Journal of Crystal Growth 409 (2015) 10–13

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Inclusion of CdS quantum DoT into beta-cyclodextrin crystal by simple rapid crystallization

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ARTICLE INFO

Article history:
Received 13 March 2013
Received in revised form
10 September 2014
Accepted 13 September 2014
Communicated by K. Deppert
Available online 20 September 2014

Keywords:
A1. Low dimensional structures
A1. Nucleation
A2. Growth from solution
B1. Oxides

ABSTRACT

Inorganic molecules have seldom been included into cyclodextrin crystal. Here in this paper we report the first example of including CdS quantum dots into cyclodextrin crystal by simple rapid crystallization. A CdS quantum dot/cyclodextrin composite has been obtained, in which quantum dots of CdS are embedded in β-cyclodextrin (β-CD) crystal. Experiments have proven that it is the rapid crystallization of cyclodextrin in acetone that results in the formation of abundant cyclodextrin nuclei, which include CdS dots into them forming the CdS quantum dot/cyclodextrin compostie. This research opens the new research field of inorganic species/cyclodextrin inclusion complex.

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1. Introduction

Cyclodextrin has been widely used as host molecules for including food, medicine and surfactants in applied science. Numerous organic guest molecules have been included into the bucket-like hydrophobic cavity of cyclodextrin [1–8], while inclusion of inorganic molecules into cyclodextrin crystal has seldom been reported. Although some papers aimed at the combination between cyclodextrin and inorganic molecules, usually cyclodextrin molecules and the inorganic molecules were combined by chemical bonding, and therefore this kind of combination cannot be regarded as inclusion of inorganic particle into cyclodextrin crystal [9,10]. So far to our knowledge, only three groups have reported the inclusion of single inorganic molecule into cyclodextrin crystal. Kwak reported inclusion of single $Fe(OAc)_2$ molecule into cyclodextrin forming cyclodextrin–$Fe(OAc)_2$ nanospheres via a physical route [11]. Gatteschi reported inclusion of single γ-Fe_2O_3 molecule into γ-cyclodextrin forming γ-Fe_2O_3/γ-cyclodextrin nanospheres via a physical route [12]. And we reported the inclusion of $Mo_xO_y^{n-}$ into β-cyclodextrin (β-CD) molecules by rapid crystallization [13]. This physical route is simple and efficient. However, the formation mechanism of such an inorganic single molecule/cyclodextrin inclusion complex via the simple physical route is still unknown. Investigation into the formation mechanism of this inclusion complex will be important and also challenging.

In our previous paper, we reported that single inorganic molecule of $Mo_xO_y^{n-}$ can be embedded between β-cyclodextrin (β-CD) molecules forming a $Mo_xO_y^{n-}$/β-CD inclusion complex when β-CD crystallized rapidly either in ice water or in a poor solvent [13]. Experiments proved that it was rapid crystallization of β-CD that lead to formation of surplus β-CD nuclei, which immediately included single inorganic $Mo_xO_y^{n-}$ molecule into them forming this inclusion complex. Therefore we can anticipate that other inorganic single molecules can also be embedded into β-CD crystal forming inorganic single molecule/β-CD inclusion complexes by this simple rapid crystallization method. We expect that CdS quantum dot can be embedded into β-CD crystal by this rapid crystallization method. Our synthesis strategy is as follows: When aqueous solution of $CdCl_2$, Na_2S and saturated β-CD are mixed, precipitation of CdS and crystallization of β-CD will go at the same time in this reaction system. We propose that if β-CD crystallizes under a naturally cooling speed, a hybrid crystal of β-CD and CdS will be obtained, in which CdS and β-CD pack into thick layers and no CdS/β-CD inclusion complex can be obtained. While when β-CD rapidly crystallizes in a poor solvent, a CdS/β-CD inclusion complex may be obtained, in which CdS quantum dot can be embedded in β-CD crystal. Experiments proved this suggestion. A CdS quantum dot/cyclodextrin composite has been obtained, in which CdS quantum dots of several nanometers in size have been embedded between the cyclodextrin molecules. Experiments proved that it was the rapid crystallization of β-CD in

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http://dx.doi.org/10.1016/j.jcrysgro.2014.09.022
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acetone that lead to such an unusual composite: When enough acetone was introduced, β-CD rapidly crystallized and abundant β-CD nuclei appeared immediately. These β-CD nuclei included CdS nanoparticles into them simultaneously. Therefore before the CdS nanoparticles grew into big particles, they had been included into β-CD molecules and a novel CdS quantum dot/β-CD composite was fabricated. To the best of our knowledge, this is the first example that CdS quantum dot can be embedded into cyclodextrin crystal via a simple physical route. This research opens the new research field of inorganic single molecule/cyclodextrin inclusion complex and also makes it possible to obtain uniform, size-controllable and stable quantum dot materials by using cyclodextrin as template via a green and efficient way.

2. Experimental procedure

2.1. Preparation of compound 1

60 g β-CD (β-cyclodextrin) and 5.7 g $CdCl_2 \cdot 2.5H_2O$ (0.025 mol) were dissolved in 500 ml deionized water by heating at about 80 °C for about 20 min. 6.5 g $Na_2S \cdot 9H_2O$ (0.027 mol) was dissolved in 300 ml deionized water. The two solutions were mixed and copious orange yellow precipitate was formed soon. The mixed solution was cooled in air for crystallization. After one day, the crystals were collected and washed with deionized water. The yellow crystal thus obtained was named compound 1.

2.2. Preparation of compound 2

120 g β-CD and 11.4 g $CdCl_2 \cdot 2.5H_2O$ (0.05 mol) were dissolved in 600 ml deionized water by heating at about 80 °C for about 20 min. 100 ml acetone was poured into the β-CD-$CdCl_2$ solution. 13 g $Na_2S \cdot 9H_2O$ (0.054 mol) was dissolved in 200 ml deionized water and then added in the β-CD-$CdCl_2$ solution. Copious orange precipitate was formed within several seconds. The mixed solution was cooled in air for crystallization. After one day, the crystals were collected and washed with deionized water and dried in air. Both yellow crystal (the yield is about 80%) and dark red crystal (the yield is about 20%) were obtained. The red crystal was picked out and named compound 2.

2.3. Characterizations

The obtained compounds were identified by HR-TEM measurements (Tecnai G2 F20 U-TWIN) and XRD analysis with a diffraction meter using Cu *K*α irradiation (D8ADVANCE). X-ray photoelectron spectroscopy (XPS) measurement was carried out on X-ray photoelectron spectrometer (ULVAC-PHI 1800). Fluorescence spectra were recorded on RF-5301PC.

3. Results and discussion

3.1. Compound 1

Precipitation of CdS and crystallization of cyclodextrin went at the same time in this $CdCl_2$–Na_2S–cyclodextrin reaction system. When acetone was not introduced, a yellow hybrid crystal (compound 1) was obtained. The yellow color indicates formation of bulk CdS and this crystal can be regarded as the co-crystal of bulk β-CD and CdS. The CdS particles bond with the OH groups of the cyclodextrin molecules via Van der Waals interactions in this hybrid crystal. The XRD pattern of compound 1 is shown in Fig. 1c. As we can see, the XRD pattern of compound 1 has integrated diffraction peaks of cyclodextrin. This indicates that

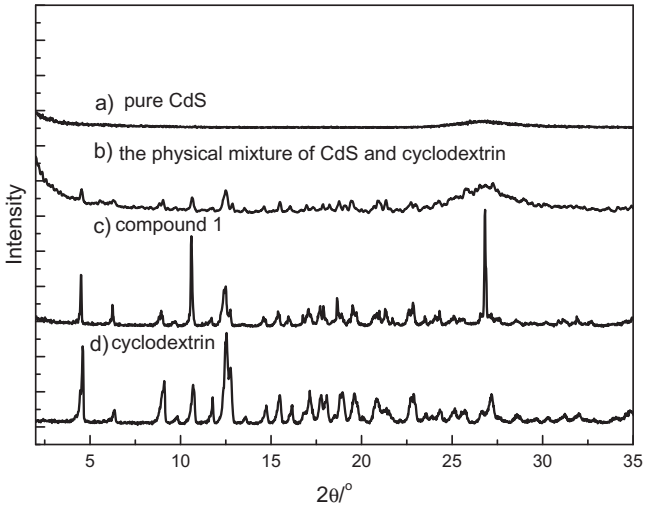

Fig. 1. (a) XRD pattern of pure CdS prepared by the coprecipitation method; (b) XRD pattern of the physical mixture of 1.2 g CdS and 1.2 g cyclodextrin; (c) XRD pattern of compound 1; (d) XRD pattern of pure cyclodextrin.

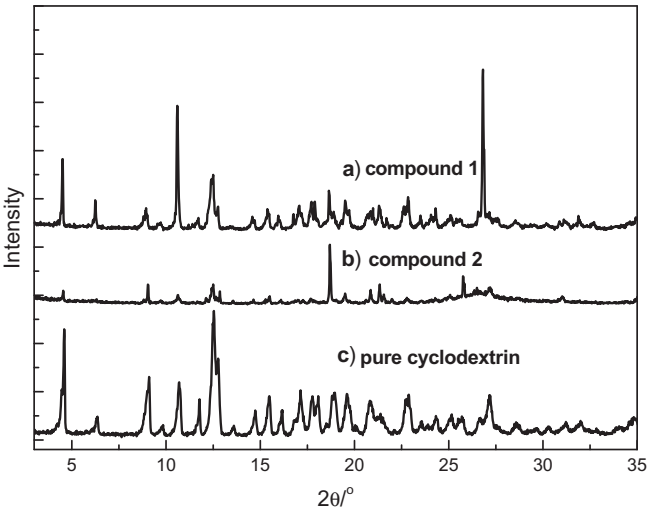

Fig. 2. (a) XRD pattern of compound 1; (b) XRD pattern of compound 2; (c) XRD pattern of pure cyclodextrin.

this is a physical mixture of bulk cycodextrin and bulk CdS, and no inclusion complex of single CdS molecule/β-CD has been formed, since the direct proof of the inclusion of single guest molecule into cyclodextrin molecules is usually the XRD patterns: usually the single guest molecule/β-CD inclusion complexes result in additional peaks in their XRD patterns besides the peaks of the starting materials, and in some cases although no additional peak can be observed, the inclusion complex results in sharply weakened or obviously shifting β-CD diffraction peaks, as many scientists have reported [14–16].

3.2. Compound 2

When 100 ml acetone was introduced into the $CdCl_2$–Na_2S–β-CD reaction system, both yellow crystal and dark red crystal were obtained. The red crystal was picked out and named compound 2. This red crystal is also a co-crystal of CdS and β-CD. And the appearance of red color here indicates formation of CdS quantum dots [12]. The XRD pattern of compound 2 is shown in Fig. 2b. As we can see, compared with the XRD pattern of pure β-CD, only a small part of cyclodextrin diffraction peaks can be observed in

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