

Synthesis and Properties of CdS Clusters

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The synthesis and properties of cadmium sulfide particles in the size regime intermediate between the bulk and molecular states has been an area of intense research, and several review articles have been recently published [1]. It has been shown that the electronic properties of these particles change dramatically when the diameter of the particle approaches the diameter of the e^-/h^+ pair created by absorption of photons [1f,2,3]. For sufficiently small particles, the exciton (e^-/h^+ pair) is thus "quantum trapped". For CdS, this occurs for particle diameters of less than 60 Å. Because of this quantum confinement, the band structure of the bulk semiconductor becomes more discrete as the particle size decreases [1a]. This is observed experimentally [4]. For such small particles, surface effects play a more important role, the reason being that a higher percentage of the atoms are on the surface. Surface defects trap the e^-/h^+ pair in shallow potential wells, which further enhance the quantum effect [1a]. The confinement of the exciton pair on the particle surface allows for interesting chemical applications such as photochemical water reduction [1d,5,6,7] and optical switching [3,8]. Since the particle size greatly affects the electronic properties of these "quantum" clusters, much effort has been put into the synthesis of materials with narrow particle size distributions.

A simple method for the synthesis of CdS is to bubble H_2S into a solution of Cd^{2+} in the presence of a thiol such as PhSH [9]. Binding of both anions to the Cd^{2+} cations present will occur, the rates of both dependent on the anion concentration. Since the thiol stops the growth of the CdS particle by "capping" the metal ion, the particle size synthesized is determined by the S^{2-}/SPh ratio present. Samples of CdS prepared in this manner can be isolated as powders and subsequently redissolved.

CdS particles have also been synthesized inside of bilayer vesicles, such as dihexadecylphosphate (DHP) [6,10]. The vesicles offer control of CdS cluster size and increase the stability of the particles, possibly through hydrophobic interactions which move the cluster into the bilayer membrane. The semiconductor particles grow to diameters of ca. 40 Å. Samples with Rh^{3+} inside the vesicles have also been made. In this system, luminescence due to the return of the excited e^-/h^+ to the ground state can be quenched by Rh^{3+} , which results in the formation of rhodium-coated CdS particles. PhSH is present as a sacrificial electron donor. Photochemical splitting of water then occurs by transfer of the excited electron from CdS to the rhodium atoms, which catalyze the formation of H_2 and O_2 from H_2O . The reaction scheme shown in Figure 1 has been proposed [10].

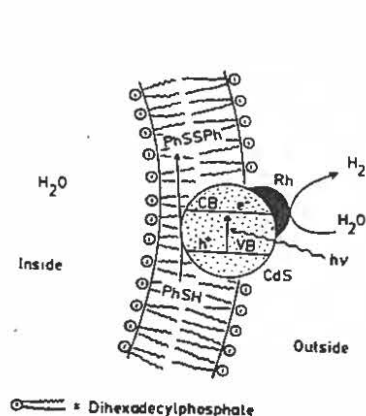


Figure 1

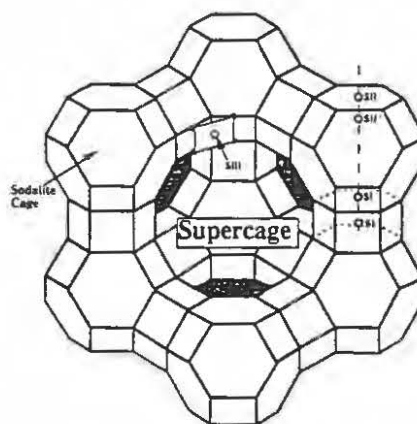


Figure 2

Yeast has also been used to grow CdS clusters [11]. Eukaryotic organisms produce short, cysteine-rich peptides as a response to the presence of cadmium ions, which are toxic to the yeast. Cadmium also stimulates the bioproduction of sulfide ions. The peptides induce the formation of discrete particle sizes by coating the clusters, thus preventing further growth. For example, CdS particles isolated from *Candida glabrata* about 85 CdS units capped by about 30 peptide units [11b]. Particle growth can be stimulated by adding free sulfide, increasing the temperature, or lowering the pH.

Even more rigid templates for the size-controlled synthesis of CdS involves the use of aluminosilicate cages. Zeolite Y, for example, undergoes cation exchange in the presence of Cd^{2+} . It has been proposed that the Cd^{2+} ions occupy the SI' sites in the smaller sodalite cages of the zeolite (Figure 2), surrounded by an octahedral array of oxygen atoms [1e,12]. Addition of H_2S replaces some of the oxygen atoms surrounding the cadmium ions with sulfides. At higher loadings of S^{2-} , adjacent sodalite cages contain CdS particles, and these particles begin to interact, forming a larger supercluster. This occurs when a specific amount of S^{2-} has been added, and is evidenced by the onset of luminescence [12a]. Zeolites with different sized cages can be used, resulting in CdS particles of different diameters.

Other materials that have been used as templates for controlled cluster synthesis include polymers [13], micelles [14], and layered metal phosphonate systems [15]. Each method has disadvantages, the most important being the difficulty of achieving a narrow distribution of particle sizes. Growing monodisperse films of semiconductor particles is also a problem, but it is necessary for optical applications. The advantages of semiconductor clusters over current systems in the areas of optical materials and the conversion of photons to chemical energy will insure that better synthetic methods will be found.

References

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