solution was measured in dilute deionized water, quinine sulphate in 0.1 M sulphuric acid was used as standard [44]. The change tendency of QY was similar that the QY got lower and lower as reflux time continued. It meant Ostwald ripening stage occurred in the initial stage of CdTe Q-dots growth [45].

3.6. Characteristics of CdTe@SiO_2 composite nanospheres LED

When reflux time was 60 min, the QY was the highest at pH 10. And the fluorescence was yellow at this time. So CdTe@SiO_2 composite nanospheres synthesized at this condition was investigated if it could be used for light-emitting diodes (LED). We fabricated a CdTe@SiO_2–GaN hybrid LED as a prototype to develop energy efficient, color-tunable, intensity-controllable, reliable and long-lived solid state lighting LED devices. GaN-based blue light emitting diodes were the excitation source for the orange emitting CdTe@SiO_2 composite nanospheres and the CdTe@SiO_2 composite nanospheres transformed blue light to emitted orange light. Fig. 6 showed the Commission International de L'Eclairage (CIE) coordinates at the corresponding voltages, and the CIE remained almost the same over a range of operation voltages. Fig. 6 also showed the normalized electroluminescence (EL) spectra normalized of a single electrode LED prototype with CdTe@SiO_2 composite nanospheres and GaN converter under different voltage. The blue light emission from the LED was transformed to orange light when it passes through the semiconductor CdTe@SiO_2 composite nanospheres. The LED had better color stability and the spectra remained almost the same in the range of operation voltages. The current density versus voltage characteristics of the single electrode LED prototype with CdTe@SiO_2 composite nanospheres and GaN converter were shown in Fig. 7, and a turn-on voltage of 2.3 V was measured on air atmosphere. And *I–V* curve showed linear behavior. The QY and color purity of our LED was low compared to silica-coated InP/ZnS nanocrystals as converter material in LED [46]. The InP/ZnS/SiO_2 nanoparticles employed displayed QY of up to 15%, the InP/ZnS/SiO_2 nanocrystals allowed the use of an inert silicone polymer and high performance LED chips with 53 lm W^{-1}. The silica encapsulation route should be applicable to various converters, and will facilitate the formation of many converter/silicone composites. In our future work, we would try to change condition to fabricate white LED which emitted a bluish, cold white light, high QY and well color-rendering properties.

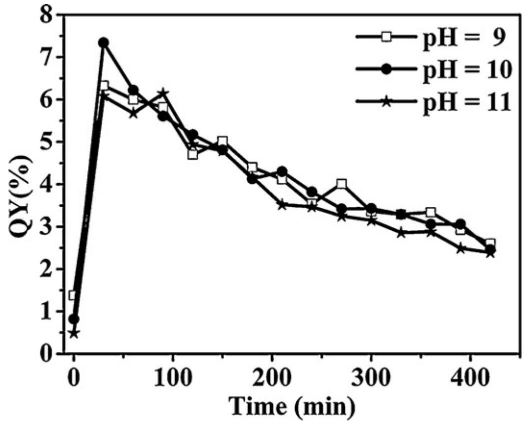


Fig. 5. The quantum yield of CdTe@SiO_2 composite nanospheres at different pH value.

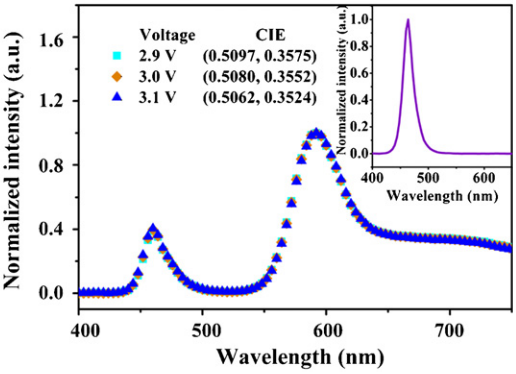


Fig. 6. EL spectra normalized of a single electrode LED prototype with CdTe@SiO_2 composite nanospheres and GaN converter under different voltage. The inset showed the CIE coordinates at the corresponding voltages and EL spectra normalized of a single electrode GaN LED prototype.

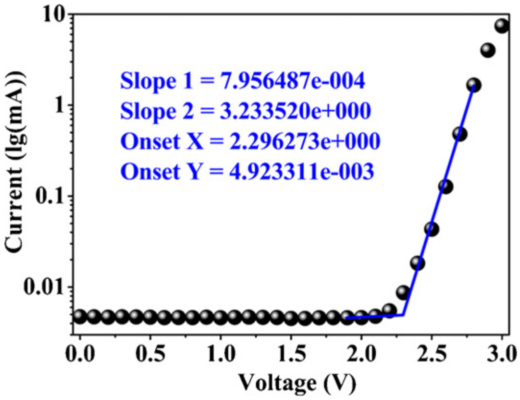


Fig. 7. Current vs voltage characteristics of the single electrode LED prototype with CdTe@SiO_2 composite nanospheres and GaN converter.

4. Conclusion

CdTe@SiO_2 composite nanospheres were synthesized by a simple heating reflux method. Systematic experimental results suggested that the Na_2SiO_3 which was on the surface of SiO_2 nanospheres was responsible for the resultant composite nanospheres. The silicic acid layer provided a sufficient protection for the CdTe Q-dots, and it caused the CdTe@SiO_2 fluorescent nanospheres stable in the open air at room temperature. MPA molecules took to the surface of SiO_2 nanospheres together with CdTe made CdTe@SiO_2 composite nanospheres dissolve in water. The single electrode LED prototype fabricated with CdTe@SiO_2 composite nanospheres had much better color stability.

Acknowledgments

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