

Water in Olive Oil Surfactantless Microemulsions as Medium for CdS Nanoparticles Synthesis

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Abstract

A simple chemical route using ternary 1-butanol/olive/water microemulsion systems without surfactant has been developed to synthesize spherical CdS nanoparticles with an average diameter of ca. 45 nm. The CdS nanoparticles were investigated by transmission electron microscopy (TEM), UV-VIS optical absorption spectrum and Fourier transform infrared (FTIR) spectroscopy measurements. By comparison with previous work, the present work confirmed the effective role of the surfactant in formation nanoparticles.

Keywords: Cadmium sulfide, Nanoparticle, Transmittance electron microscope, Infrared spectroscopy

1. Introduction

At the moment nanostructural materials have become attractive because of their unique characteristics that can hardly be obtained from conventional bulk materials (Alivisatos, 1996) owing to their quantum size and surface effects. In particular, much attention has been paid to synthesis of semiconductor materials due to their excellent prospective in optical, electronic and magnetic functionality, and so on (El-Sayed, 2004).

To date there are many methodologies available for synthesizing CdS nanocrystals, such as soft chemical reaction, solid-state reaction, sol-gel process, sonochemical preparation (Mane, et al., 2000; Henshaw, et al., 1996), microwave heating (Wada, et al., 2001), photoetching (Torimoto, et al., 2001). However, water-in-oil (w/o) microemulsions or reverse micelles technique is one of the most recognized methods due to its several advantages, for instance, soft chemistry, demanding no extreme pressure or temperature control, easy to handle, and requiring no special or expensive equipment. Synthesis of nanoparticles in water-in-oil microemulsions, can yield particles nearly monodisperse in size (Ethayaraja, et al., 2007; Caponetti, et al., 2006; Tan, et al., 2011). In this investigation, we have developed a method to produce CdS nanoparticles of small sizes using new microemulsions systems without surfactant. These ternary mixtures consisting of an inexpensive non-toxic oil (Olive oil), a short chain-alcohol and water represent thermodynamically stable dispersion of nanometer-sized water drops in a continuous oil medium. There are two motivations behind this work. One due to the literature concerning the preparation of CdS nanoparticles by use of water-in-oil microemulsion without surfactant is quite scarce (Ghows, et al., 2011). The other for continuation my previous work for study the roles of surfactant and cosurfactant in the formation of CdS nanoparticles (EL-Hefnawy, 2012). Thereby, in this paper, CdS nanoparticles were prepared in ternary 1-butanol/olive/water microemulsion. CdS nanoparticles are extensively characterized using TEM, UV-VIS spectrophotometer, and FTIR spectroscopy. The structural aspects of this surfactantless microemulsion were discussed by the comparison with my previous work.

2. Experimental

2.1 Materials

Virgin olive oil was obtained from the local market. 1-butanol (99% pure) was purchased from Sigma. Cadmium chloride and sodium sulfide were purchased from Merck. These reagents were used as received. Deionized Millipore Milli-Q water was used in all the experiments.

2.2 Construction of Phase Diagram

In order to find the concentration range of all components [olive oil/1-butanol/water] in which they form surfactantless microemulsions, phase diagram was constructed using the water titration method. Olive oil and

1-butanol were mixed at the weight ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1. These mixtures were diluted dropwise with water, under moderate agitation. The samples were classified as microemulsions when they appeared as clear liquids. Phase diagram is presented in Figure 1.

2.3 Synthesis of CdS Nanoparticles

To prepare the microemulsion, the oil phase and 1-butanol were mixed by magnetically stirring until the mixture became transparent. Divide the mixture into two parts, and the two different microemulsions were prepared as follows: the CdCl_2 aqueous (0.012 M) was added into one of the parts then the reverse microemulsion of CdCl_2 was obtained; the $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ aqueous (0.012 M) was added into the other part of mixture until the mixture became transparent, then the reverse microemulsion of Na_2S was prepared. All experimental processes were under magnetic stirring. The two reverse microemulsions were mixed and magnetically stirred at room temperature of 27°C for about 15 min.

2.4 Characterization

TEM was used to examine the morphology of the CdS nanoparticles on a JEOL transmission electron microscope (model: JEM- 1230, Japan operating at 120 kV attached to a CCD camera). The particle size values were automatically registered from a program of Gatan camera digital micrograph software. The UV-Vis spectra were recorded in a range from 200 to 1000 nm using Shimadzu UV-1601PC UV-visible spectrophotometer. Microemulsion solution without any salt was used as a reference for UV-visible absorption measurements. When equal volumes of microemulsions containing CdCl_2 and Na_2S were mixed in a cuvette, a deep yellow color instantaneously appeared, confirming the formation of CdS nanoparticles. Fourier transform infrared (FT-IR) measurements were carried out using Perkin Elmer Spectrum1 FT-IR with a resolution of 4 cm^{-1} .

3. Results and Discussion

The TEM images of CdS nanoparticles prepared at reverse microemulsion system are shown in Figure 2. It can be seen that nanoparticles have spherical morphology with an average diameter of ca. 45 nm. We can find from this figure that the morphology of the particles is almost homogeneous. In the previous work (EL-Hefnawy, 2012), it was observed that microemulsion with the ratio of water to surfactant (ω_o) = 5 was suitable to get the finest particle size 16 nm. It was significant to increase ω_o from 5 to 15 as the particles increase gradually in this response. Thereby, the surfactant with ω_o =10 and 15 is unable to prevent the agglomeration of CdS particles. This observation will be more confirmed in the present work. In the present work, CdS nanoparticles were prepared in ternary 1-butanol/olive/water microemulsion without surfactant with aqueous phase% = 3.9 that is identical to the ratio of aqueous phase in microemulsion with ω_o = 5 in the previous work. Compared with the results obtained from this previous work, the present results demonstrate that this method can fabricate CdS nanoparticles with large dimensions (average diameter ca. 45 nm). This result confirms that the surfactant (SDS) plays a critical role in the formation of CdS nanoparticles with small dimensions. SDS and 1-butanol adheres to the surface of the nanoparticles served as a protective layer to prevent them from aggregating to larger particles (Sun, et al., 2002; Weller, et al., 2002; Mei, et al., 2006; Huang, et al., 2004; Vidal, et al., 2006). This conclusion is further support to previous results (EL-Hefnawy, 2012), and interprets why the synthesized CdS nanoparticles in surfactantless microemulsions were formed with large dimensions. The absence of SDS in this work left 1-butanol to adhere alone with nanoparticles. Thereby, 1-butanol was unable alone to prevent the agglomeration of CdS particles.

Figure 3 shows the UV-VIS optical absorption spectrum of CdS nanoparticles synthesized in surfactantless microemulsion. We can estimate that an UV-VIS optical absorption excitonic peak of the nanoparticles is at ca. 330 nm, and shows a blue shift from that of bulk CdS (530 nm) crystals. This result is in agreement with the value of the reported literatures (EL-Hefnawy, 2012; Henglein, et al., 1989).

FTIR measurement has been made in the wave number range 400 cm^{-1} to 4000 cm^{-1} . The FTIR spectra is shown in Figure 4. CdS particles showed two stretching bands, asymmetric and symmetric, around 2920.2 cm^{-1} and 2852.6 cm^{-1} are associated with C-H stretching. There are weak to medium absorption bands at 630 cm^{-1} and 725 cm^{-1} possibly due to Cd-S stretching. Hence the existences of above mentioned bands identify the presence of CdS.

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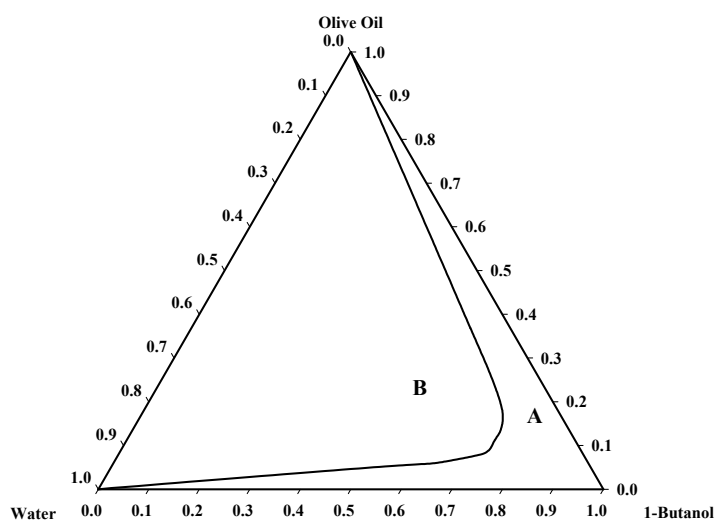


Figure 1. Phase diagram of water/ oil/ 1-butanol mixtures at 27 °C. The area A indicates the microemulsions domain.

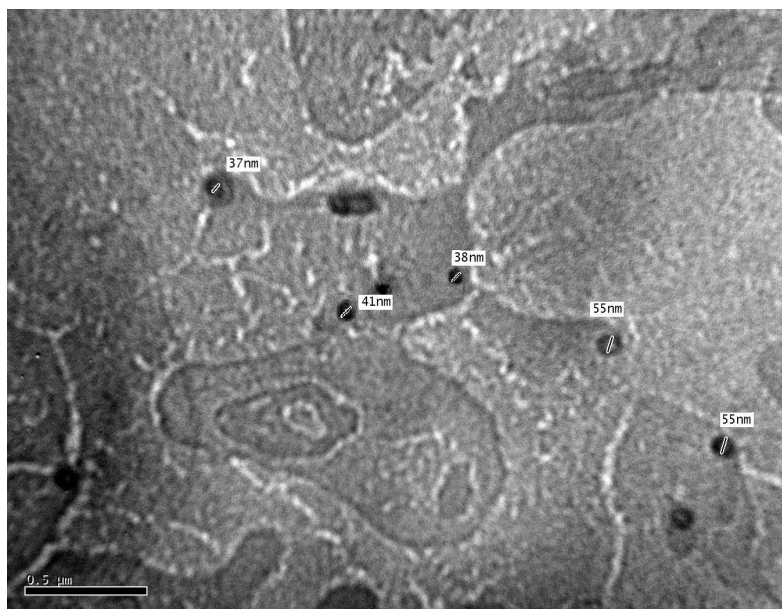


Figure 2. TEM images CdS nanoparticles in microemulsion at aqueous phase% = 3.9

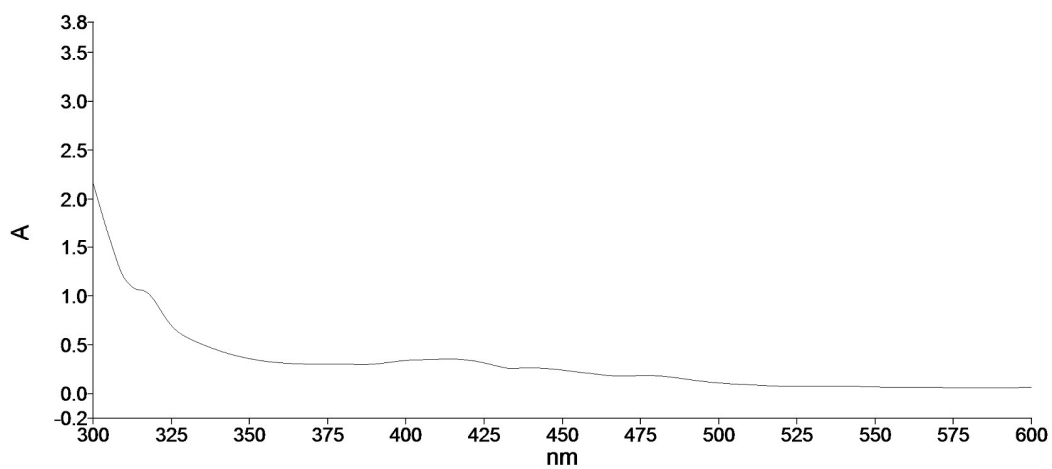


Figure 3. UV- VIS absorption spectrum of the CdS nanoparticles in 1-butanol/Olive oil/water microemulsion with aqueous phase% = 3.9

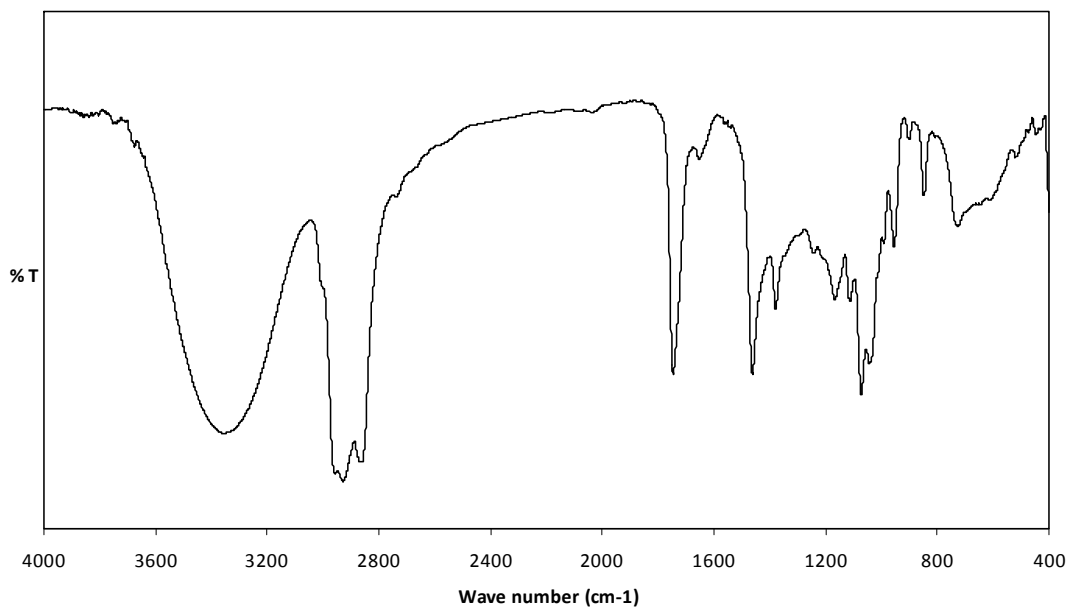


Figure 4. IR spectra of the CdS nanoparticles in 1-butanol/Olive oil/water microemulsion with aqueous phase% = 3.9