Original Article

Synthesis and Optical Characterizations of the Fluorescence Silica Nanoparticles Containing Quantum Dots

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Abstract: The quantum dots coated by silica is fluorescence material class with great biocompatibility, low toxicity and water-solubility, that is suitable for bioapplications. This work presents the synthesis of SiO₂ coated CdTe/ZnSe (named CdTe) quantum dots (CdTe@SiO₂ nanoparticles) via a wet chemical route called modified Stöber method. The compounds tetraethylorthosilicate (TEOS) has used as precursors, aminopropyltriethoxysilane (APTES) is as electric neutralizer, and ammonium hydroxide is used as catalysts. The size of CdTe@SiO₂ nanoparticles was estimated about 70 to 150 nm depending on the quantities of H₂O, APTES, and catalysts. The emission behaviours of SiO₂ coated quantum dots was effected by ratio of substances participating in the reaction and synthesis conditions. with the ratio (by volume) of suitable substances: TEOS:solution of QDs:NH₄OH:APTES:H₂O being 1.5:1.5×10⁻²:0.8×10⁻²:4×10⁻²:3×10⁻⁴:5×10⁻², the prepared silica nanoparticles containing quantum dots show high fluorescence emission efficiency, with the fluorescence intensity is higher than that of uncoated CdTe/ZnSe quantum dots. This is a positive result in the technique of manufacturing luminescent silica nanoparticles containing quantum dots. The results show an ability to use the CdTe@SiO₂ nanoparticles for biological application.

Keywords: Stöber method, fluorescence SiO₂ nanoparticles, CdTe quantum dots, aminopropyltriethoxysilane precursor, ammonium hydroxide catalysts.

1. Introduction

Nowadays, quantum dots have emerged as a new class of fluorescent probes for in vivo biomolecular and cellular imaging because they are highly photo-stable with broad absorption spectra, narrow size-
tunable emission spectra covering from ultraviolet (UV) to infrared (IR) region. They have long fluorescence lifetimes and remarkably resistant to photobleaching [1-8].

Despite numerous such advantages due to the exhibition of high-quality fluorescence, it would be difficult to use quantum dots in biomedical applications because of several drawbacks including high toxicity, low dispersion in water or biological environments, and fluorescence blinking. These problems can be solved by creating intermediate layers or coating the shells around the quantum dots. The core/shell structure supports quantum dots have longer-term optical stability and higher quantum yield. Silica is one of the optimal options to problems of quantum dots. When surrounded by chemically inert silica shells, quantum dots could be prevented from the effects of the environment on the optical properties. Furthermore, silica nanoparticles not only were non-toxic and transparent for visible light regions, but they can be well dispersed in biological environments, have high biological compatibility, and are easy to bind with biological entities [9-12]. However, they did not discuss about changing emission properties of SiO$_2$ coated quantum dots due to different reaction conditions. There are several chemical routes known for the synthesis of silica nanoparticles in solution. But the most common approach is Stöber method which has involved grafting of organic groups by chemical reaction of pre-synthesized silica particles with certain coupling agents [13, 14]. This simple method can be carried out with non toxic solvents such as water or ethanol, and has been modified to incorporate quantum dots inside the silica nanoparticles and reform high uniform beads. However, these techniques face a common problem that the fluorescent efficiency of the sample is significantly reduced [15-21]. Although there were some work have done to improve the manufacturing process, the fluorescence efficiency of quantum dots after silica coating still decreases. This degeneration is probably related to surface traps formed during silica formation [18]; due to TEOS hydrolysis [20], the influence of ammonia catalysts, or exchange the ligands of silane precursors can damage the surface of the quantum dots [16]. For this reason, the researches in order to prevent this decline are essential.

Several researches of preparing single quantum dot in a silica sphere were published. Thomas Nann and coworkers have synthesized silica coated quantum dots by using oil-in-water microemulsion system with cyclohexane as the “oil” phase and Synermonic NP-5 as the surfactant [22]. Xingguang Su et al, Yunhua Yang and Mingyan Gao who were successful in synthesis of aqueous CdTe quantum dots embedded silica nanoparticles by reverse micelle method [21, 23, 24]. They inserted many quantum dots in each silica particle using PDDA (polydimethylidiallyl ammonium chloride) to balance the electrostatic repulsion between CdTe quantum dots and silica intermediates. Although this method created high quality silica nanoparticles, however, it used toxic solution effect on healthy of researcher and environment. In comparison with reverse micelle method, Stöber method used a nontoxic solvent, ethanol, as reaction media. Thomas Nann and Paul Muvanlney created single silica coated single quantum dot by using TEOS to colloidal stable seed particles in an EtOH/H$_2$O/NH$_3$ mixtures [22]. Yoshio Kobayashi et al used NaOH in their Stöber method. They presented effect concentration of TEOS and concentration of NaOH on formation process of silica shell and properties of SiO$_2$ coated quantum dots [25, 26, 27], but they have no discussion about changing emission properties of SiO$_2$ coated quantum dots due to different reaction conditions.

In this work, the CdTe/ZnS quantum dots are coated by a silica layer in ethanol solvent via Stöber method using ammonium hydroxide (NH$_4$OH) as catalysts. Effect of reaction substances (TEOS, NH$_4$OH, APTES and water) ratios on the perform of CdTe@SiO$_2$ nanoparticles and their optical properties were investigated. The size of CdTe@SiO$_2$ nanoparticles was estimated about 70 to 150 nm. The emission behaviours of SiO$_2$ coated quantum dots was effected by ratios of substances participating in the several researches of preparing single quantum dot in a silica sphere were published. Thomas Nann and coworkers have synthesized silica coated quantum dots by using oil-in-water microemulsion system with...
cyclohexane as the “oil” phase reaction and synthesis conditions. In our work, with a solution volume of CdTe/ZnSe quantum dots of 80 µl (containing about $10^{15}$ quantum dot particles/mL), the proportion (by volume) of suitable substances was obtained. With this ratio, the silica nanoparticles containing quantum dots have exhibited a high fluorescence emission efficiency, the fluorescence intensity is higher than that of uncoated CdTe/ZnSe quantum dots. This is a positive result in the technique of manufacturing luminescent silica nanoparticles containing quantum dots. The results show an ability to use the CdTe@SiO$_2$ nanoparticles for biological application.

2. Experiments

The CdTe/ZnS quantum dots were synthesized as-prepared in [8] with 4-5 nm in size. For synthesis of fluorescence SiO$_2$ nanoparticles with CdTe quantum dots via Stöber method, tetraethylorthosilicate (TEOS, Sigma Aldrich) were used as precursors, NH$_4$OH (Sigma Aldrich) was used as catalyst in sol gel process. Due to the negatively charged CdTe/ZnS quantum dot surface (because of presence of the carboxyl COO$^-$ group) and the silica network formed through hydrolysis and condensation processes is also negatively charged [27], APTES ($C_9H_{23}NO_3Si$) was used as electric neutralizer for easily growing of SiO$_2$ shell on the quantum dots face. Ethanol (Merck) and purified water from Millipore were used in the synthesis. The synthesis route of fluorescence SiO$_2$ nanoparticles with CdTe quantum dots by modified Stöber method is described in figure 1. The mixture of CdTe quantum dots and APTES was ultrasonic vibrated in ethanol and then was added in the ethanol solution containing TEOS magnetic stirred before. After that, the ammonium hydroxide catalyst was added in the solution to create the reaction to form silica particles containing the quantum dots inside. The solution was magnetic stirred for 24 hours. The silica-coated quantum dots (CdTe@SiO$_2$) nanoparticles samples then have been cleaned by centrifugation in ethanol.

Based on the equations of hydrolysis and condensation reaction, we chose fix amounts of ethanol solvent and TEOS precursor are chosed of 15 ml and 150 µl; amount of solution containing CdTe /ZnS quantum dots is 80 µl (with a concentration of about $10^{15}$ particles / mL). The amount of other substances is changed to investigate their effect on the emission of quantum dots. The amounts of substances are given in tables 1, 2 and 3.

The size and shape of CdTe@SiO$_2$ nanoparticles were determined by transmission electron microscopes (TEM, JEM 1011). Absorption spectra were measured using JASCO-V570-UV-Vis-NIR spectrometer. The fluorescence spectra were recorded on a Cary Eclipse spectrofluorometer (Varian).
3. Results and Discussion

The CdTe@SiO₂ nanoparticles were synthesized as colloidal particles dispersed in aqueous or ethanol solutions. The solution of prepared nanoparticles samples is opaque white, that is color of silica. Figure 2 presents the TEM image of one sample of CdTe@SiO₂ nanoparticles. It shows that the particle shape is spherical with the average diameter of about 110 nm with high monodispersion. The results show the success of synthesis SiO₂ nanoparticles containing CdTe/ZnS quantum dots. The size of silica nanoparticles vary from 70 to 150 nm depending on the concentration of reactants and the catalyst of the synthesis.

Table 1. Amounts of substances for survey by amount change of APTES

| Ethanol (ml) | TEOS (µl) | QDs CdTe (µl) | NH₄OH (µl) | APTES (µl) | H₂O (µl) |
|-------------|-----------|---------------|------------|-----------|---------|
| 15          | 150       | 80            | 400        | 0         | 700     |
| 15          | 150       | 80            | 400        | 1.5       | 700     |
| 15          | 150       | 80            | 400        | 3         | 700     |
| 15          | 150       | 80            | 400        | 4.5       | 700     |

Table 2. Amounts of substances for survey by amount change of NH₄OH

| Ethanol (ml) | TEOS (µl) | QDs CdTe (µl) | NH₄OH (µl) | APTES (µl) | H₂O (µl) |
|-------------|-----------|---------------|------------|-----------|---------|
| 15          | 150       | 80            | 200        | 3         | 700     |
| 15          | 150       | 80            | 400        | 3         | 700     |
| 15          | 150       | 80            | 600        | 3         | 700     |
| 15          | 150       | 80            | 800        | 3         | 700     |

Table 3. Amounts of substances for survey by amount change of H₂O

| Ethanol (ml) | TEOS (µl) | QDs CdTe (µl) | NH₄OH (µl) | APTES (µl) | H₂O (µl) |
|-------------|-----------|---------------|------------|-----------|---------|
| 15          | 150       | 80            | 400        | 3         | 300     |
| 15          | 150       | 80            | 400        | 3         | 500     |
| 15          | 150       | 80            | 400        | 3         | 700     |
| 15          | 150       | 80            | 400        | 3         | 900     |

Fig.2. TEM image of CdTe@SiO₂ nanoparticles.
The measurement of absorption spectra in UV – VIS region of the CdTe quantum dots and CdTe@SiO$_2$ nanoparticles was performed at room temperature. Figure 3A và 3B presents the absorption spectra of CdTe quantum dots and CdTe@SiO$_2$ nanoparticles with the same concentration of CdTe quantum dots. The absorption spectrum of CdTe@SiO$_2$ nanoparticles is a sloping line that has not absorption peak in comparison with that of CdTe quantum dots. This can be explained that due to the interaction between CdTe quantum dots and host silica matrix, and the distribution of quantum dots in one silica particle is inhomogeneous; the absorption peak of CdTe@SiO$_2$ nanoparticles cannot be observed. The absorbance of CdTe@SiO$_2$ nanoparticles is higher than that of CdTe quantum dots due to the contribution of absorption of silica matrix.

The results in our work show that, coating silica shell hardly affects on emission wavelength from CdTe quantum dots. The shape of fluorescence spectra of CdTe@SiO$_2$ nanoparticles is similar to that of uncoated CdTe quantum dots. However, ratios of substances participating in the reaction have significant influence on perform of CdTe@SiO$_2$ nanoparticles and their fluorescent intensities.

3.1. Effects of APTES Electric Neutralizer

Firstly, we prepare silica-coated CdTe/ZnS quantum dots, but in coating silica process APTES is not used (non APTES CdTe/SiO$_2$). Figure 4 shows a comparison of the fluorescence spectra of CdTe/ZnS quantum dots and that of silica-coated quantum dots non APTES.

Figure 4 presents the fluorescence spectra of CdTe@SiO$_2$ nanoparticles prepared with various amounts of APTES. It can be seen that, the appearances of fluorescence spectra of CdTe@SiO$_2$ nanoparticles prepared with different APTES amounts are almost unchanged compared to that of uncoated CdTe quantum dots. But there is significant
difference in emission intensity of CdTe@SiO$_2$ nanoparticles samples prepared with and without APTES. When APTES was used in during the silica coating reaction, the resulted CdTe@SiO$_2$ samples have a much greater fluorescence intensity than that of non APTES CdTe@SiO$_2$. This shows the role of a neutralizer in the coating of silica for quantum dots. The APTES helps silica shells growing on the surface of the quantum dots. When coated with silica shell, quantum dots become more stable, their surface is not damaged, the emission efficiency increases. In our experiment, with 3 samples using APTES amounts of 1.5; 3 and 4.5 µl, the sample using 3 µl has the highest fluorescence intensity. Samples with lower (1.5 µl) and higher (4.5 µl) APTES amounts give lower fluorescence intensity. Following this result, we choose neutralizing agent APTES amount of 3 µl for the next experiments.

**3.2. Effects of NH$_4$OH Amount**

In the Stöber method, the amount of NH$_4$OH catalyst plays an important role for the granulation process, it both provides water for the hydrolysis reaction and creates a high pH environment to promote condensation. To investigate the effect of the amount of catalyst on the formation and optical properties of silica nanoparticles containing quantum dots, we fabricated samples with different catalyst amounts. The amounts of other substances is given in Table 2.

![Fig 4. Comparison of fluorescence spectra of quantum dots CdTe/ZnS and CdTe@SiO$_2$ non APTES](image)

![Fig 5. Fluorescence spectra of CdTe@SiO$_2$ with various amounts of APTES](image)

![Fig 6. Comparison of fluorescence spectra of CdTe@SiO$_2$ nanoparticles with catalyst content of 200 and 400 µl versus the fluorescence spectra of uncoated CdTe/ZnS quantum dots.](image)
Fig. 6 shows the comparison of fluorescence spectra of CdTe@SiO₂ nanoparticles with catalyst content of 200 and 400 µl versus the fluorescence spectra of uncoated CdTe/ZnS quantum dots. It can see that fluorescence intensity of 200µl-catalyzed CdTe@SiO₂ sample is stronger than that of uncoated silica quantum dots. In our opinion, with a small amount of catalyst, hydrolysis reaction is incomplete, CdTe dots are coated with siO₂, but the shell is thin, protected by thin shell quantum dots have strong emission. This result on fluorescence spectra of CdTe@SiO₂ nanoparticles is worth noting because the emission intensity is mostly lower comparing with uncoated CdTe quantum dots. But TEM images of CdTe@SiO₂ nanoparticles (Fig.7) reveal that at NH₄OH amount of 200 µl (fig.7a) the particles do not have good dispersion, the sample has many small particles and there is clustering phenomenon, creating large particles. This can be explained that, at the little amount of NH₄OH catalyst, it is not enough for a complete hydrolysis reaction. At higher catalysts amount (400 µl), the samples have good dispersion, the particles are spherical and uniform in size (Fig.7b).

Following this result, amounts of NH₄OH catalyst in our experiments have to be of 400 µl or more.

Fig.8 depicts fluorescence spectra of CdTe @ SiO₂ nanoparticles with different amounts of catalysts. The fluorescence intensity of CdTe@SiO₂ samples all decreased compared to that of the uncoated CdTe/ZnS sample, but the fluorescence intensity reduction in samples with 400 µl and 600 µl NH₄OH are not significant.

Fig.8. Fluorescence spectra of CdTe @ SiO₂ nanoparticles with different amounts of catalyst.
The fluorescence intensity of the sample decreases with increasing amount of the catalyst. This result is believed to be the initial CdTe quantum dots without silica coating, dispersed well in distilled water with a pH of 5.0 to 7, when increasing NH₄OH catalyst amount, the pH of the medium increases, influences to the emission of quantum dots. Following this result, NH₄OH catalyst in our experiments has amount of 400 µl or higher. Therefore, silica nanoparticles formed are spherical, uniformly size and fairly dispersed. So the in order to prepare samples with the best fluorescence, the amount of catalyst is an important factor. In our experiment, the catalyst amount of 400 µl is optimal, which corresponds to the molar ratio of NH₄OH: TEOS to 2.6. This result is close to the report of Yoshio Kobayashi [26].

3.3. Effects of water amount

The total amount of water in the silica hydrolysis reaction affects the size and the number of formed particles. When water amount in hydrolysis reaction changes, the shape, size, and the dispersion of CdTe@SiO₂ nanoparticles also diversified. The amounts of other substances is given in Table 3.

Fig.9 shows TEM images of CdTe @ SiO₂ nanoparticles with different water content. The H₂O amount of 300 µl is not enough for the hydrolysis reaction to totally occur, the SiO₂ particles have not been formed but only form clusters of different sizes. The increase of water amount promotes the hydrolysis reaction, the number of Si molecules Si(OC₂H₅)₄(OH)x increases rapidly until a saturation value is reached. At 500 µl of water, the particles are relatively formed, but the particles are still not completely spherical, not very well dispersed and have a clustering phenomenon. With 700 µl of water, the desired particle sizes can be controlled by amount of water in the reaction.

The fluorescence spectrum of CdTe@SiO₂ nanoparticles (fig.10) reveal that the photoluminescent intensity of the samples tends to decrease as the amount of water increased, except for water amount of 300 µl. Increasing of water amount corresponds to increasing of SiO₂ particle size. The silica particle size increases corresponding to the thickness of the silica shell surrounding CdTe/ZnS quantum dot being thicker. The thick SiO₂ layer is cause a deterioration in the optical properties of the quantum dots, the emission of quantum dots is obstructed by a thick silica shell. At 500 µl H₂O, the water amount is enough for the hydrolysis reaction, so silica particles have formed, quantum dots are protected by the silica shell, that prevent the influence of the solution environment to quantum dots, resulting in increased their fluorescences. With less water (300 µl), the silica particles do not form, leading to quantum dots are affected by the environment, resulting in lower intensity fluorescence emission.

![Fig.9. TEM images of CdTe @ SiO₂ nanoparticles with different water content: 300 µl (a), 500 µl (b) and 700 µl (c).](image-url)
In summary, using the Stöber method to coat quantum dots by silica shell, the amount of water and the amount of other substances involved in the reaction plays an important role in the formation of single dispersed particles as well as optical properties of silica nanoparticles containing quantum dots. In our experiment, the ratio of amount reaction participants ethanol: TEOS:solution of QDs:NH4OH:APTES:H2O which to formation samples with uniformly sized particles, good dispersion and fluorescence being stronger than that of uncoated quantum dots was 1.5:1.5×10^{-2}:0.8×10^{-2}:4×10^{-2}:3×10^{-4}:5×10^{-2} by volume.

4. Conclusion

The SiO2 nanoparticles containing CdTe/ZnS quantum dots (CdTe@SiO2) have been synthesized successfully via Stöber method. By detailed investigating manufacturing process we found the ratio of substances involved in the reaction to preperate silica nanoparticles containing quantum dots of CdTe/ZnS of good quality. The CdTe@SiO2 nanoparticles have good emission, mono-dispersion, and good stability in solution. Fluorescence being stronger than that of uncoated quantum dots, this result is worth noting because the emission intensities were mostly lower comparing with that of uncoated CdTe quantum dots. This indicates that the prepared CdTe@SiO2 nanoparticles are suitable for bioapplications.

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