Catalytic Effect of Ag$^+$ in Colloidal CdS-Induced Photooxidation of Aniline

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The efficiency of colloidal CdS-induced oxidation of aniline is enhanced by doping Ag$^+$. The luminescence of CdS particles containing low Ag$^+$ is quenched by added aniline. At high concentrations of Ag$^+$ ($\geq$10%) no quenching of emission is observed. It is understood by the formation of Ag_2S phase on the surface of CdS particles which prevents photogenerated holes to interact with the adsorbed aniline. The catalytic action of Ag$^+$ is attributed to the efficient charge transfer at CdS-Ag_2S interface upon irradiation to the adsorbed redox species.

In recent years, a number of photocatalytic reactions initiated by colloidal semiconductors have been investigated for the elucidation of the mechanism of their catalytic action.[1] CdS is among widely explored photocatalyst as its absorption extends into the visible region.[2-4] Lately, we have shown that the oxidation of aniline by photogenerated holes at CdS surface leads to the formation of azobenzene with a quantum yield of 0.15.[4] In the present work we report that colloidal CdS particles containing Ag$^+$ further enhanced the efficiency of this reaction by about 40%. Reber and Rusek[5] have achieved efficient H_2 production from platinized suspensions of CdS modified by Ag_2S.

The slow addition of 1 to 20 percent silver (concentration of Ag$^+$ is given in percent of the equivalent CdS concentration) to the stirred colloidal CdS promoted the red luminescence of CdS (Figure 1a) without bringing any shift in the emission wavelength in agreement with the findings of Spanhel et al.[6] An amount of 2 percent Ag$^+$ caused about three fold increase in luminescence efficiency and does not bring any change in its electronic spectrum in the visible region (Figure 1b). At this concentration a large part of silver is known to remain dissolved in the CdS lattice.[5,6] The luminescence intensity of these particles is reduced in the presence of aniline (Figure 2). An increase in concentration of aniline beyond 5 x 10^{-3} M, however, did not cause any additional quenching of emission. An increase in the concentration of Ag$^+$ to 4 percent enhanced the luminescence yield of CdS further by about 1.5 times but the extent of quenching of emission of these particles by aniline is appreciably decreased. The CdS solution containing 10 percent Ag$^+$ did not demonstrate any quenching effect. At high concentrations of Ag$^+$ (> 2 percent), the onset of absorption is red shifted due to the formation of Ag_2S at the interface of CdS and a large portion of silver is then present in the form of Ag_2S phase (Figure 1b).

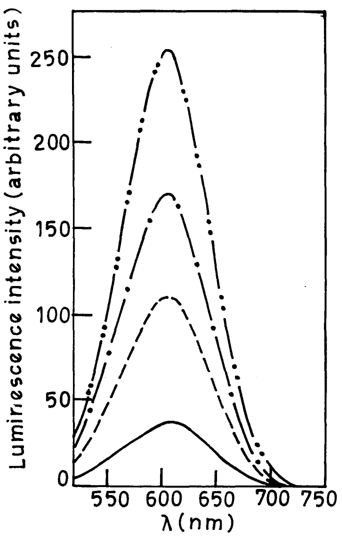

Figure 1(a). Luminescence spectra of 0.25 mM colloidal CdS containing various concentrations of Ag$^+$ (in percent of the equivalent CdS concentration) at pH 10.5.:– 0; -- 2; -–4; ---- 10. Excitation wavelength 400 nm.

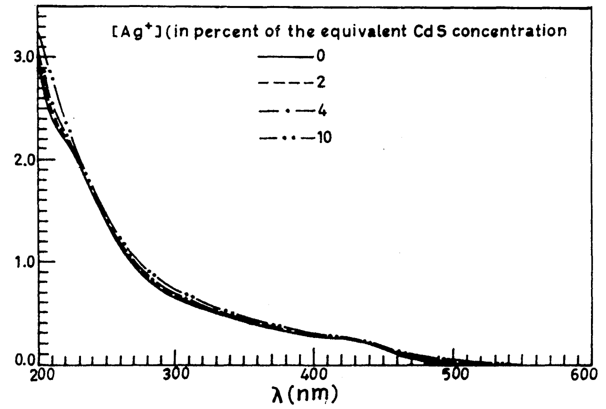

Figure 1(b). Absorption spectra of 0.25 mM CdS containing various concentrations of Ag$^+$ (in percent of the equivalent CdS concentration) at pH 10.5.: –0; - - 2; --- 4; ---- 10 .

Aniline is found to get adsorbed on the surface of both type of colloidal CdS particles, i.e. with and without having Ag$^+$. The amount of adsorbed aniline was similar for both type of particles and at low concentrations of aniline the adsorption data followed the Langmiur isotherm. At high concentrations of aniline, the adsorption behaviour matches with the Type-II isotherm and thus corresponds to multilayer adsorption.

The photoirradiation of reaction mixture containing silver doped CdS (0.64 mM) and 10 mM aniline in the visible region ($\geq$ 400 nm) results in the formation of azobenzene as the only product which is confirmed by GCMS [m/e 182(42) P, 105 (23), 77(B), 51(35), 50(8), 44(77)] and was estimated by GC[7]. The photocatalytic activity of CdS is increased by increasing [Ag$^+$]. This was, however, not proportionate to the amount of added Ag$^+$ (Figure 3). An addition of 2 percent of Ag$^+$, which remains largely dissolved in the CdS lattice, improved the quantum efficiency of azobenzene by 30% and a further increase in [Ag$^+$] upto 15

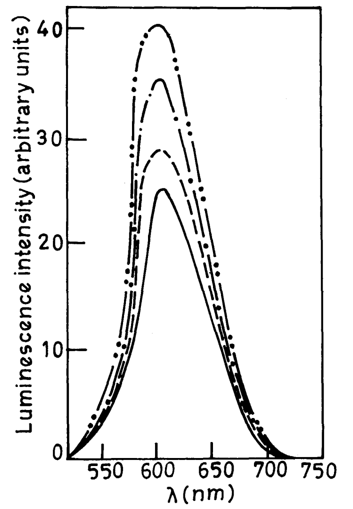

Figure 2. Luminescence spectra of 0.25 mM colloidal CdS containing 2 percent Ag^+ (of the equivalent CdS concentration) in presence of various concentrations of aniline at pH 10.5.: -‥- 0;--- 0.5 mM;--1.0 mM; — 5.0 mM. Excitation wavelength 400 nm.

percent enhanced it slightly to 40%. At high $[Ag^+]$ (>2%) a certain fraction of light is now absorbed by Ag_2S phase which does not contribute towards product formation.[8] The catalytic activity of these particles is found to diminish upon aging. In the absence of aniline, Ag^+ added in increments increasingly prevented the photocorrosion of colloidal CdS.

An increase in red photoluminescence of silver modified CdS particles is understood by the creation of more of these radiative centres involving anion vacancies.[4,6,9,10] At low $[Ag^+]$, the anion vacancies are possibly created at CdS/Ag_2S microheterojunctions (Figure 1b). The quenching of photoluminescence of these particles by aniline is explained by scavenging of the photogenerated holes by the adsorbed aniline. The lifetime data of CdS emission followed three-exponential decay at 600 nm and had an average lifetime ($<\tau>$) of about 10 ns. In a typical case, an addition of 2 percent of Ag^+ enhanced $<\tau>$ of colloidal CdS to 80 ns which is decreased to 28 ns in the presence of 10 mM aniline. It thus supports the hypothesis of charge transfer to the adsorbed aniline. The fact that this emission could not be quenched completely, indicates that the process of charge transfer to the redox couple involves complex mechanism. At higher concentrations of silver, Ag_2S forms a separate phase surrounding colloidal CdS. The adsorbed Ag_2S may not allow photogenerated holes to diffuse to the surface of the particles. In other words the trapped hole cannot be intercepted by the adsorbed aniline directly and thereby no quenching of emission is observed. In addition to the formation of Ag_2S, free Cd^{2+} released in the solution might also contribute to the non-quenching effect due to the formation of $Cd(OH)_2$ layer at the interface.

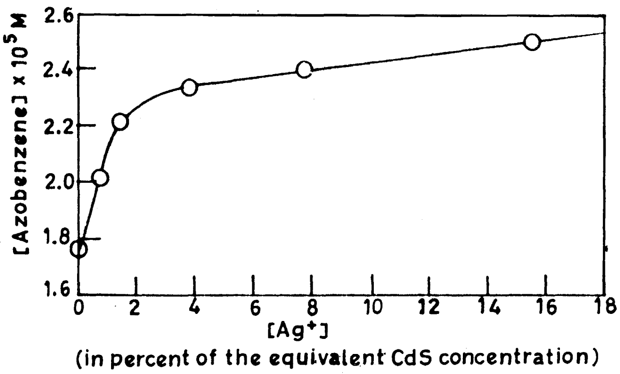

Figure 3. Yield of azobenzene as a function of the concentration of Ag^+ after 5 min. of irradiation.

Increased photocatalytic activity of colloidal CdS containing silver ions can be attributed to the occurrence of the following two processes. Silver sulphide phase assists in the trapping of electrons and holes at $CdS\text{-}Ag_2S$ micro heterojunctions. The trapped charge carriers are then efficiently scavenged by the adsorbed redox species, O_2 and aniline, due to their prolonged lifetime. In the absence of aniline, the hole (S^-) reacts with colloidal Ag_2S which is evidenced by reduced anodic photocorrosion of CdS.

In conclusion, silver containing colloidal CdS generates microheterojunctions consisting of $CdS\text{-}Ag_2S$ phases. The photoirradiation of such particles causes a better charge separation leading to the increased reactivity of generated electron-hole pair with the adsorbed species.

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