



for example, can be oxidized to 3-methyl-2-butenal in 72% yield, when treated with BTSC. Since the vinyl addition to ketones yields the tertiary alcohols, this sequence provides a way to synthesize the α,β -unsaturated carbonyl compounds with two carbon elongation from ketones. Phenyl substituted enones or enals produced by this procedure underwent carbon-carbon double oxidation, and alkanophenone was obtained as a major final product.

We are currently studying other features of this interesting reagent.

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Effect of EDTA on the Formation and Stability of CdS Colloidal Semiconductor

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Colloidal CdS semiconductor particle has much of the desired characteristics for using it in solar energy conversion systems and photocatalytic reactions.^{1,2} The semiconductor particle is usually prepared *in situ* from cadmium salt solution by addition of sulfide solution or by exposure to H₂S gas. The properties of the particle are greatly dependent on the size of the particle,³ which varies with preparation mode. In CdS-mediated photochemical reduction reaction, e.g. water splitting, the photogenerated electron of the semiconductor is transferred to oxidant. For sustained reaction, the presence of sacrificial electron donor which supplies electrons to the positive holes of the semiconductor particles is required. Ethylenediaminetetraacetate (EDTA) is frequently utilized for the purpose.^{4,7} However, EDTA forms complex CdEDTA²⁻ with Cd²⁺. Thus the presence of EDTA in solution is expected to affect the formation and behavior of CdS colloid. Present communication reports results of investigations on this aspect.

Colloidal CdS was prepared by mixing 1.0×10^{-3} M CdCl₂ solution with 1.5×10^{-3} M Na₂S solution at equal volume ratio. Both solutions contained desired concentration of Na₂EDTA ($0-3.0 \times 10^{-3}$ M) and pH of the solutions was adjusted to 8.0 ± 0.3 with HCl/NaOH. Formation of CdS colloid was detected by yellow coloration visually and followed by absorption spectra. The spectra were taken after vigorous vortex of the mixtures aged for desired period. Figures 1a-c show absorption spectra of the mixtures after 10 min, 24 hrs and 48 hrs of mixing. The most remarkable effect of EDTA was retardation of CdS colloid formation. In the absence of EDTA, the mixture showed yellow color instantaneously.

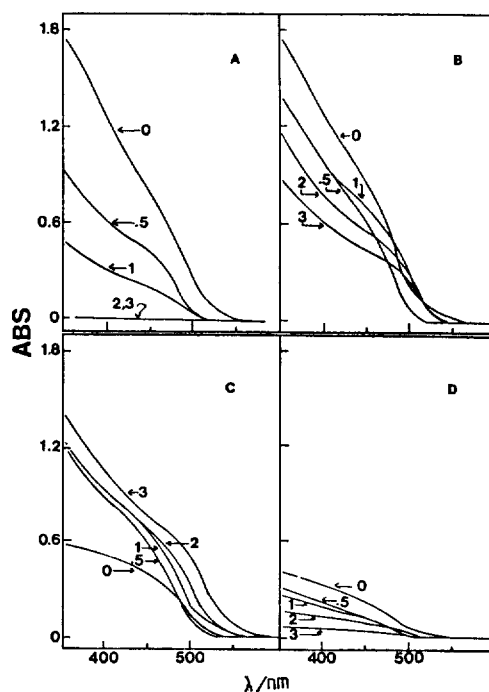


Figure 1. Absorption spectra of solutions after mixing 1.0×10^{-3} M CdCl₂ and 1.5×10^{-3} M Na₂S solutions in equal volume ratio in the presence of EDTA at pH 8: A, after 10 min; B, after 24 hrs; C, after 48 hrs. Solutions for spectra D included 6×10^{-4} M Tris and other conditions were the same as C. The concentrations of EDTA in mM unit are shown in Figures.

However, presence of EDTA blocked CdS colloid formation, *i.e.* yellow coloration of the solution, for a period of 3-5 min in $0.5-1.0 \times 10^{-3}$ M EDTA, about 1 hour in 2.0×10^{-3} M EDTA and as long as 24 hrs in 3.0×10^{-3} M EDTA. Even in the presence of 3.0×10^{-3} M EDTA, the free Cd^{2+} in the initial mixture is about 2000 times supersaturated, compared to the calculated equilibrium concentration in 0.75×10^{-3} M sulfide solution.⁸ Therefore CdS colloid formation is clearly retarded kinetically by EDTA. This is quite similar to the phenomena observed in CuS precipitation.¹⁰

The other effect of EDTA on CdS colloid formation was dependency of absorption edge of the colloidal solutions on the concentration of EDTA. Absorption edge is defined as the intersection of the base line with the tangent drawn to the shoulder.¹ Weller *et al.* showed theoretically and from comparison with many experimental data that absorption edge of CdS particle increases sharply with the diameter of the particle and reaches a constant wavelength ca. 510 nm for macrocrystalline solid.³ As can be seen from Figure 1a, the absorption edge of initially formed CdS colloid in the presence of 0.5×10^{-3} and 1.0×10^{-3} M EDTA is at shorter wavelength than the value for CdS obtained in the absence of EDTA. The absorption edges shift to longer wavelength as time passed (Figure 1b, 1c), but still appeared near or at shorter wavelength than that formed in the absence of EDTA. This implies that the CdS colloidal particles formed in presence of 0.5×10^{-3} and 1.0×10^{-3} M EDTA have smaller size. This infers that, in the low concentration of EDTA, nucleation of CdS particle is not significantly inhibited and the major effect of EDTA is retardation of growth of CdS nuclei. On the other hand, CdS colloidal solutions obtained in large excess of EDTA ($2.0-3.0 \times 10^{-3}$ M) exhibited absorption edge at longer wavelength indicating the formation of large CdS particles (see Figure 1c). This can be attributed to inhibition of nucleation as well as growth of CdS particle by the high concentration of EDTA.

EDTA also had large effects on the precipitation of CdS particles and scattering of light from the solutions. The relative scattered light intensity was monitored from a Hitachi 650-10S spectrofluorimeter with incident light of wavelength 600 nm. CdS colloidal solution prepared in the absence of EDTA flocculated to precipitate and scattered light strongly as soon as the Cd^{2+} and sulfide solutions were mixed. On the other hand, solutions formed in the presence of EDTA gave little initial scattering. As time passed after mixing the solutions, scattering from solutions containing $2-3 \times 10^{-3}$ M EDTA was significantly enhanced and formation of precipitate was observed. However, scattering from solutions with 0.5×10^{-3} and 1×10^{-3} M EDTA virtually unchanged and no precipitation was observed upto 48 hours. This, in part, can be attributed to difference in the size of CdS particles depending on the concentration of EDTA: the larger particles formed at high concentration of EDTA scatter light more strongly and sediment faster than the smaller particles formed at low concentration of EDTA. However, we can not rule out the possibility that EDTA affects flocculation of CdS particles. If this is held, the flocculation seems to be prevented to the greatest extent when [EDTA] is $0.5-1 \times 10^{-3}$ M.

We also tested the effect of other chelating agents, tartrate and phosphate. Though these are also known to form complexes with Cd^{2+} , the presence of these chelating agents

as high as 2×10^{-2} M had little effect on the CdS colloid formation: mixing of the Cd^{2+} and sulfide solutions gave instantaneous yellow coloration and precipitation.

2-Amino-2-(hydroxymethyl)-1,3-propanediol (Tris) is widely used as a buffer near pH 8 and is known to form complexes with divalent metal ions.¹¹ Presence of low concentration of Tris had little effect on the formation of CdS colloid in the absence of EDTA. But Tris enhanced the retarding effect of EDTA remarkably. For example, no appreciable yellow color of CdS colloid was detected in 24 hrs in the presence of as low as 6×10^{-4} M Tris and 1.0×10^{-3} M EDTA; with the same concentration of EDTA in the absence of Tris, the color appeared in about 5 min. The absorption spectra of the solutions after 48 hrs of mixing are shown in Figure 1d.

So far, we have demonstrated that the sacrificial electron donor EDTA for CdS mediated photoredox reactions has large effects on the *in situ* formation and stability of the CdS colloidal semiconductor particle. The smallest size and highest stability of the CdS colloid can be achieved with near stoichiometric concentration of EDTA with respect to Cd^{2+} . The commonly used Tris buffer system has synergetic effect for retardation of the colloid formation by EDTA, and care should be exercised in choosing buffer. Studies on the detailed mechanism and further effects of EDTA and other agents on the CdS colloidal systems are underway.

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8. Formation constant of CdEDTA^{2-} is 2.9×10^{16} and the fraction of EDTA existing as EDTA^{4-} at pH 8 is 5.4×10^{-3} .⁹ Thus the concentration of the free Cd^{2+} in the initially 5×10^{-4} M Cd^{2+} solution with 3.0×10^{-3} M EDTA at pH 8 is about 1×10^{-15} M. The fraction of sulfide present as S^{2-} at pH 8 is 1.0×10^{-7} as $\text{p}K_1$ and $\text{p}K_2$ of H_2S are 7.2 and 14.9, respectively. Solubility product constant of CdS is 3.6×10^{-29} , while $[\text{Cd}^{2+}][\text{S}^{2-}] = 7.5 \times 10^{-26}$ in the initial stage of the experimental condition.
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