Enhancement of Photocatalytic Oxidation Activity by Surface-Modified CdS Nanoparticles of High Photostability

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High photostable CdS nanoparticles modified with alkyl group were prepared by an improved microemulsion technique using hexanethiol (RSH) as co-surfactant. The surface-modified CdS nanoparticles (R-CdS) catalyzed the photooxidation of 4-chlorophenol *via* continuous bubbling oxygen under UV light. The photocatalytic oxidation activity of R-CdS nanoparticles was enhanced due to the high photostability generated by heat-treatment.

The utilization of semiconductor nanoparticles as photocatalysts to initiate interfacial redox reactions has evoked great interest in recent years.[1,2] The photogenerated electron-hole pairs can be trapped and react with the molecules at the particle surface. When the semiconductor particle size falls below a critical diameter of 10 nm, the charge carriers appear to behave quantum mechanically. As a result of this confinement, the band gap increases and the band edges shift to yield larger redox potentials. The increased driving force would increase the rate constant of charge transfer.[3] In addition, the long-lived photogenerated carriers would also be appeared due to the size-quantization.[4,5] Thus the quantum-size semiconductor particles should result in an enhancement of the photocatalytic activity for redox reactions induced by photogenerated carriers.[2,6]

CdS is one of the most efficient semiconductor photocalalysts, but it has been only used in a large number of studies on photocatalytic reductions due to its photoanodic corrosion.[6,7] It is highly desirable if CdS can also be activated using visible light in addition to UV light. Hence it may provide a possible alternative for direct utilization of solar energy to carry out photocatalytic oxidization such as photodegradation and photosynthesis. Therefore, it is crucial to increase the photostability of CdS.[7]

In the present work, surface-modified CdS nanoparticles were prepared by using co-surfactant hexanethiol ($C_6H_{13}SH$) as capping reagent in an inverse microemulsion. The high photostability of R-CdS nanoparticles (S_{II}) was achieved for the first time by heat-treatment so as to form compact CdS cores by removing water from the inside of the nanoparticles (S_I) (Figure 1). In addition, the heat-treatment also resulted in the strong chemical surface-modification by the reaction between excess cadmium and $C_6H_{13}SH$ at the surface of CdS nanoparticles. This is the first attempt to photocatalytically oxidize toxic organic compounds[3] with continuous bubbling oxygen as electron scavenger by R-CdS nanoparticles. An enhancement of the photocatalytic activity has been clearly observed to photodegrade 4-chlorophenol under UV light.

The procedure for the preparation of R-CdS nanoparticles was as follows. Microemulsion A consisted of 72.2 wt% heptane, 12 wt% aqueous solution of 0.1 M $Cd(NO_3)_2$ and 15.8 wt% surfactant of AOT/$C_6H_{13}SH$ at molar ratio of 1 to 5. Microemulsion B consisted of 73.8 wt% heptane, 10 wt% aqueous solution of 0.1 M $(NH_4)_2S$ and 16.2 wt% surfactant of AOT/$C_6H_{13}SH$ (1/5 molar ratio). Equal amount of the microemulsion A and the microemulsion B were mixed with stirring for half an hour at room temperature. The mixed microemulsion changed slowly from transparent to translucent and it was subjected to centrifugation. The precipitate was washed with heptane several times and recovered by centrifugation. It was dried by evacuating heptane under reduced pressure, and the final product was labeled as sample I (S_I). Sample II (S_{II}) was prepared directly by heat-treating (*via* refluxing) the mixed microemulsion under nitrogen to remove H_2O and replace AOT by $C_6H_{13}SH$ completely from CdS nanoparticles in the suspension. The dried S_{II} was obtained by the identical procedure to S_I.

S_I was almost covered with the capping reagent (-C-S stretching at 700 cm^{-1}) besides a very small amount of residual AOT (-SO_3Na at 1000, 1100-1300 cm^{-1} and -C=O at 1740 cm^{-1}) and some water as verified by IR and UV analysis. The similar result has also been reported for surface-capped CdS nanoparticles prepared by the method of M. L. Steigerwald *et al.*[6] However, S_{II} was completely modified with the capping reagent without any residual AOT on the surface of R-CdS nanoparticles. It was also free of water because the strong water absorption peak at 1900 nm no longer appeared in the near-infrared absorption spectrum of S_{II} in tetrahydrofuran. Thus the heat-treatment in our improved method is a key success to prepare pure chemical surface-modification nanoparticles (Figure 1). There was not much difference in their particle sizes of R-CdS before and after heat-treatment as viewed by TEM. The particle sizes were about 4 nm in diameter. The clear excitonic peaks for both S_I and S_{II} indicated monodispersive distribution in their similar absorption spectra, from which the same particle sizes were also estimated as compared with TEM results.[8]

Under the irradiation of 200 W low pressure mercury lamps, photocatalytic oxidation experiments were carried out in a quartz tube with a 10 mL tetrahydrofuran solution containing 1 mM 4-chlorophenol and 1 g/L R-CdS nanoparticles. Oxygen was continuously bubbled into the solution throughout the entire experimental process. Figure 2 illustrates the photooxidation of 4-chlorophenol catalyzed by R-CdS nanoparticles (S_I and S_{II}) as a function of irradiation time. The relative concentration of 4-

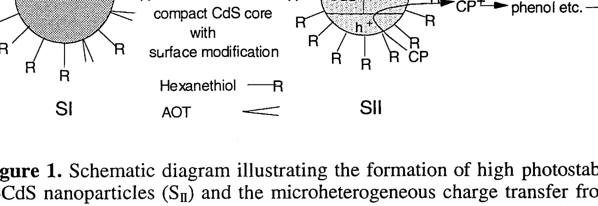

Figure 1. Schematic diagram illustrating the formation of high photostable R-CdS nanoparticles (S_{II}) and the microheterogeneous charge transfer from the valence band of the R-CdS nanoparticles to 4-chlorophenol molecules.

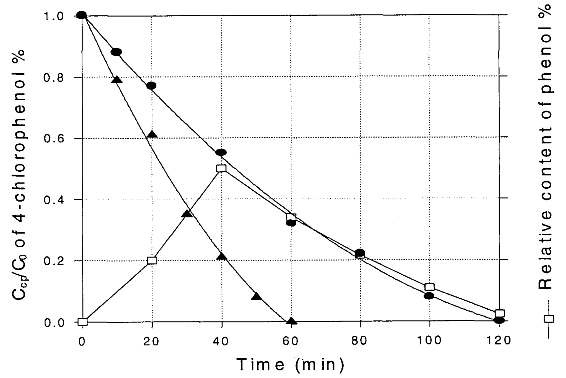

Figure 2. C_{cp}/C_0 *vs.* time plots showing the photodegradation of 4-chlorophenol photocatalytically oxidized by R-CdS nanoparticles for S_I (filled circles) and S_{II} (filled triangles). Relative content of phenol *vs.* time plot showing the kinetic process of phenol photocatalytically oxidized by R-CdS nanoparticles for S_{II} (open squares).

chlorophenol (C_{cp}/C_0) decreases steadily with irradiation time. It is found that heat-treatment is crucial to the enhancement of photooxidation activity of R-CdS nanoparticles. The R-CdS nanoparticles (S_{II}) with chemical surface-modification at the surface of compact CdS cores exhibit high photostability and can generate more stable long-lived excitation states than that of S_I, from which high oxidizing activity can be achieved.[5,9] The photodegradation experiment of 4-chlorophenol in the absence of R-CdS was carried out to compare with the above experiment. No photodegradated products were observed in this process.

During the photocatalytic oxidation process, S_{II} was very stable as no significant difference for their absorption spectra was observed under a long time (more than 10 h) irradiation, and similar particle sizes before and after the photocatalytic process were verified by TEM. But S_I was not stable enough from being oxidized. The solution color changed from initially light yellow to slightly white turbid and finally colorless with white precipitates at the bottom of the reacting vessel under long time UV irradiation. H. Yoneyama *et al.* have reported that the CdS nanoparticles can be photocorroded to the extent that gives the absorption onset equal to the wavelength of the irradiated photons.[10] It indicates that the complete photocorrosion of the CdS nanoparticles can be carried out and generate white inorganic salt which precipitates in the organic phase under the high frequency irradiation of 253.7 nm UV light. It was the case for S_I, but S_{II} was not photocorroded under such an irradiation in the presence of oxygen, indicating its high photostability.

The schematic diagram in Figure 1 illustrates that the CdS nanoparticles were coagulated into compact cores (S_{II}) by heat-treatment to remove water from its inside, and then the strong chemical surface-modification took place at the interface of S_{II}. The compact structure of CdS cores can hinder oxygen from going inside of the cores in R-CdS nanoparticles. Thus the photogenerated electrons can be captured by the outer oxygen as electron scavenger which is brought into contact with the surface of the CdS cores, the remaining photogenerated holes inside can be removed instantly by those oxidizable species at the surface of R-CdS. This implies that R-CdS nanoparticles were not easy to be oxidized with the attack of holes. On the other hand, the surface-modified layer should not be oxidized in the photocatalytic process. This is because those photogenerated carriers captured by the surface-capped layer at the interface can transfer back to the CdS particles and recombine again with opposite charges newly generated in the valence/conduction bands. If the species capture the carriers through contact with the surface of CdS, they will be oxidized or reduced because the charged species will leave the CdS surface and the carriers cannot transfer back to recombine again. The results for S_{II} indicate that the surface-modified layer of R-CdS was indeed photostable. Otherwise, the CdS nanoparticles without the surface-modified layer (stabilizer) can result in aggregation of nanoparticles to be further photocorroded and no longer disperse in the organic solvent.

However, it was not the case for S_I because the CdS cores were not compact enough and chemical surface-modification was incomplete, where some water and AOT were still present. Oxygen can still access to the inside of CdS cores, and capture the photogenerated electrons *via* direct contact with CdS. Large amount of holes can be generated inside of CdS cores and not removed instantly. Thus the photocorrosion of the R-CdS nanoparticles will take place easily with attack of lots of holes.

Phenol and hydroxylated biphenyl intermediates were detected during the photocatalytic oxidation of 4-chlorophenol. Figure 2 also shows the formation of phenol during the photooxidation catalyzed by S_{II}. C. P. Huang *et al.* have reported the photocatalyzed oxidation pathways of 2,4-dichlorophenol by CdS powder with continuous bubbling oxygen. Hydroxygenated biphenols and phenol were also found in the weak basic environment.[7] The mechanism could be proposed as follows: chlorinated phenols can be adsorbed on CdS surface with high adsorption density in acidic environment, this implies that almost no water molecules could occupy the CdS surface. Hence direct oxidation by photogenerated holes is the major oxidation way. However, these species (4-chlorophenol) will not be adsorbed easily on the CdS surface in the weak basic environment due to its electrostatic repulsion and lack of specific chemical interaction. This implies there is enough empty surface that can be occupied by surface adsorbed water and OH^- on the CdS. The hydroxyl radicals produced *via* oxidation of water and hydroxyl group result in the attack of hydroxyl radical as the predominant oxidation way. Hence hydrogenerated biphenols and phenol intermediates were generated in our weak basic system.[7]

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