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Controlled Formation of CdS Particles in Multibilayer Cast Films of Amphiphilic Cyclams[1]

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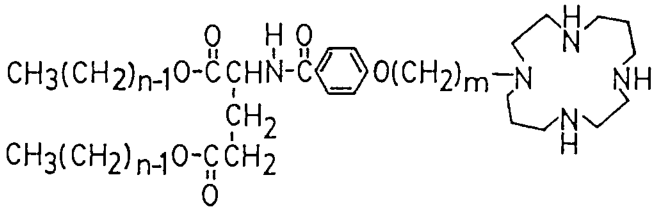
Quantum sized cadmium sulfide particles were prepared by reaction of H_2S gas with Cd^{2+}-cyclam complexes preorganized in cast multibilayer films. The particle size was affected by the chemical structure of the bilayer component as well as by phase transition characteristics.

In recent years, "small-particle" research has been a topic of increasing interest.[2,3] Reduction of particle sizes to the nanometer range is accompanied by altered electrical, magnetic and chemical properties[2] and produces scientifically as well as practically attractive materials. A prerequisite for systematic studies of the quantum size effect is to establish a general synthetic procedure with controlled particle sizes. CdS particles were extensively studied. Their size control has been accomplished by using a variety of reaction media such as aqueous[4] and non-aqueous[5] solutions, reversed micelles,[3] vesicles,[3] BLMs,[3] surface monolayers,[6] polymer films,[7] clays,[8] zeolites,[9] Langmuir-Blodgett films,[10] peptides[11] and yeast cells.[12] We have reported that free standing cast films of regular multibilayer structure serve as convenient matrices for syntheses of two-dimensionally crosslinked organic polymers,[13] oriented iron oxide particles[14] and ultrathin siloxane networks.[15] In addition, metal chelates have been introduced into the inter-bilayer space with macroscopic ordering.[16] These organized metal chelates appear particularly attractive as starting materials of inorganic clusters. We describe in this paper the preparation of CdS clusters in



1 (n,m) = (14,2),(14,6),(16,6),(16,10)

cast multibilayer films which contain preorganized cadmium complexes.

Cyclam-containing double chained amphiphiles 1 were sonicated in water with an equimolar amount of aqueous $CdCl_2$ to give transparent Cd^{2+} bilayer complexes (ca. 10 mM). Transparent cast films were obtained by spreading the dispersions onto fluorocarbon sheets and allowing them to stand at room temperature (ca. 20 °C). Subsequently, the cast films were exposed to H_2S for 9 h at 15 °C or 80 °C and then kept in vacuo.

^{113}Cd MAS-NMR measurement (Bruker AC250) for the cast films was conducted before and after H_2S treatment. Relative to cadmium perchrolate hexahydrate standard, 1(14,6)-Cd^{2+} cast film gave an NMR signal at 321 ppm, which shifted to 707 ppm upon exposure to H_2S at room temperature. These chemical shifts are in good agreement with that of simple Cd^{2+}-cyclam complex (324.5 ppm), which was prepared by mixing aqueous $Cd(ClO_4)_2$ with an equimolar amount of unsubstituted cyclam, followed by evaporation of water, and with a reported value for cadmium sulfide (705.8 ppm),17) respectively. The formation of CdS particles was further confirmed by means of XPS measurement (Perkin Elmer, PHI5300 ESCA system). The content of the S atom in the 1(16,6)-CdS film prepared at 15 °C and 80 °C were estimated to be 1.0 per cadmium in each case, from the relative area of the Cd_{3d} and S_{2p} peaks.

Subsequently, the cast films were subjected to differential scanning calorimetry (Seiko Instruments, DSC 120). Gel-to-liquid crystal phase transition characteristics of cast films before and after exposure to H_2S are summarized in Table 1. All the non-exposed films gave endothermic peaks in the range of 50 °C to 70 °C. H_2S treatment lowered the peak temperature for cast films of 1(14,2) and 1(14,6), whereas 1(16,6) and 1(16,10) showed rises of the peak temperature. These data indicate that phase transition characteristics are maintained after generation of CdS in cast films.

These 1-CdS composite films were soluble in organic solvents such as chloroform. ^1H-NMR spectrum of 1(14,6)-CdS composite film in $CDCl_3$ was different from that of Cd^{2+} complex of 1(14,6) and was quite similar to that of 1-HCl. These NMR data indicate that Cd^{2+} ions become detached from the bilayer surface upon introduction of H_2S, and resulting protonated cyclam units are absorbed on the particle surface. Figure 1 compares absorption spectra of 1(14,2)-CdS and 1(16,10)-CdS composites dissolved in chloroform. They are identical to that of the original cast films. It is known that bulk CdS start to absorb close to 520 nm (corresponding to a band gap of 2.4 eV photon energy) and the optical absorption edge show blue-shifts as the particle size decreases.2) The absorption threshold observed for cast films is shifted to shorter wavelengths compared to bulk CdS. In addition, CdS generated at 15 °C displayed a larger shift than the

Table 1. DSC Characteristics of Cast Films

Sample	Peak top (T_C) / °C	ΔH / kJ mol^{-1}	ΔS / J $K^{-1}mol^{-1}$
1(14, 2)-Cd^{2+}	49.6$^{a)}$, 53.8	24, 13	76, 40
1(14. 2)-CdS	38.7	28	90
1(14, 6)-Cd^{2+}	62.7	19	57
1(14, 6)-CdS	36.2, 50.5$^{a)}$	10, 23	32, 72
1(16, 6)-Cd^{2+}	50.1	35	107
1(16, 6)-CdS	49.3, 59.2$^{a)}$	4, 25	12, 74
1(16,10)-Cd^{2+}	59.5	25	75
1(16,10)-CdS	48.6, 62.7$^{a)}$	3, 22	9, 66
	70.3	2	5

a) Main peak.

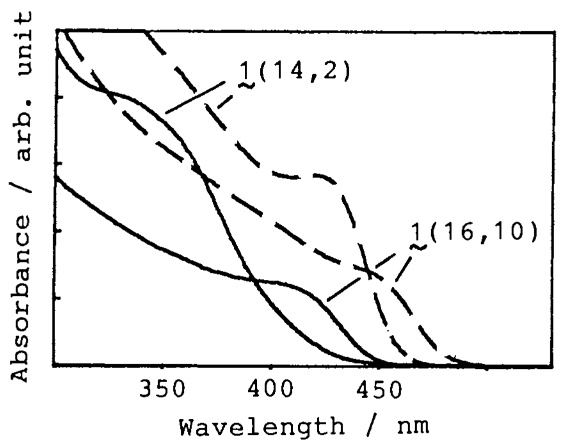


Fig. 1. Absorption spectra of **1**-CdS in chloroform solution.
solid line ; CdS generated at 15 °C.
broken line ; CdS generated at 80 °C.

Table 2. Absorption threshold of CdS formed in preorganized cast films of **1**(n,m)-Cd^{2+}

Amphiphile	λ / nm$^{a)}$	λ / nm$^{b)}$
1(14, 2)	410 (27 Å)$^{c)}$	460 (41 Å)
1(14, 6)	440 (32 Å)	460 (41 Å)
1(16, 6)	445 (35 Å)	470 (46 Å)
1(16,10)	445 (35 Å)	480 (53 Å)

a) Temp 15 °C. b) Temp 80 °C.
c) estimated particle size according to Ref. 18.

80 °C - sample. These data clearly show that the size quantization occured depending on the physical state of cast films. The observed absorption thresholds are summarized in Table 2, together with the particle diameter estimated according to the literature.$^{18)}$ All these films gave absorption edges around 460 nm (d $\approx$ 41 Å) when CdS particles were prepared at 80 °C (above T_C). On the other hand, absorption thresholds were affected by the amphiphilic structure, when CdS was prepared at 15 °C. These results indicate that the kinetics of particle growth is influenced by spatial arrangement and/or mobility of Cd^{2+}/cyclam complexes in the crystalline film, as well as by the physical state (crystal vs. liquid crystal) of the film. Apparently, cadmium ions gain much more mobility in the liquid crystalline film, resulting in the formation of larger particles (460 nm species). It is noteworthy that observed absorption onsets are blue shifted from the bulk value even when CdS was prepared in the liquid crystalline

film. Therefore, coagulation of the growing particles is effectively suppressed by the layered amphipile, due to adsorption of the cyclam moiety on CdS surface.

It is established that cast films of synthetic bilayer membranes are superior templates for controlled preparation of quantum sized CdS particles. The chemical structure of the ligand amphiphile as well as the physical state of the bilayer influence the kinetics of particle growth. Different spectral onsets observed below T_c imply possible fine tuning of the semiconductor band gap by changing the amphiphilic structure. High solubility of these composite quantum-particles in organic solvents may lead to novel photoreactions in organic media.

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