Single w/o microemulsion templating of CdS nanoparticles

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We report the synthesis of monodispersed CdS nanoparticle with tunable size by controlling the reaction aging time in a single water in oil (w/o) microemulsion system. The w/o microemulsion system consists of nonionic surfactant poly (oxyethylene)$_5$ nonyl phenol ether (NP5), poly (oxyethylene)$_{10}$ nonyl phenol ether (NP10), cyclohexane and aqueous solution (cadmium salt and thioacetamide). Thioacetamide (TAA) has been utilized as a source for slow release of sulfur ions in the *in situ* synthesis of CdS. UV-Visible spectra shows obvious blue shift for the CdS nanoparticles as compared to the bulk material due to quantum size effect. CdS nanoparticle size depends on the reaction aging time where longer reaction aging time yields bigger particles. CdS nanoparticles growth behaviour as a function of reaction aging time in the microemulsion system was characterized by UV-Visible spectroscopy. The particle growth follows a power law with an exponential in the order of 0.17. Energy Filter Transmissions Electron Microscopy (EFTEM) reveals monodispersed CdS nanoparticles with standard deviation, σ less than 8%.
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1. Introduction

Over the past decades, extensive studies have been carried out to synthesize nanosized II–VI semiconductor particles. Some of the II–VI semiconductors which have been synthesized include CdS [1, 2], PbS [3, 4], ZnS [5] and NiS [6]. These nanoparticles have novel properties due to the quantum confinement effects of nanoparticles, which show a characteristic band gap widening. II–VI semiconductors have attracted lots of attention in the field of optics due to their strong particle size dependent optical property [7], solar cell energy application [8] and catalysis e.g., NiS as desulfonization catalyst [9]. Various methods have been introduced to synthesize monodispersed II–VI semiconductor nanoparticles, such as solvothermal synthesis [10], gamma irradiation [11], hard template [12, 13], laser ablation [14] and reverse micelles [15–17]. In this report, CdS was chosen as a model semiconductor particle because they have been extensively studied [18, 19] and are readily characterized by means of UV-Visible spectroscopy. CdS has direct band gap energy of 2.52 eV, which causes an absorption edge at around 510 nm in the UV-Visible absorption spectrum. The band gap energy can be tuned around 2.6–3.0 eV by varying the size of CdS nanoparticle.

Here, we report the synthesis of CdS nanoparticles using single w/o microemulsion nanoreactor system. Thioacetamide (TAA) was introduced into the water cores that serve as a slow release of sulfur source.

Thioacetamide hydrolyzes and releases sulfur ions in the presence of water as shown in the following stoichiometry:

$$CH_3CSNH_{2(aq)} + 2H_2O$$
$$\rightarrow H_2S_{(aq)} + CH_3COO^-_{(aq)} + NH^+_{4(aq)}$$
$$H_2S \rightarrow 2H^+ + S^{2-}$$
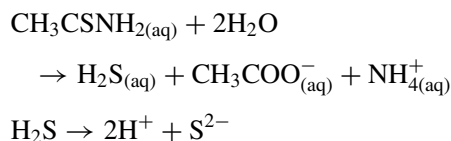
It is emphasized that the particles were produced via single microemulsion processing route whereby S^{2-} ions react with Cd^{2+} ions in the surfactant stabilized by tiny aqueous nanodroplets (5–20 nm) dispersed in the organic solvent. There had been increasing numbers of reports on the synthesis of nanoparticles with various size controlled by the size of the aqueous droplet [20, 21]. *Li et al.* [22] reported that double microemulsion processing route will tend to produce smaller particle compared to single microemulsion processing route. However, the present single microemulsion processing route is able to synthesize small sized CdS nanoparticles by utilizing TAA as the sulfur source.

2. Experimental

The starting materials were nonionic surfactant poly (oxyethylene)$_5$ nonyl phenol ether (NP5), poly (oxyethylene)$_{10}$ nonyl phenol ether (NP10), cadmium
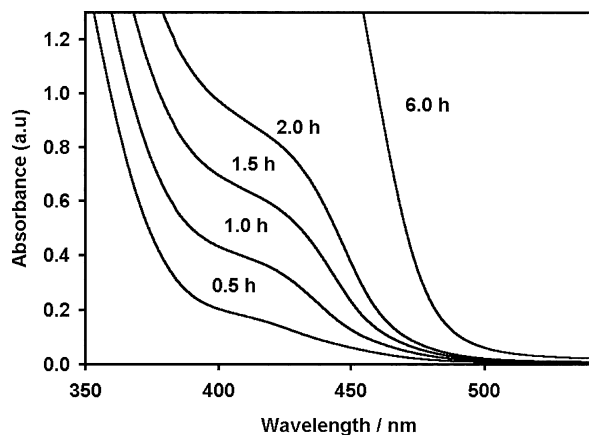

Figure 1 UV-Visible spectrum for CdS nanoparticles formed in the aqueous core of microemulsion at increasing time.

nitrate (>99.0% purity) and thioacetamide (>99.0% purity) which were purchased from Fluka and cyclo-hexane from Merck (>99.5% purity) whereas ethanol (99.5% purity) and diethyl ether (99.8% purity) were both obtained from BDH. All materials were used as received without further purification. Deionized water (18.2 MΩ) was used throughout the sample preparation. Thioacetamide solution was prepared daily prior to sample preparation.

A typical route to synthesize CdS nanoparticles in a single microemulsion system was achieved by mixing 10 wt% aqueous phase consisting of TAA solution (1.0 M) and cadmium nitrate solution (0.2 M) with 36 wt% surfactants (NP5 and NP10 in weight ratio 2:1) and 54 wt% cyclohexane. The well-mixed w/o microemulsion appeared to be optically transparent.
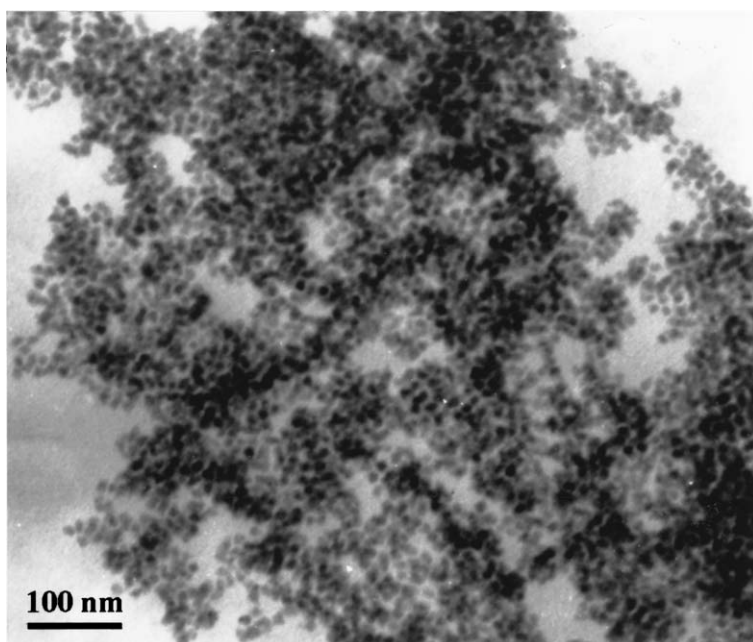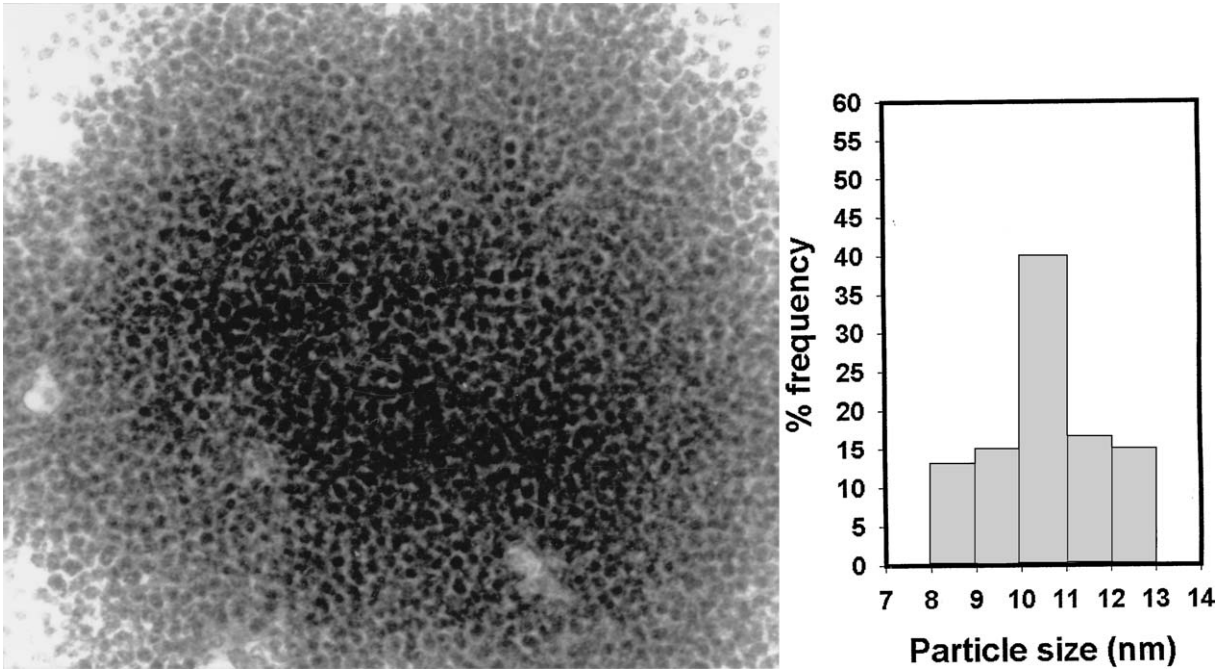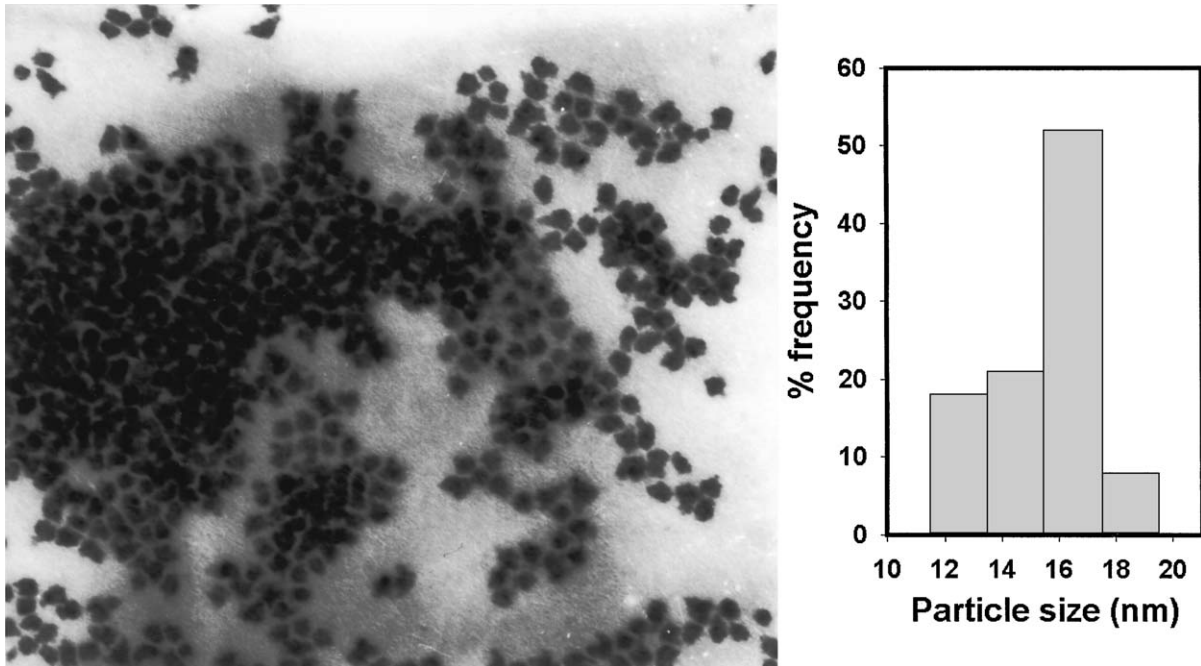

(a)
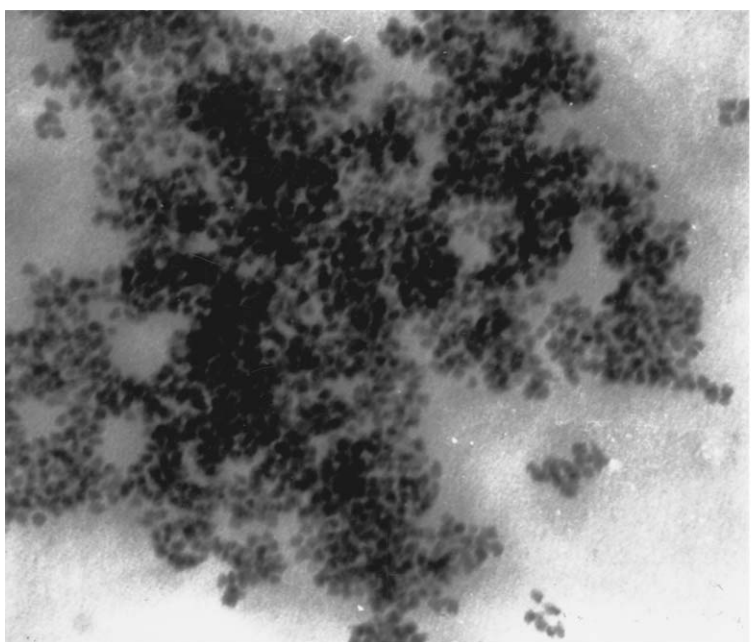
(b)

Figure 2 EFTEM micrographs for CdS nanoparticles after various reaction aging time: (a) 0.5, (b) 1.0, (c) 1.5, and (d) 6.0 h. All four electron micrographs were taken at the same magnification. Histogram for particle size distribution is shown at the right of each micrograph. (*Continued*)

(c)

(d)

Figure 2 (Continued).

The homogenous samples were left standing at room temperature to allow slow reactions. The nanoparticles growth behaviour in the microemulsion matrix was characterized as a function of time using Perkin Elmer Lambda 35 UV-Visible spectrometer. The UV-Visible spectra were recorded immediately after mixing all the reactants at various reaction aging time. Metal sulfide was extracted by washing the microemulsion matrix using mixture of ethanol/diethyl ether solution (vol% 1:1) at various reaction aging time. Each washing involved dispersing the particles in diethyl ether/ethanol solution via sonication. The dispersions were centrifuged to recover light yellowish CdS powders. The clear supernatant was removed and the washing process was repeated at least four times before the powder was re-dispersed in 50/50-vol% diethyl ether-ethanol solution. The resulting CdS nanoparticles was characterized by LEO 120AB Energy Filter Transmission Electron Microscope (EFTEM) operated at 120 kV accelerating voltage. A small drop of CdS nanoparticles dispersed in diethyl ether/ethanol solution with 1% of dode-canethiol as a capping agent was spread on the carbon-coated copper grid (400 mesh, Agar Scientific) and was allowed to evaporate at room temperature before observation under EFTEM.

3. Results and discussion

Thioacetamide (TAA) hydrolyzes in the aqueous solution and releases H_2S slowly at room temperature. The

slow hydrolysis of TAA in water allows CdS nanoparticles growth in the microemulsion system to be monitored as a function of time by UV-Visible spectrometry. The absorption spectra for as synthesized CdS nanoparticles (Fig. 1) shows clear blue shift from the bulk material where the absorption edge for reaction aging time of 0.5, 1.0, 1.5, 2.0 and 6.0 h are 461, 465, 467, 472 and 481 nm respectively. The position of the absorption edge is size dependence due to quantum confinement effect. This relationship was made quantitatively by calculation of the energy for the first electronic excited state of the particles and hence provides the basis for particle size estimation. By applying the well-known Brus equation [23], CdS nanoparticle size, d can be estimated as follows:

$$d = \frac{\frac{3.6e^2}{(4\pi \in)} - \left\{\left[\frac{3.6e^2}{4\pi \in}\right]^2 - 4(E_g - E)\frac{h^2}{2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right)\right\}^{\frac{1}{2}}}{2(E_g - E)}$$

(1)

where E_g and E is the band gap energy of the bulk and nanoparticle semiconductor respectively, e is electron charge, $\in$ is dielectric constant, h is Planck constant while m_e and m_h are electron effective mass and hole effective mass respectively.

Fig. 2 shows EFTEM observation of extracted CdS nanoparticles after various reaction aging time (0.5, 1.0, 1.5 and 6.0 h) where longer reaction aging time resulted in larger particles. This result is in accord with growth behaviour observed from UV-Visible spectrometry. Fig. 2a shows monodispersed CdS nanoparticles with average size of 6.5 nm after 0.5 h of reaction. CdS nanoparticles with mean size of 8.5 nm were obtained after 1.0 h of reaction (Fig. 2b), 12.5 nm after 1.5 h of reaction (Fig. 2c) and after 6 h, the particles grew to larger particles giving mean size of 16.5 nm. This shows that CdS nanoparticle size can be easily tuned by varying the reaction aging time. The particle size distribution histogram was plotted by calculating the size of about 200 CdS nanoparticles for each TEM micrograph and the CdS particles show narrow size distribution with standard deviation, σ less than 8%.

Particle size estimated from UV-Visible absorption spectra and mean particle size obtained from EFTEM micrograph was plotted as a function of reaction aging time in Fig. 3. The particle size estimated from UV-Visible spectra was 7.5 nm after 0.5 h of reaction aging time and reached the size of 9.1 nm after 1.5 h. The particles size reaches $\sim$10 nm after $\sim$4.0 h and $\sim$11.5 nm after 6.0 h. The growth rate seems to become plateau after 4 h of reactions aging time. CdS nanoparticles growth obtained from the UV-Visible spectra shows power law behaviour as follow:

$$d \propto t^{0.17}$$

(2)

The particle size was found to scale with reaction aging time on the order of 0.17. This result however is differ from the Lifshitz-Slyozov Wagner Law (LSW) [24] for the kinetics of growing process of an ensemble
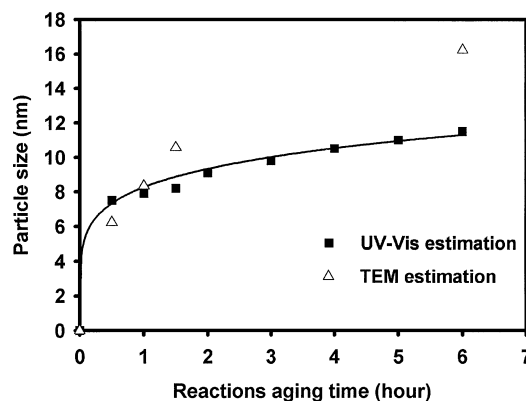

Figure 3 Particle size as a function of reaction aging time estimated from both UV-Visible spectra (close rectangle) and electron micrographs (open triangle). A power law fits particle size estimated from UV-Visible data with exponential value of 0.17.

of particles, where

$$d \propto t^{0.33}$$

(3)

The LSW law is an approach to describe a situation whereby if two particles of different sizes are present in a liquid or aerosol, it is thermodynamically favorable for the larger or more stable particle to grow at the expense of the smaller particle. In the present system, the particle growth process happened in a confined nanoreactor, provided by the nanosized aqueous droplet dispersed in microemulsion. However, particle size counted from the EFTEM micrographs is bigger than that of UV-Visible estimations. This may be due to the continuing growth of CdS nanoparticles during the extraction process.

4. Conclusion

We have synthesized monodispersed CdS nanoparticles with narrow size distribution in a single microemulsion system. The nanoparticles growth in the single microemulsion system exhibits a power law growth with exponential value of 0.17. Synthesis of CdS nanoparticles in microemulsion using TAA as sulfur source provides a simple route in controlling the particle size by varying the reaction aging time.

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