

Wet-Chemical Synthesis of ZnTe Quantum Dots

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ABSTRACT

ZnTe quantum dots (QDs) have been very attractive because of their potential applications in optoelectronic devices operating in the blue-green region of the spectrum. This paper describes a convenient one-step synthesis of high-quality ZnTe QDs in high-temperature organic solution with high yield. Anhydrous zinc chloride was dissolved in phenyl ether under argon protection and oleic amine was used as coordinating agent. Complex solution of metal tellurium in trioctylphosphine (TOP) was injected into the hot reaction mixture as a source of tellurium. The reaction was complete in several minutes and the resulting QDs were isolated by centrifugation and re-dispersed in hexane. The produced spherical ZnTe QDs are monodispersed and their sizes could be controlled simply by varying the growth temperature. The morphology and phase structure were investigated using TEM and XRD. Photoluminescence (PL) spectra were also studied and quantum size effects were observed as well.

INTRODUCTION

Nanomaterials have drawn enormous interest from the scientific community because of their novel electronic, magnetic, optical, chemical and mechanical properties, which make them highly attractive for many important technological applications. Of the various types of nanocrystals, semiconductor nanocrystals have been the most intensively studied because of their quantum confinement effects and size- / shape-dependent photoemission.¹ ZnTe quantum wells (QWs) and quantum dots (QDs) have been very attractive due to their potential applications in optoelectronic devices operating in the blue-green region of the spectrum². The development of uniform nanometer-sized semiconductor QDs is essential in fabricating novel materials for electronic applications. Wet chemical growth of semiconductor QDs in high-temperature solution has been demonstrated as a powerful method to control the crystallinity, morphology, size and size distribution. However, such studies on the preparation of colloidal ZnTe QDs are very limited,³⁻⁶ most likely owing to a lack of appropriate synthetic approaches. Y.-W. Jun and co-workers reported a route for preparing ZnTe QDs based on thermolysis of organometallic compound.³ Direct combination reaction of metal zinc and tellurium has also been investigated for this purpose.^{5,6} However, all these processes need either considerably high-temperature or long reaction time.³⁻⁶ Furthermore, the morphology of resulting QDs was not satisfying. Synthesis of high quality of ZnTe QDs is still essential.

In this report, we describe a convenient wet-chemical approach to synthesize size-controlled ZnTe QDs in organic solution simply using ZnCl₂ and metal tellurium as the reactants. The reaction temperature is relatively low and the resulting ZnTe QDs are well crystallized with a quasi-spherical shape. We realize that oleylamine plays a very important role in the reaction. We also investigate the morphology and phase structure.

EXPERIMENT

Metal tellurium (99.99%), trioctylphosphine (TOP), oleylamine (70%) were purchased from Aldrich and used as received. ZnCl_2 anhydrous was dried in an oven at $130\text{ }^\circ\text{C}$ for one week before use. The morphology and phase structure were observed using a transmission electron microscope (TEM) (JEOL 2010) operating at 120 kV and an X-ray diffractometer (XRD) (Philips X-pert system) operating with a $\text{Cu K}\alpha$ ($\lambda = 0.1541\text{ nm}$) X-ray source. The UV-Vis absorption spectra were recorded with an Agilent 8453 spectrophotometer and photoluminescence spectra were determined with a Perkin-Elmer LS45 Luminescence spectrometer.

The detail of a typical synthesis of ZnTe QDs is described as the follows. 0.136 g of ZnCl_2 (1 mmol,) was added to the mixture of phenyl ether (15 mL) and oleylamine (1.0 mL) at room temperature and the resulting system was gradually heated to $150\text{ }^\circ\text{C}$ under vacuum, forming a homogeneous and clear solution. A 0.5M Te-TOP stock complex solution was pre-prepared by stirring metal tellurium and tri-n-octylphosphine (TOP) at room temperature in a glove box. 1.0 mL of Te-TOP stock solution was injected into the Zn-oleylamine complex solution when the temperature of the system was increased to $210\text{ }^\circ\text{C}$. The resulting mixture was then heated at $210\text{ }^\circ\text{C}$ for 5 minutes. ZnTe QDs were subsequently separated by adding excessive ethanol followed by centrifugation. The ZnTe colloids were re-dispersed in hexane, producing a clear QD suspension solution with yellow color.

DISCUSSION

As prepared, ZnTe QDs exist in a quasi spherical-shape with a particle-size of 6~9 nm as showed in TEM (Fig. 1). In most cases, oleic acid was used as a stabilizing agent in high-temperature organic solution approach. However, we realized that the presence of oleylamine was one of the key factors to form ZnTe QDs. Oleic acid without oleylamine would not result in a formation of any QDs. If a mixture of oleic acid and oleylamine was introduced into the reaction, no ZnTe QD formed, either. The freshly prepared QD colloidal suspension was pale yellow. It usually slowly turned dark brown in one or two days due to the possible QD aggregation. If a little bit of TOP was added into the colloidal system immediately after preparation, the aggregation process could cease; whereas addition of oleylamine didn't stop the aggregation. We therefore believe that TOP acts as capping ligand, whereas oleylamine plays a role of not only a coordinating agent to form Zn-oleylamine complex but also a reducing agent in the reaction. Previous studies indicated that a direct reaction between metal zinc or zinc salts and tellurium could result in very little ZnTe QDs leaving most reactant unreacted⁵. Yadong Li etc. suggested that this might be due to the fact that tellurium was not easily to be reduced to anion. They employed hydrazine as the reducing agent as well as the solvent, and obtained ZnTe Nanorods.⁵ In our investigation, we used oleylamine, which coordinated with zinc anion, to enable the dissolution of ZnCl_2 in organic solvent and to act as reducing agent simultaneously to promote the formation of ZnTe QDs.

The reaction temperature is another important parameter. In temperature range of $170\text{-}210\text{ }^\circ\text{C}$, we observed that the higher temperature, the smaller QDs produced. Fig.1 shows TEM images of

roughly- spherical shaped ZnTe QDs with average sizes of $6.2 (\pm 0.8)$ and $7.9 (\pm 0.9)$ nm for samples grown at 190 and 170 °C, respectively. It is generally believed that, for a primarily formed single-phase crystal with ultra-small size, their surfaces must be polyhedral containing high-index crystallography planes⁷ which have a tendency to grow along direction(s) where the crystallography facet(s) possess low surface energy. Based on this consideration, a dynamic injection technique has previously been developed to control the size of QDs.⁸⁻¹⁰ It involves multiple injections of portions of pre-stocked precursor solution into hot reaction system in certain intervals of time to maintain continuous growth of QDs. Using this technique, we have successfully tuned the average size of ZnTe QDs up to 15 nm in diameter. The average sizes of crystallites estimated from XRD patterns by the Scherrer equation are close to those calculated from TEM images.

The resulting QDs possess high crystallinity. Powder X-ray diffraction (XRD) and TEM selected area electron diffraction (SAED) patterns are shown in Fig 2. All detectable diffraction peaks/rings can be indexed from the cubic structure ZnTe, and the cell parameter was in good agreement with the reported data (Joint Committee on powder Diffraction standers card no. 15-764). No characteristic peaks of Zn or Te were observed.

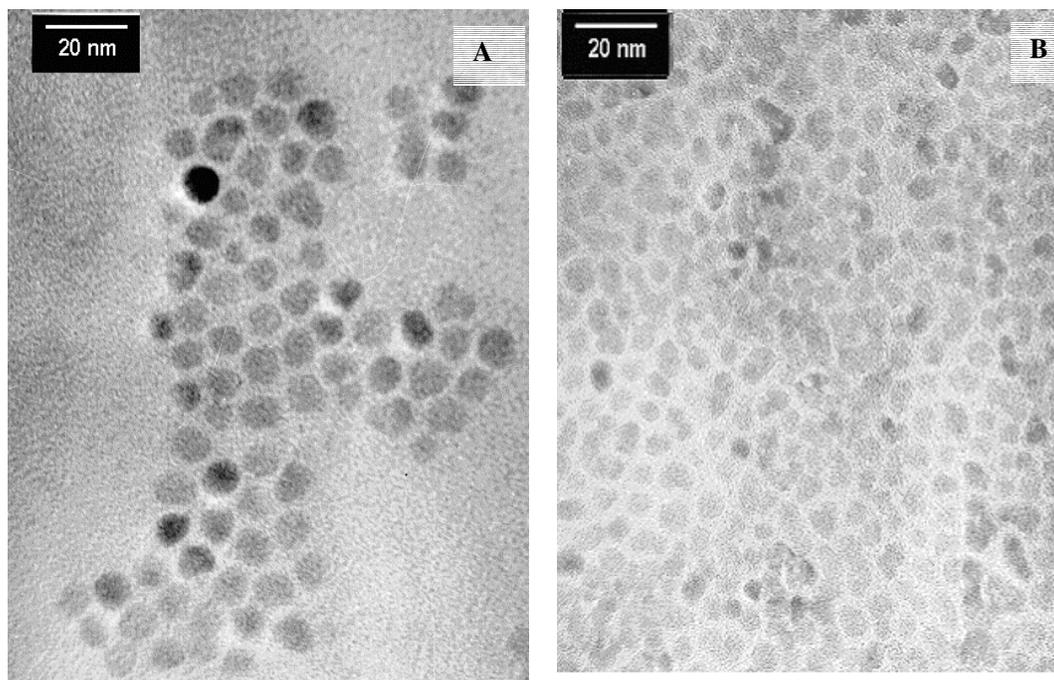


Fig.1 TEM Images of ZnTe quasi- spherical QDs grown at (A) 170 °C and (B) 190°C

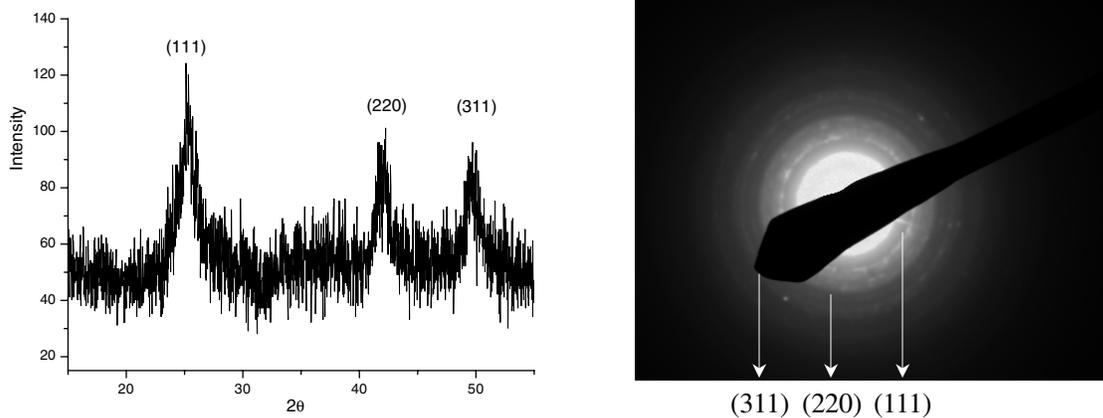


Fig.2 (A) Powder X-ray diffraction (XRD) pattern of ZnTe QDs, and (B) TEM selected area electron diffraction (SAED) pattern of ZnTe QDs

Optical properties were also investigated by UV absorption and photoluminescence. Fig.3 shows optical spectra of ZnTe QDs prepared at different growth temperatures. It is well known that the exciton Bohr radius (R_B) plays an important role in quantum confinement effect. If $R/R_B < 4$ (R is the radius of particles), the quantum confinement is very obvious. For ZnTe, the calculated R_B is about 6.2 nm.¹¹ In our synthesis, the R/R_B of the resulting ZnTe QDs is much smaller than 4. Therefore, ZnTe QDs have a relatively strong quantum confinement effect and exhibit remarkable blue-shift in photoluminescence compared to the position of the 548 nm (2.26 eV) of bulk ZnTe. Similar blue shifts are also observed in UV-VIS absorption.

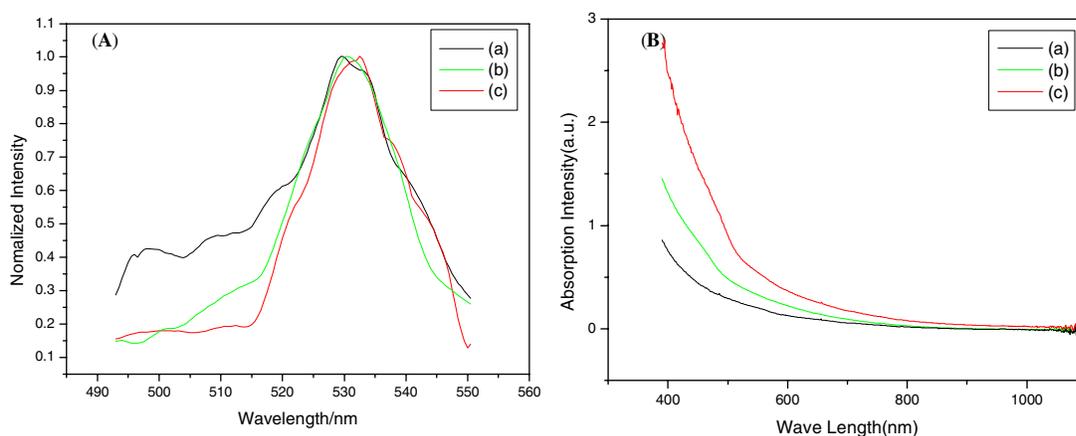


Fig.3 Optical spectra of ZnTe QDs grown at (a) 170 °C, (b) 190 °C, (c) 210 °C respectively. (A) Photoluminescence spectra, (B) UV-VIS absorption spectra

CONCLUSIONS

In conclusion, we have developed a convenient wet chemical method to prepare high-quality ZnTe QDs in a high-temperature organic solution system with considerably high yield. The average size of the resulting ZnTe QDs can be controlled simply by varying the

growth temperature and by employing a multi-injection technique. The morphology and phase structure were also investigated using TEM and XRD. Optical spectra were studied and quantum size effects were observed as well.

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