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Research Article

Thickness-Controllable Silica Coating of CdTe QDs by Reverse Microemulsion Method for the Application in the Growth of Rice

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Herein, we report the synthesis and surface modification of CdTe quantum dots (QDs) and the application in the rice growth. Water-soluble thioglycolic acid (TGA) stabilized CdTe quantum dots were synthesized firstly and then the surface modification was conducted. II–VI semiconductor nanocrystals prefer to be coated with silica as inert materials to improve their chemical properties. The toxicity of QDs reduced after the modification. Silica coated QDs were used in the growth of rice seed and the effect was discussed. In our knowledge it is the first time we report that the silica coated QDs had nice effect on the growth of rice.

1. Introduction

Colloidal II–VI semiconductor nanocrystals (quantum dots) have shown nice size-dependent optical properties with narrow bandgap [1] like CdS [2], CdSe [3], CdTe [4], CdHgTe [5], HgTe [6], and ZnSe [7] which exhibit great potential as a labeling material due to their unique size-tunable photoluminescence. In the past 20 years, great progress has been made in the synthesis of the quantum dots, and the quantum dots have applications for fluorescent biological research [8–12].

However, QDs have disadvantages in their applications: toxicity due to the heavy metal ions [13], the chemical stabilities, and oxidation in the surface area. To solve these problems, coating QDs with inert materials like silica would be a good choice [14]. Silica coating of semiconductor nanocrystals has received specific effects [15–17]. The methods of silica coating can be divided into two groups, that is, the reverse microemulsion method and Stober method. For the aqueous QDs, the reverse microemulsion (water in oil) can be used in silica coating with better controlling of particle size than the Stober method. As for the Stober method, the silica sphere is usually large as 200 nm and bigger. By the reverse microemulsion method, the particle size can be controlled in a range of 30–150 nm [18] so that the reverse microemulsion method is more suitable. In our reported work, not only 40 nm of silica coating can be synthesized but also 400 nm of silica coating can be synthesized by the reverse microemulsion method.

In the past ten years, nanotechnology and nanomaterials were widely applied as life science [19]. But the research about their applications in agriculture began relatively late. Some work reported that silver nanoparticles reduced bacterial contaminations during tissue culture of *Araucaria excelsa* var. Glauca [20]; multiwall carbon nanotubes (MWNTs) had the ability to enhance the proliferation of callus cells of tobacco (*Nicotiana tabacum*) and make tomato produce two times more flowers and fruits [21, 22]; TiO_2 and MWNTs significantly promoted the germination, seedlings growth of tomato (*Lycopersicon esculentum*), and spinach (*Spinacia oleracea*) [23, 24]. Khodakovskaya et al. even illustrated

MWNTs have the potential to act as plant growth regulators [22]. Some results proved several kinds of nanomaterials had the positive effects at every stage of plant life cycle and showed great capacity to regulate the plant growth and development. We investigated that silica coated CdTe QDs had good effects on the rice root growth.

2. Experimental Section

2.1. Chemicals. Cd $(CH_3COO)_2*2H_2O$ (Aldrich, 99%), tetraethyl orthosilicate (TEOS) (98%), thioglycolic acid (TGA) (98%), sodium hydroxide, polyoxyethylene octyl phenyl ether (TritonX-100), cyclohexane, n-hexanol, ethanol, and ammonium solution were purchased from Sigma-Aldrich.

2.2. Synthesis of CdTe QDs Stabilized by Thioglycolic Acid. CdTe QDs were synthesized according to the method reported previously [25]. First of all, 0.08 mmol of Na_2TeO_3, 0.4 mmol of Cd $(CH_3COO)_2*2H_2O$, and 160 mg of $NaBH_4$ were prepared. Secondly, the Cd $(CH_3COO)_2*2H_2O$ was dissolved in 50 mL deionized water and then poured into a flask with a magnetic bar. The solution was kept stirring. After that 100 mL of deionized water was added followed by the 36 μL of TGA into the flask. Then the pH of the solution was adjusted to 11.5 by 2 M NaOH (several drops); next the Na_2TeO_3 was dissolved in 50 mL deionized water. After 5 minutes, Na_2TeO_3 with $NaBH_4$ was added to the solution; other five minutes later, the flask was connected to a reflux condenser and through the opening at 100°C—up to 1 to 7 hours under air conditions. Finally, after cooling the filtered solution was poured into the bottle and stored in 4°C without washing.

2.3. Synthesis of Silica Coated CdTe QDs. Silica coated QDs were prepared according to previous reports by the reverse microemulsion method [16]. In detail, 4 mL of the solution prepared CdTe QDs was washed one time by 4 mL of isopropanol. The microemulsion solution was combined by 15 mL of cyclohexane, 2.25 mL of Triton X-100, and 1.5 mL of n-hexanol under the N_2 atmosphere for half an hour (solution 1). Then 40 μL of ammonia solution (25% by weight) was introduced and several drops of 1 M NaOH were added to make the pH to 12 (solution 2). The washed CdTe QDs dissolved in 1 mL of solution 2 (solution 3). Then the solution 3 was introduced into the prepared solution 1 (microemulsion liquid system). After 10 minutes of stirring, fixed amount of PDDA was introduced. 200 μL TEOS was introduced under vigorous magnetic stirring. The reaction system was then sealed and kept in the dark; mixture was stirred at room temperature for 3 days. Isopropanol, ethanol, and water were used for washing the CdTe @ silica composite particles. In each washing process, a sonicator was needed. Firstly the ratio 1 : 1 with isopropanol was centrifuged; after that the precipitate was dissolved in the ethanol and deionized water. Finally CdTe @ silica composite particles were dissolved in the deionized water stored in 4°C.

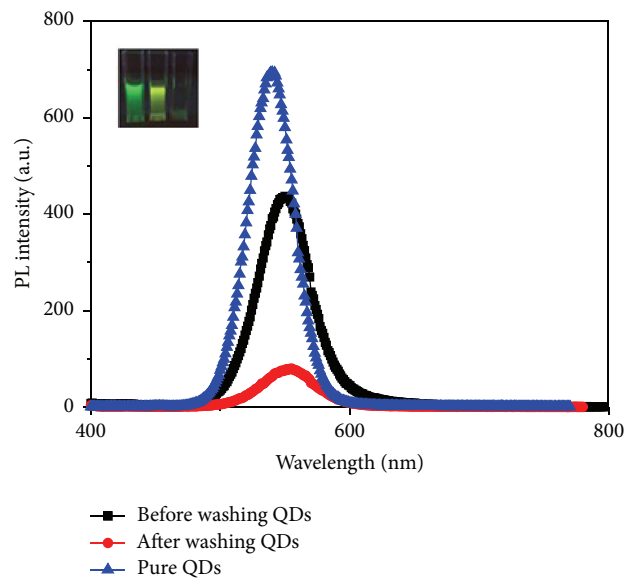


Figure 1: Fluorescence spectra of pure uncoated QDs, silica coated before washing QDs, and silica coated after washing QDs.

2.4. Rice Seed Germination and Root Development. Rice (*Oryza sativa* cv. 'Nanjing 45') seeds were immersed in a 0.1% potassium permanganate ($KMnO_4$) solution for 24 h for sterilization. After rinsing three times with deionized water, the seeds were soaked in 100 mL 1/2 MS solution with silica coated QDs suspensions at various concentrations (0.13 μM, 0.26 μM, and 0.52 μM) in thermostat incubator (25 ± 1°C, 60% rH, and 16/8 light/day) for germination, which 1/2 MS with no silica coated QDs was used as a control. The root length was measured at 8, 11, and 15 days after treatment. Each treatment was conducted with thirty seeds, and the results were presented as increasing percent of ten seedlings root length average from 8 to 11 and 11 to 15 days.

2.5. Characterizations. Steady-state photoluminescence (PL) spectra were measured on an Edinburgh Instrument FLS920P fluorescence spectrometer. TEM machine model used for the images of CdTe@SiO_2 is Philips-CM20 with the operation voltage 200 kV.

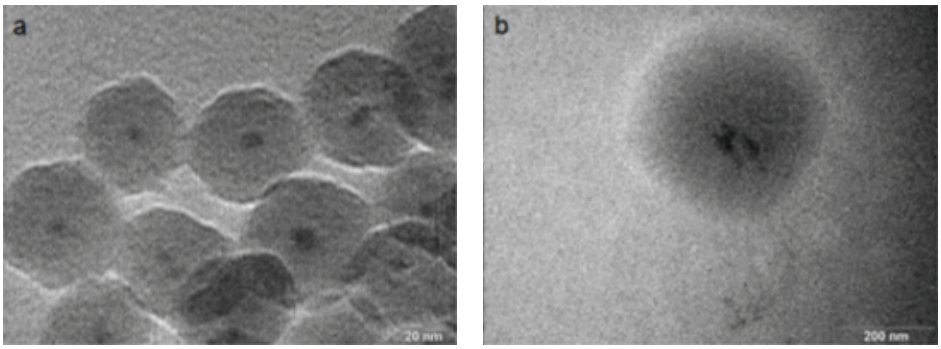
3. Results and Discussion

3.1. Silica Coating of CdTe QDs and Thickness Controlling. The fluorescence spectra and particles before and after silica coating were shown below in Figure 1.

After the reverse microemulsion method, the silica coated QDs are oil-soluble. After being washed in the ethanol and water, water-soluble silica coated QDs were available. After the washing, the amounts of QDs reduced so that the PL intensity decreased.

Transmission electron microscopy (TEM) images of silica coated QDs sample were presented in Figure 2.

As Figure 2 showed the nice effect with the coating is spherical and uniform. The chemical properties of QDs may



(a) (b)

Figure 2: TEM images of samples of good silica coating of QDs under the suitable adjustment of conditions. (a) The size of silica is 40 nm; (b) the size of silica is 400 nm.

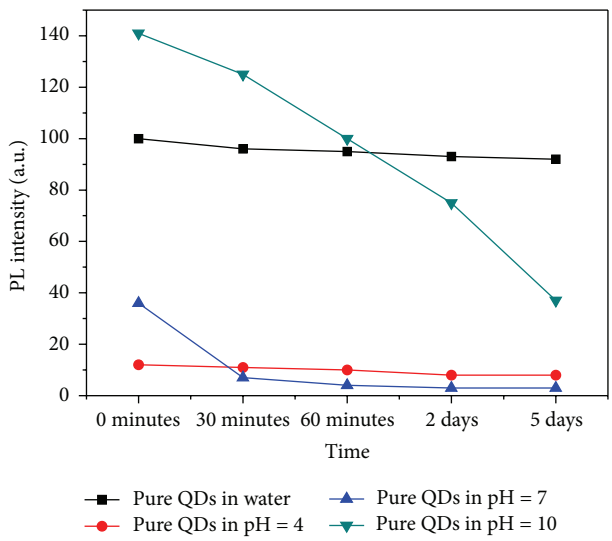


Figure 3: PL spectra of pure QDs in the different buffers tested for different times.

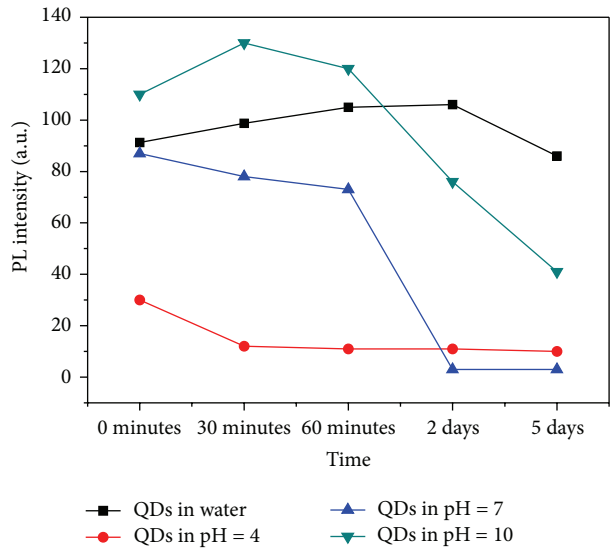


Figure 4: PL spectra of silica coating of QDs in the different buffers tested for different times.

be better and also the stability. What is more, we can adjust the thickness of silica coating by controlling the amount of TEOS; the thickness of the silica coating is as large as 400 nm in comparison to the previous 40 nm.

3.2. Stability Test between the Pure Uncoated QDs and Silica Coated QDs. The pure CdTe and silica coated after washing CdTe QDs were tested for stability in water and the buffers with different pH (4, 7, and 10 corresponding) for 4 days. Results are presented in Figure 3 for uncoated samples and in Figure 5 for silica coated.

From Figure 3 we can realize that the pure QDs in the water are stable, in the buffer with pH = 10 had an increase of PL than that of in the water, in the buffers with pH = 7 and pH = 4 are of low PL compared to that of in the water. What is more, the buffer with pH = 4 can quench the QDs in a short time, which implied that the QDs are sensitive to the pH of solution.

From Figure 4 we can observe that the PL of silica coated QDs in the buffer with pH = 10 had a slight increase at first compared to the pure uncoated QDs in the pH = 10. And the PL of silica coated QDs in the buffer with pH = 7 had a higher increase than the pure QDs in the pH = 7. And the PL of silica coated QDs in the buffer with pH = 4 was slightly higher than the pure uncoated QDs. With the good effect we can infer that the stability of silica coated QDs is better than the pure uncoated QDs.

3.3. Rice Seed Germination and Root Development. Each treatment was conducted with thirty seeds, and the results are presented as increasing percent of ten seedlings root length average from 8 to 11 and 11 to 15 days.

As we can observe from Figure 5 that the rice roots with silica coated QDs were longer than the rice roots without silica coated QDs inside. The pure QDs significantly inhibited the growth of root due to its toxicity. The different increment

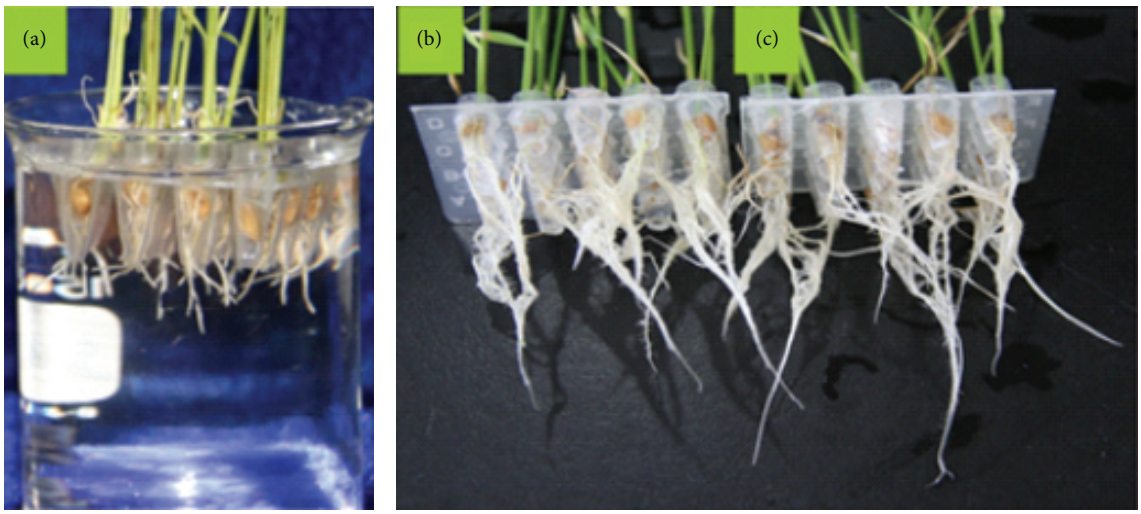


Figure 5: Image of rice roots (a) with pure QDs; (b) without QDs; and (c) with silica coated QDs.

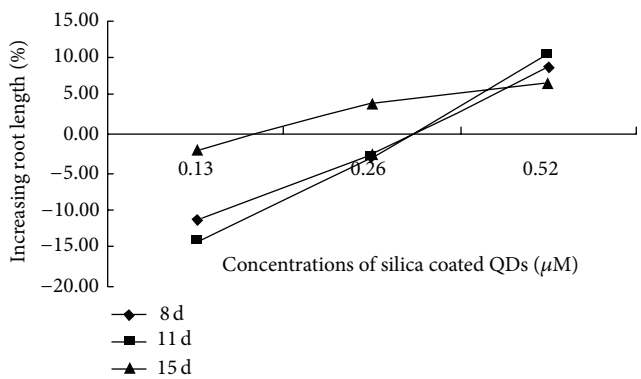


Figure 6: Effects of silica coated QDs at different concentrations on rice root length.

of different concentrations of silica coated QDs was shown below as Figure 6.

To test the action of the synthesized silica coated QDs, we placed the seeds in 1/2 Murashige and Skoog solution supplemented with different concentrations of silica coated QDs (0.13 μM, 0.26 μM, and 0.52 μM). As shown in Figures 5 and 6, all the treatments led to the growth of the increasing percent of root length. Silica coated CdTe QDs did not have toxic effect but promoted root elongation of rice seedlings. The roots grew faster in shorter time under low concentrations. The results were different from many other researches about the nanomaterials affecting the plant growth [26–29]. Many investigations in the past were negative mainly due to the toxicity of nanoparticles. For example, TiO_2 nanoparticles significantly inhibited the germination rates, root lengths, and biomasses of tobacco seedlings [30]. Iron ions/NPs did not affect the physiological parameters with respect to water control. Conversely, Cu ions/NPs reduced water content, root length, and dry biomass of the lettuce plants [31]. Toxicity of CuO NPs was mainly due to NPs solubilization in the media [32]. However, there are some nanoparticles that can promote the growth of plant. Iron nanoparticles can enhance root elongation of *arabidopsis thaliana* by triggering cell wall loosening [33]. Silica coated QDs are minority nanomaterials that are helpful in the growth of plants. And the mechanism needs to be further studied.

4. Conclusion

Silica coating of CdTe QDs particles has successfully been prepared by a reverse microemulsion method and the thickness of silica sphere can be varied from 40 nm to 440 nm. The amount of TEOS is critical for the experiments. The stability test was made which approved the better stability of silica coated QDs than pure uncoated QDs. At last the 40 nm size of silica coated CdTe QDs had good effect on the rice roots growth for the first time reported.

Conflict of Interests

The authors declared that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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