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Synthesis and Characterization of the CdS Platelet Particles in Octylamine-water System

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The anisotropic CdS platelets were synthesized in the lamellar bilayer phase region of the octylamine-water binary system. The influence of the synthesis conditions of the system components on morphology and size of the platelets was examined. Atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) studies have shown thickness and face size of the synthesized particles. Platelets with face sizes ranging from 50 to 250 nm and thickness from 10 to 30 nm have been synthesized at room temperature. In addition, HRTEM micrographs show that the synthesized platelets are poly crystal.

Key words: CdS, Platelet particles, Self-assembly, Octylamine-water

I. Introduction

The synthesis of nanosize powders is of considerable importance to the microelectronics industry because of the pervasive drive to miniaturize components. The ability to synthesize nanosize particles and control their properties is important in many industrial areas of modern technology such as catalysis, ceramic processing, pharmaceutics, and photography.[1] Many approaches have been explored for the preparation of spherical, or equi-axed, ultrafine particles, including the use of colloids and micelles to successfully control aggregation.[2,3]

However, scant attention has been paid to the fabrication of anisotropic nanoscale particles, which often possess unique physical and chemical properties. The control of particle morphology is a complex processing which requires a basic understanding of solid state chemistry, solution chemistry, and the mechanisms and kinetics of interfacial reactions. Amorphous particles are usually spherical due to their isotropic growth, while single crystal particles assume their intrinsic crystallographic habits. Specific adsorption of ions, complexes, organic compounds, etc., may result in a variety of morphologies of colloidal micro crystallites by restraining or sometimes promoting growth of the facets to which they are absorbed.[4] The morphology of particles can be controlled by nucleation and growth mechanism. These hosts posses inorganic inclusions such as anisotropic cages, channels, and layers with dimensions from a few angstroms to hundreds of nanometers. As well as providing geometric control and stabilization of particle clusters, these inclusions may have a profound influence on the physical and chemical properties of the clusters.[5]

Among the various materials which can be used as a host matrix, amphiphilic molecules and their self-assembly associations have great potential for the synthesis of anisotropic shape particles. The spontaneous association of amphiphiles under equilibrium conditions, well-defined micelles are well known in interfacial chemistry. The configuration of the micelles depend on surface free energy which is dictated by several competing factors such as repulsive forces between head groups, hydrophobic attraction between hydrocarbon chains, interactions between aggregates at high surfactant concentrations, and the relative sizes of the polar and hydrophobic moieties of the amphiphile.[6] The neat phase bilayers consisting of alternating layers of aqueous and amphiphilic molecules can be used as templates to growth platelet metal hydroxide or semiconductor particles. Indeed binding of the CdS at the polar head group is an important feature in templating resultant particles to produce a controlled morphology, then there should be a correlation between the aqueous phase thickness and the resulting particle thickness. The desired self-assembly structure can be produced by manipulating the amphiphile composition, the concentration of amphiphile and salt, counter-ion valence, and the presence of co-surfactants.[7]

The objective of this study is to determine the influence of synthesis conditions on the size and morphology of the CdS particles. The possible growth mechanisms and criteria for the formation of anisotropically shaped particles will be discussed.

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II. Experimental

All starting materials were reagent grade. Cadmium itrate tetrahydrate (>98% purity, Fisher Scientific) and odium sulfide nonahydrate (98%, Aldrich Chemical Com-)any) were used without further purification. Sodium sul-ide nonahydrate was kept refrigerated until just before the)reparation of aqueous solution. Octylamine-water micro-:mulsion system was used to form neat bilayer phases. The amphiphile used in this system was octylamine (Ald-ich Chemical Company). The experimental procedure for)reparing CdS particles by microemulsion is schemati-:ally illustrated in Fig. 1. Two neat bilayer phases were)repared containing Cd^{2+} and S^{2-} ions, respectively. The :olutions were shaken vigorously. After standing for at east 30 minutes to ensure equilibration, the cationic and inionic neat bilayer phases were mixed together in the /olume ratio of 1:1, followed by vigorous shaking again. CdS particles were precipitated immediately and the solu-:ion color changed to yellow. The particles were separated)y centrifugation and they were dispered in ethanol. Sev-:ral approaches were used to determine the influence of :he water/surfactant molar ratio on the particle size and norphology. In order to verify the particles which had :abular shape, morphological analysis was initially con-lucted using high-resolution transmission electron micros-copy (HRTEM). HRTEM and AFM were used to provide characterization to determine face sizes and thickness,

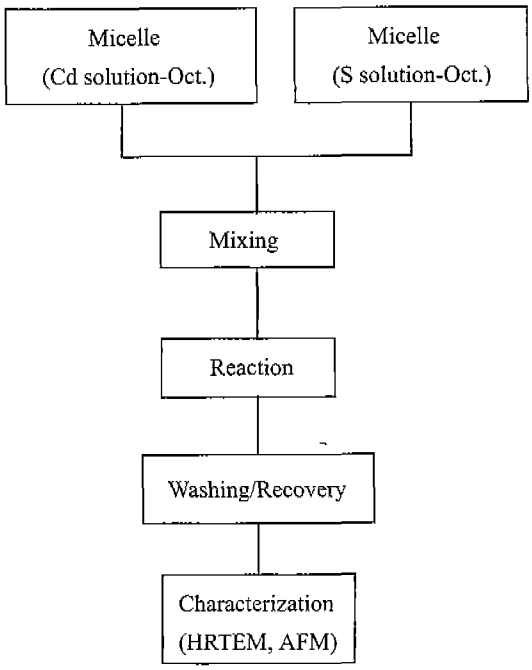

Fig. 1. Flow chart for the synthesis of the CdS platelet particles in the octylamine-water system.

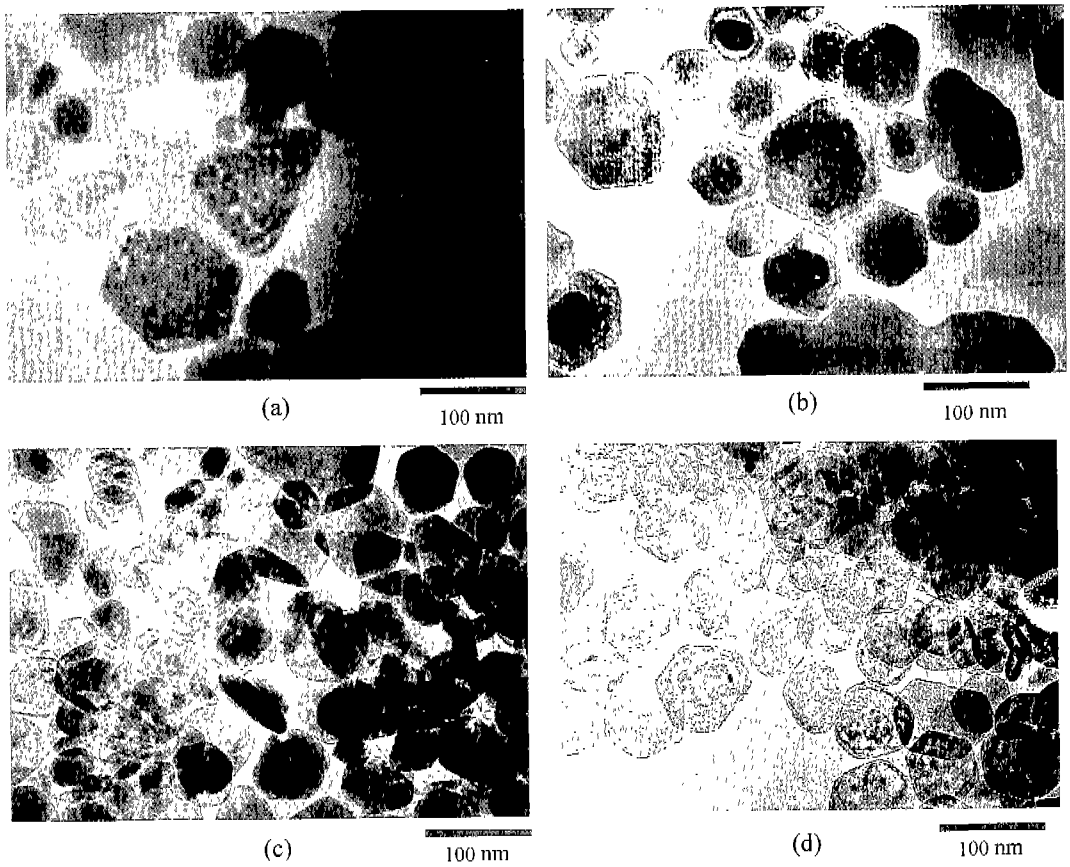

Fig. 2. TEM micrographs of the CdS platelet particles as a function of surfactant amount in the octylamine-water system; (a) 60 wt%, (b) 50 wt%, (c) 40 wt% and (d) 30 wt%.

respectively. HRTEM was used to obtain detailed data about the morphology and the crystal structure of the particles.

III. Results and Discussion

The microemulsion system was used to produce hexagonal plate-like CdS particles through the neat bilayer phases. The formation of anisotropic platelets is very sensitive to the composition of the phase as well as to processing parameters such as reagent concentrations and water/surfactants weight ratio. The fundamental reaction takes place in the reactor of the aqueous layer is as follows:

$$Cd^{2+}(aq) + S^{2-}(aq) \rightarrow CdS(s) \quad (1)$$

At 25°C, log K(CdS) is equal to −26.1, with a stoichiometric solubility for CdS(s) of 10^{-13}M.

Thus, the reaction goes practically to completion, with very little Cd^{2+} or S^{2-} remaining in solution at equilibrium.[8,9] Fig. 2 shows that several microemulsion systems produced nanoscale platelet-shaped CdS particles from their neat bilayer phases(octylamine-water), however the size and distribution of the resulting particles were different. Variation of the experimental conditions showed that there are upper and lower limits of concentration of the Cd^{2+} metal ion. For the octylamine-water system, the weight ratio of oil/water was varied from 0.40 to 1.85, through the bilayer region of the phase diagram,[10] to control the size and thickness of the particles. Above 0.5 M, the neat bilayer phase is not the stable phase, and the resulting CdS particles were randomly shaped rather than platelets. Below 0.002 M, no CdS particles were obtained as

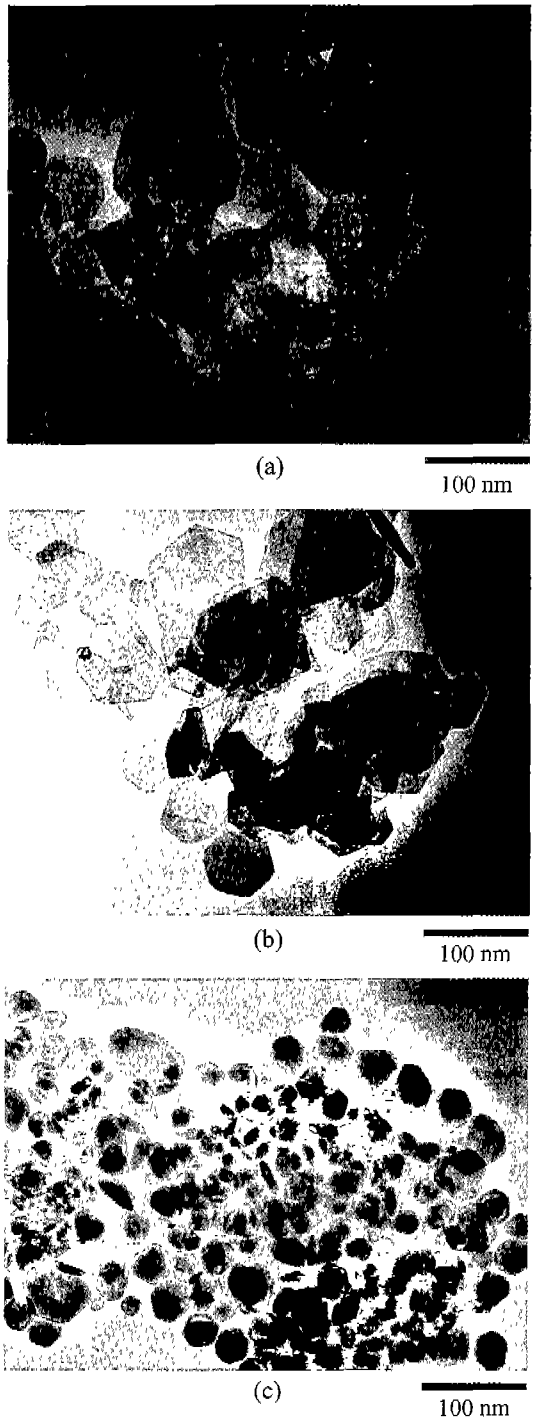

Fig. 3. TEM micrographs of the CdS platelet particles in the 40 wt% octylamine-60 wt% water system as a function of solution concentration; (a) 0.01 mol, (b) 0.02 mol and (c) 0.03 mol.

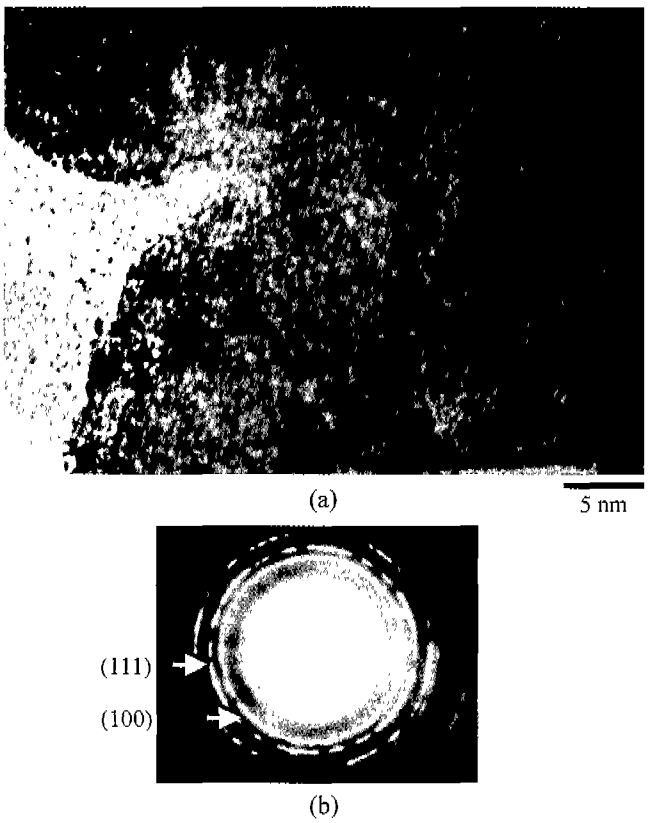

Fig. 4. HRTEM micrograph(a) and Diffraction pattern(b) o the CdS platelet particle in the 40 wt% octylamine-60 wt% water system.

precipitates.

Fig. 3 shows the effect of the starting solution concentrations in the octylamine-water system. Since the water in the micro-emulsion system came from the aqueous CdS solution, the increase in the CdS concentration also increased the cation and anion contents in the system. This change led to the formation of the CdS platelets particles increase and the size of the synthesized CdS platelet particles decreased in the system.

The synthesized CdS platelet particles in neat bilayer phase consisted of smaller primary particles (Fig. 4a), and the TEM diffraction pattern in Fig. 4b shows that the platelets were polycrystalline CdS. It was observed that the platelets have circular or ellipsoidal face morphologies. The agglomeration of the primary particles make platelet shaped in this system because it is energetically more favorable. The lattice fringes in the high-resolution bright field image demonstrated that the platelets were poly crystal (Fig. 4a).

Since the thickness fringe studies by HRTEM did not provide results precise enough to determine platelet thickness, these measurements were conducted with AFM (Fig. 5). During the AFM studies, contact mode was used to determine the size and the thickness of the platelets on the atomically flat freshly cleaved mica substrate surface. The platelets were washed three times with ethanol to dissolve and remove the organic layer. The wide size distribution results from the primary particle agglomeration that forms over the surfaces of the amphiphilic molecules.

IV. Conclusion

The anisotropic shaped CdS particles were successfully synthesized in self-assembled laminar bilayers at room temperature. Thin laminar aqueous layers down to about 10 nm thickness were produced with the use of amphipilic octylamine molecules. It was observed that the thickness of the aqueous layers between the bilayers was also increased up to 30 nm with increasing water/surfactant ratios. This affected the size of the platelets that were formed in between these bilayers. Variations in surfactant/water weight ratio and solution concentration led to the formation of platelets in size range of 50 to 250 nm, and a thickness of 10 to 30 nm. These results indicate that the thickness of platelets can be controlled by the thickness of aqueous layers. HRTEM verified that the synthesized platelets were phase pure, poly crystal cadium sulfide so this demonstrates that the synthesis of nanosize phase pure cadium sulfide is possible in the octylamine self-assembly systems.

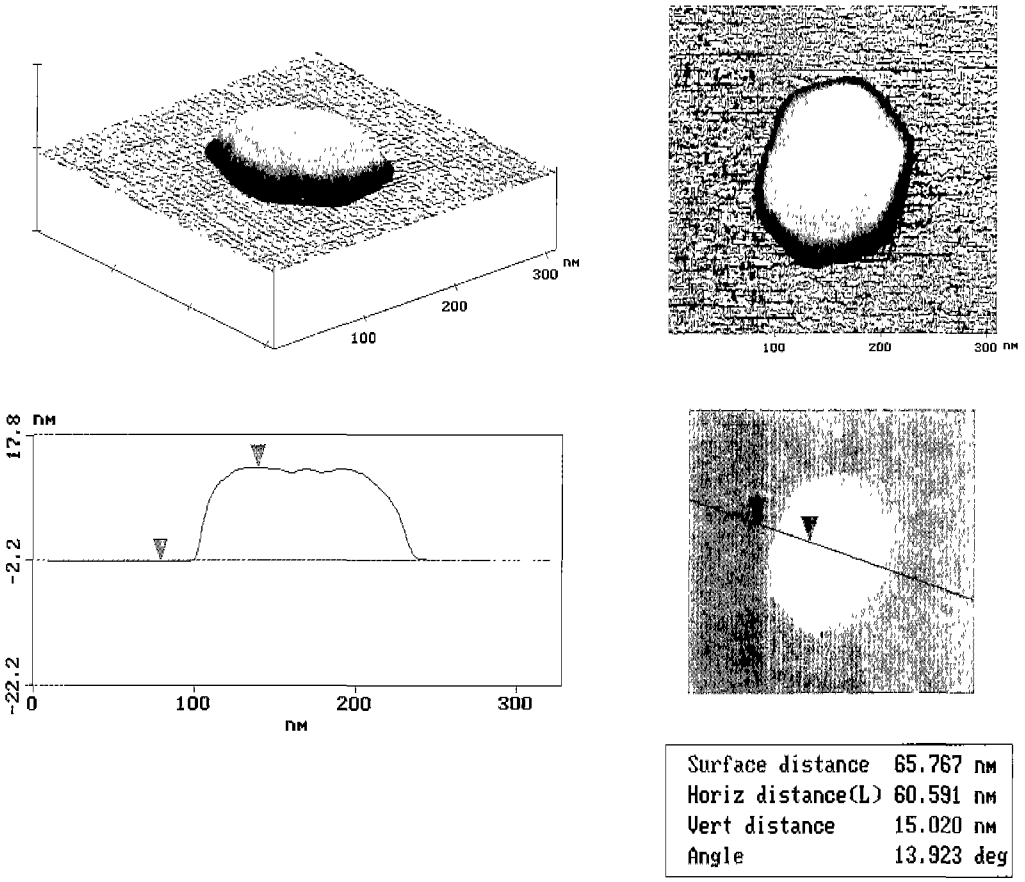

Fig. 5. AFM micrograph of the CdS platelet particles in the 30 wt% octylamine-70 wt% water.

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