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The synthesis of cadmium sulfide nanoplatelets using a novel continuous flow sonochemical reactor

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ABSTRACT

A continuous flow sonochemical reactor was developed capable of producing metastable cadmium sulfide (CdS) nanoplatelets with thicknesses at or below 10 nm. The continuous flow sonochemical reactor included the passive in-line micromixing of reagents prior to sonochemical reaction. Synthesis results were compared with those from reactors involving batch conventional heating and batch ultrasound-induced heating. The continuous sonochemical synthesis was found to result in high aspect ratio hexagonal platelets of CdS possessing cubic crystal structures with thicknesses well below 10 nm. The unique shape and crystal structure of the nanoplatelets are suggestive of high localized temperatures within the sonochemical process. The particle size uniformity and product throughput are much higher for the continuous sonochemical process in comparison to the batch sonochemical process and conventional synthesis processes.

1. Introduction

Cadmium sulfide (CdS) nanoparticles (NPs) exhibit quantum confinement effects as they approach the Bohr exciton radius below 10 nm. CdS is predominantly used as a buffer layer in different solar cells based on materials like CIGS [1], CIS [2] and in CdSe–Zn [3]. This critical layer improves photovoltaic device performance as well acts as a wide band transparent window to incoming sunlight. CdS is also used in a myriad of applications including lasers, waveguides, solar cells, photodetectors, photocatalysts and photodiodes [4]. To enable these applications, precise process control is necessary to minimize particle size distribution at small particle sizes.

It has been found that generally the particle size distribution for nanoparticles is narrower for sonocrystallization than for other comparable synthesis methods such as microfluidic-based routes. Table 1 shows a corresponding comparison of coefficient of variation (CV) based on data reported for these nanoparticle synthesis routes. Cadmium selenide data is compared since it is chemically similar to CdS in synthesis and structure.

In the sonochemical synthesis route, heating by cavitation and bubble implosion provides a potential route to high temperature reactions from a liquid phase. Sonochemistry has been used for the synthesis of nanoparticles of various semiconductor materials like CdS [11,12] and PbS [13,14] in batch modes. It has been demonstrated that a surfactant free approach using sonochemistry can be used to generate well dispersed CdS NPs [11]. However in batch mode, long residence times measured in hours can make process control more difficult due to the chemistry being exposed to the US energy multiple times. Further, batch US chemistries are difficult to scale-up. In continuous sonochemical synthesis, residence times can be reduced from several hours to less than a minute making it easier to control reaction conditions. Also, conventional solution processing does not yield high aspect ratio particles or high temperature phases. In general, very little research has been performed on continuous sonochemical synthesis [15,16].

In this paper, a continuous flow sonochemical reactor is developed and used to continuously produce a metastable crystal structure in the form of high aspect ratio CdS platelets. The sub 10 nm thick platelets exhibit good particle size control without the use of surfactants. The method is compared with batch sonochemistry and conventional heating to delineate the advantages.

2. Development of a continuous flow sonochemical reactor

A flow cell reactor was developed to couple an ultrasonic (US) horn with the nanoparticle chemistry of interest. Ultrasound attenuates as a function of distance in front of the horn.

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Table 1
Nanoparticle size distributions reported in the literature.

Material	Avg size (nm)	SD (nm)	CV (%)	Synthesis approach	Author
CdSe	8.0	0.6	8.0	Sonochem	Mastai et al. [5]
CdSe	3.0	0.6	19.7	Sonochem	Mastai et al. [5]
CdSe	4.0	0.7	17.0	Sonochem	Mastai et al. [5]
CdSe	5.5	0.6	10.2	Sonochem	Mastai et al. [5]
CdS	4.5	1.0	22.2	Microfluidic reactor	Peterson et al. [6]
CdS	5.2	0.3	6.0	Microfluidic reactor	Wan et al. [7]
CdS	5.5	0.9	16.4	Sonochem*	Wang et al. [8]
CdS	11.5	6.5	56.3	Sonochem*	Wu et al. [9]
CdS	8.5	3.5	40	Sonochem*	Gao et al. [10]

* Data derived from results presented in the paper.

Attenuation is an exponential function, strongly dependent on the attenuation coefficient (α) as given by [17]

$$I = I_0 \exp(-2\alpha d)$$

where I is intensity at distance d from the source, I_0 being initial intensity. The acoustic pressure amplitude as a function of distance from the horn has been modeled using the equation [18].

$$P(d) = \rho c v |2\sin\left(\frac{\pi}{\lambda}\left(\sqrt{d^2 + a^2} - d\right)\right)|$$

where $P(d)$ is the acoustic pressure amplitude as a function of distance d, ρ is the density of the liquid, c is velocity of sound in the liquid, v is the velocity amplitude of the horn, λ is the wavelength of the sound and a is the radius of the horn tip.

A key factor in the design of the flow cell was to reduce the residence time of the flow chemistry within the reactor. Shorter residence times would lead to the potential for higher, more uniform power densities adjacent to the horn and less exposure to bulk temperatures. A horn with a maximum power inverter rating of 750 W (model VCX 750) and an interfacing flow cell (630-0495) were acquired from Sonics and Materials, Inc. To reduce fluid residence time within the flow cell, the internal volume of flow cell was modified through the use of an insert. Fig. 1 shows a schematic of the internal volume of the reactor with and without the flow insert. The flow cell insert reduced the flow cell volume from 65 ml to 8 ml. The critical dimension in the insert was the clearance between the horn outer diameter and the inner diameter of the insert itself. This had to be sufficiently larger than the critical bubble size in order to prevent vapor lock restricting the outflow of processed reactants. The flow insert was made of UHMWPE

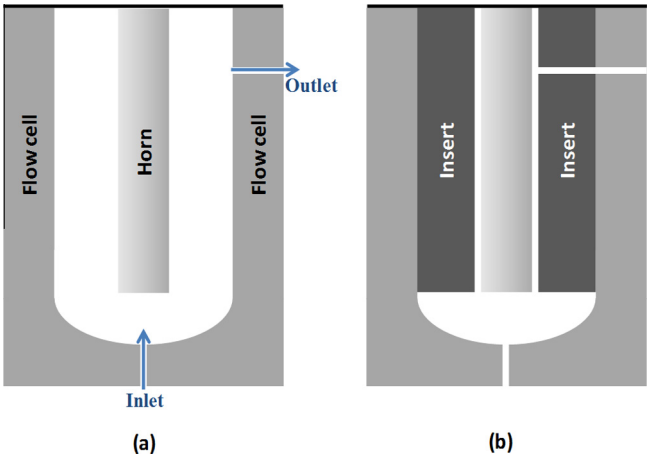

Fig. 1. Cross-section of continuous flow reactor (a) without insert and (b) with insert.

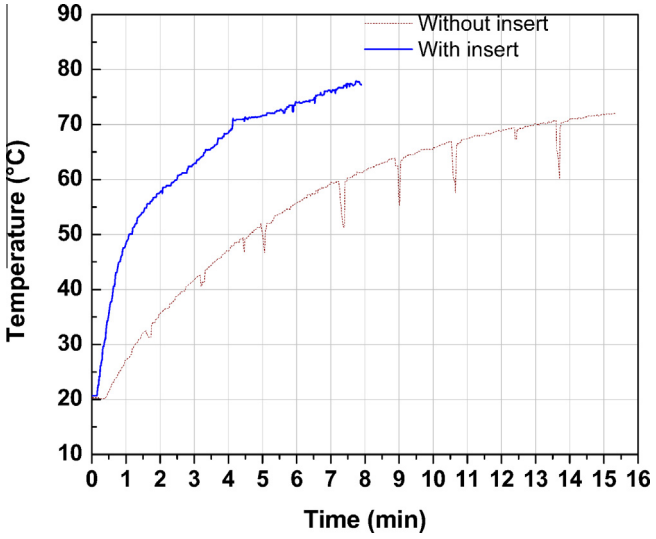

Fig. 2. Effect of volume reduction on heating rate.

due to its low density, high elasticity, high softening point and low cost.

The use of the insert was found to provide several benefits. First, Fig. 2 shows the effect of the flow cell insert on the time needed for the bulk temperature to reach steady state in pure water. It can be clearly observed that it takes approximately one-third the amount of time to reach 70 °C for pure water. Second, the curve collected without the insert shows several points at which the temperature suddenly drops off. This is due to temperature accumulation adjacent to the horn leading to bubble accumulation and disruption of power transfer. This suggests that the use of the flow cell insert led to better temperature uniformity within the flow cell as originally intended. A schematic of the final continuous flow setup is shown in Fig. 3.

3. Experimental methods

Based on prior literature [10], a cadmium chloride and thiourea reactant chemistry was chosen for sonochemical synthesis of cadmium sulfide nanoparticles. This chemistry involves processing at 85 °C [19,20]. The reaction mechanism involves forming a cadmium–thiourea complex – $Cd[SC(NH_2)_2](OH)_2$ which is aided by ammonia released from ammonium chloride–ammonium hydroxide buffer. This controls the release of Cd ions for precipitation into CdS and hence affects the kinetics of the reaction, aimed at controlling the particle size. Table 2 shows the conditions chosen for the reaction in batch and continuous modes. The chemistry was first evaluated in batch mode to check feasibility.