

## Formation of Q-state CdS Colloids using Ultrasound

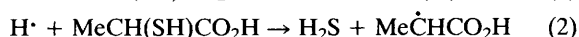
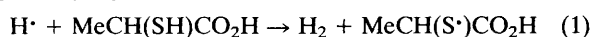
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The formation of quantum-sized CdS particles has been achieved by the irradiation of aqueous solutions of Cd<sup>2+</sup>-thiol-sodium hexametaphosphate with 20 kHz ultrasound.

The absorption of high-intensity ultrasound by water can produce H<sup>•</sup> and OH<sup>•</sup> radicals in solution.<sup>1-6</sup> In the presence of solutes dissolved in the water these primary radicals can be scavenged leading to the formation of other radicals and a host of chemical reactions.<sup>6-8</sup> It has been shown that both the primary and secondary radicals are able to react with aqueous metal ions or metal complexes to yield colloidal metals<sup>9-11</sup> and metal oxides.<sup>12</sup> We have also found that the size of the colloidal particles produced is quite small, <10 nm.<sup>9</sup> This particular observation prompted us to examine the formation of semiconductor colloids to see if the mechanism of particle formation initiated *via* ultrasound would produce quantum sized, or Q-state particles.

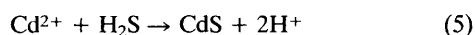
It is known from radiation chemical studies that attack of H<sup>•</sup> on certain thiols leads to the release of H<sub>2</sub>S.<sup>13-15</sup> For example, in the case of 2-mercaptopropionic acid, the relevant reactions are given by eqns. (1) and (2).



The H<sup>•</sup> species produced by sonication of water can in principle participate in the above reactions if sufficient thiol is present in solution to prevent the recombination reactions (3) and (4) which occur predominantly within the cavitation



bubble.<sup>8,16</sup> The more surface active the additive, the greater the scavenging efficiency of the solute.<sup>5,9</sup> The H<sub>2</sub>S produced by reaction (2) can then be reacted further with, for example, Cd<sup>2+</sup>,<sup>15</sup> eqns. (5) and (6).



To gain some estimate of the importance of reaction (2) in a sonochemical process we monitored the spectral changes following sonication of solutions of Cd<sup>2+</sup>-thiol-sodium hexametaphosphate (HMP). The latter component was required to minimise the formation of UV-absorbing Cd(thiol) complexes.<sup>15</sup> The sonication system used was a conventional 20 kHz horn sonifier, operating at 15 W cm<sup>-2</sup>. All solutions were purged with N<sub>2</sub> for 15 min before sonication and then maintained under an atmosphere of N<sub>2</sub> during sonication. In all the sonication experiments the temperature was maintained at 20 ± 4°C to prevent any bulk thermal reaction of Cd<sup>2+</sup> with the thiols which can occur at reasonable rates at temperatures >40°C. At room temperature no noticeable thermal reaction was observed for any of the thiols used over several days.

The changes in absorption of a solution of Cd<sup>2+</sup>-DL-penicillamine [(Me<sub>2</sub>C(SH)CH(NH<sub>2</sub>)CO<sub>2</sub>H]-HMP as a function of the time of sonication are shown in Fig. 1. The absorption bands produced are essentially the same as those observed for Q-state CdS particles of different sizes. Also shown are the fluorescence spectra observed from the particles formed in the sonicated solution. These fluorescence spectra are similar to those observed in the radiation chemical formation of CdS particles in the presence of HMP and 3-mercaptopropane-1,2-diol.<sup>15</sup>

The effect of the thiol type on the particle size was also

examined and the results are shown in Figs. 2 and 3. Both figures show that sonication produces CdS particles which are in the Q-state range and that the type of thiol present determines the size of the particle formed after any particular amount of sonication. The wavelengths for the onset of absorption of the CdS particles produced at different times of sonication and in the different thiol systems are shown in Table 1. We also deliberately saturated a solution of Cd<sup>2+</sup>-2-mercaptopropionic acid-HMP with H<sub>2</sub>S gas to give the spectrum shown in Fig. 2. It is clear that exposure of the solution to a high local concentration of H<sub>2</sub>S produces a larger wavelength absorption threshold, hence larger particles than by the sonochemical 'titration' of the Cd<sup>2+</sup> in solution. The absorption spectra obtained following sonication were reason-

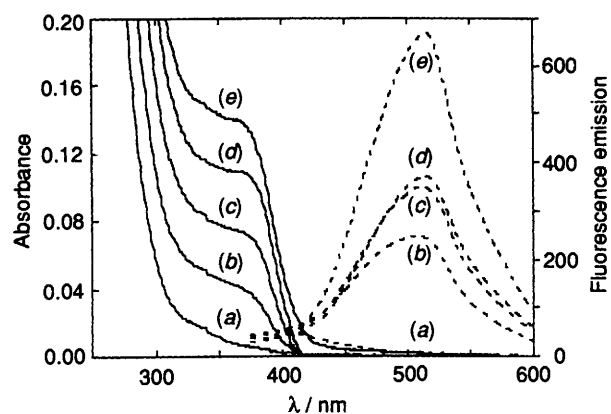


Fig. 1 Absorption (—) and emission (---) spectra (arbitrary units) obtained from Cd<sup>2+</sup> (2 × 10<sup>-4</sup> mol dm<sup>-3</sup>)-DL-penicillamine (0.1 mol dm<sup>-3</sup>)-HMP solutions. Before sonications (a), after 20 (b), 40 (c) and 60 min sonication (d) and upon equilibration overnight (e). The bulk solution temperature was maintained between 18.0 and 23.5°C, pH = 5.6. The excitation wavelength for the emission spectra was λ = 320 nm.

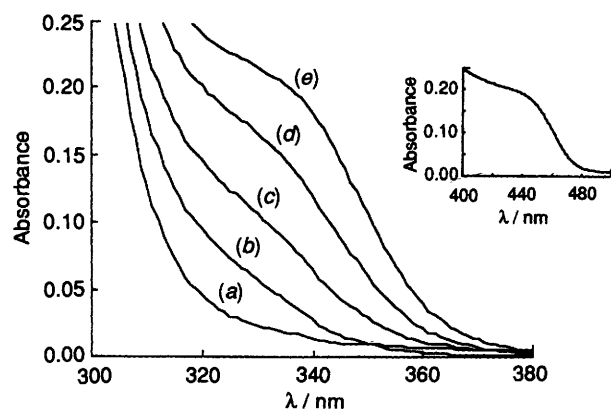
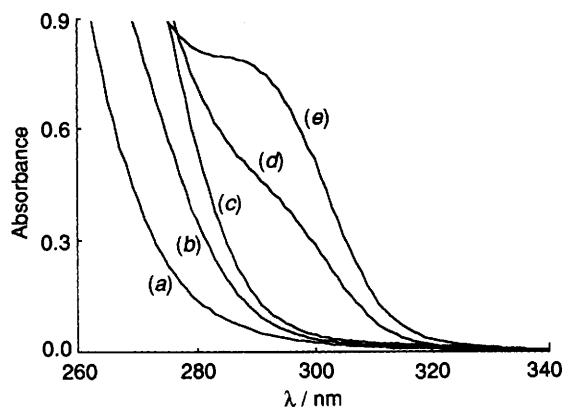


Fig. 2 Absorption spectra obtained from Cd<sup>2+</sup> (2 × 10<sup>-4</sup> mol dm<sup>-3</sup>)-2-mercaptopropanoic acid (0.1 mol dm<sup>-3</sup>)-HMP solutions. Before sonication (a), after 20 (b), 40 (c) and 60 min sonication (d) and upon equilibration overnight (e). The bulk solution temperature was maintained between 18.5 and 21.4°C, pH = 5.0. The insert shows the resultant absorption spectrum obtained after H<sub>2</sub>S saturation of a similar solution.

ably stable, and only after prolonged standing was there a shift to higher wavelengths, indicative of an increase in the mean particle size. Table 1 also lists the wavelengths for the onset of absorption after equilibration for 24 h of the sonicated solution, prepared using the different thiol systems.

It is interesting that the sonochemical formation of CdS particles can yield colloids which approach the cluster size range.<sup>16</sup> They are relatively stable in this form presumably because of adsorption of the thiol-HMP onto the particle surface. This is very similar to the observations reported from the  $\gamma$ -radiolysis of Cd<sup>2+</sup>-3-mercaptopropane-1,2-diol-HMP solutions.<sup>15</sup> The results also show that sonochemical reactions



**Fig. 3** Absorption spectra obtained from Cd<sup>2+</sup> ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>)-3-mercaptopropanoic acid (0.1 mol dm<sup>-3</sup>)-HMP solutions. Before sonication (a), after 20 (b), 40 (c) and 60 min sonication (d) and upon equilibration overnight (e). The bulk solution temperature was maintained between 18.0 and 21.5°C, pH = 5.0.

**Table 1** Wavelength of the onset of absorption obtained at various sonication times in Cd<sup>2+</sup>-thiol-HMP systems<sup>a</sup>

Thiol	Onset $\lambda$ /nm			
	$t^b$ /min			
	20	40	60	<i>c</i>
DL-Penicillamine	404	408	409	411
2-Mercaptopropionic acid	347	355	361	365
3-Mercaptopropionic acid	294	297	315	317

<sup>a</sup> Cd<sup>2+</sup> ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>)-thiol (0.1 mol dm<sup>-3</sup>)-HMP ( $1.5 \times 10^{-4}$  mol dm<sup>-3</sup>). <sup>b</sup> Time of sonication. <sup>c</sup> For solutions left to equilibrate for 24 h after sonication for 60 min.

can mimic the radiation-initiated chemical process in the same controlled way. It is the low local concentration of H<sub>2</sub>S produced in solution by sonication which is conducive to the formation of ultrasmall semiconductor particles. This is probably due to the fact that at low CdS nucleation rates, efficient capping of the Q-state particles occurs before they can aggregate. In contrast, when H<sub>2</sub>S gas is bubbled through a Cd<sup>2+</sup>-thiol solution, a higher nucleation rate can be expected with the primary particles coalescing before thiol stabilization occurs.

R. A. H. acknowledges the support of a Australian Postgraduate Research Award. P. M. is supported by a QEII Fellowship. This work was sponsored by the Australian Research Council grant scheme.

Received, 2nd December 1993; Com. 3/07147B

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