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Evolvement of soft templates in surfactant/cosurfactant system for shape control of ZnSe nanocrystals

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ABSTRACT

The evolution of soft templates in the synthesis of ZnSe nanocrystals realized through a surfactant/cosurfactant system was investigated and a micelle formation process model was proposed. Through freeze-fracture electron microscopy, it was proven that template micelles were formed in the zinc precursors. Furthermore, it was found that a long stirring period was essential for achieving the lowest energy state of the soft templates which were used for synthesizing monodisperse ZnSe quantum dots.

1. Introduction

Synthesis of high-quality nanocrystals (NCs) has attracted dramatic attention in recent years [1–5]. Researchers have used organometallic approaches and alternative approaches to prepare high quality semiconductor nanocrystals with different sizes, shapes, optical properties and composites [5]. The ZnSe NCs with low toxicity, high photoluminescence quantum yield (QY) and good crystal structure is an attractive subject in this field and would be a suitable substitute to the cadmium NCs which are more widely studied [6,7].

In cadmium based quantum dots (QDs), a commonly accepted part of the hot-injection synthesis procedure is that a cadmium precursor should be dried under vacuum before injecting chalcogenide precursors at high temperature [8,9]. However, the change of cadmium precursors during the heat-vacuum process is not clear. Recently, we reported a simple method of shape-controlled synthesis of ZnSe NCs [10]. However, the shape control mechanism which may be related to the evolution of the zinc precursors has not yet been clarified. In this work, the possible process model and mechanism of ZnSe nanocrystal shape control by soft templates in surfactant/cosurfactant system was proposed. And the micelle templates which formed in the zinc precursors for shape control of ZnSe NCs were captured and characterized to prove the proposed micelle evolution model. In addition, monodispersed nanocrystals were easily achieved by using the micelles at the lowest energy as templates.

2. Experimental details

The preparation of ZnSe QDs with different shapes was performed based on a previously published method [10]. Alternative stirring periods of the zinc precursors were carried out before they were heated to high temperature (~300 °C) to investigate the soft template thermal energy evolvement. FFEM (freeze fracture electron microscopy) was used to capture the soft templates formed in zinc precursors. The zinc precursors, which were prepared according to the published method [10] and stirred at 70 °C for different durations, were taken out by a syringe and swiftly deep-frozen by liquid nitrogen. Then, cryo-fracturing and shadowing (Hitachi HUS-5GB, carbon and platinum) were carried out for the transmission electron microscopy (TEM, Hitachi H-800) characterization. The raw solution of ZnSe QDs was purified by repeated extraction and centrifugation with a mixture of a lowly polar solvent (such as hexane, chloroform, benzene, and toluene) and a highly polar solvent (such as methanol, acetone and ethanol). Meanwhile, the raw chemicals of zinc precursors and the stirred zinc precursor samples were measured by the FTIR spectra. For FTIR (Thermo Nicolet Avatar 360) spectroscopy measurements, the spectra were obtained by

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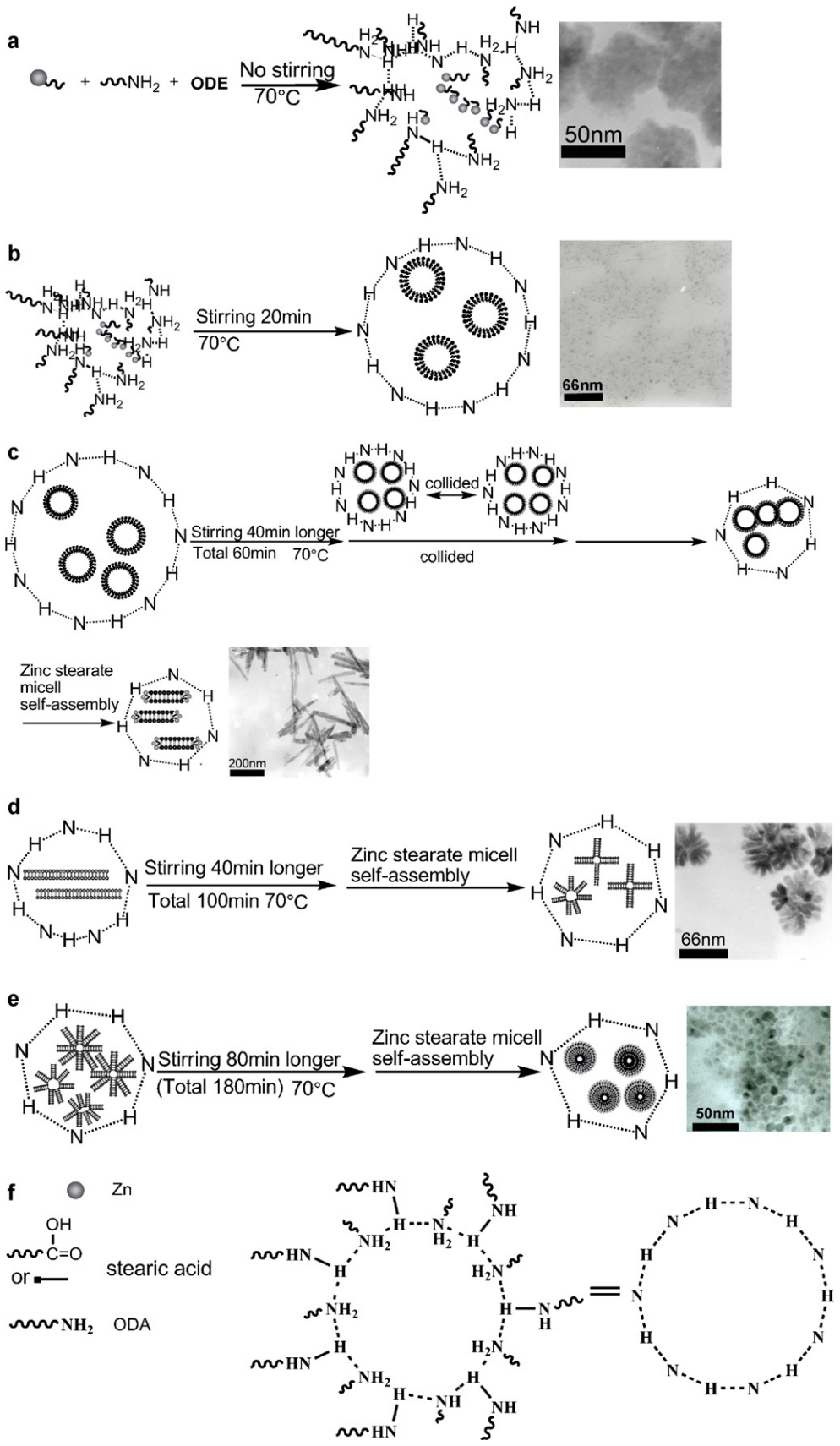

Fig. 1. A proposed model for the self-assembly process of surfactants to form micelles and TEM images (right insets) of the prepared ZnSe NCs which were synthesized from the micelles templates: (a) cotton fibre like nanocrystals synthesized when zinc precursors were stirred for 0 min, (b) uncompacted global nanocrystals synthesized when zinc precursors were stirred for 20 min, (c) nanotubes synthesized when zinc precursors were stirred for 60 min, (d) nanoflowers synthesized when zinc precursors were stirred for 100 min, (e) nanodots synthesized when zinc precursors were stirred for180 min, (f) symbols used in the process model.