

# JAST

Journal of Analytical Science & Technology

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# Journal of Analytical Science & Technology

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# Photocatalytic Efficiency Analysis of CdS Nanoparticles with Modified Electronic States

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## ABSTRACT

For the photooxidative reaction of olefin, colloidal CdS nanoparticles (NPs) show enhanced efficiency of photocatalytic activity compared to bulk CdS. We find that the enhanced activity is due to the enlarged surface area of the colloidal CdS NPs as well as enhanced energetic coupling between the colloidal CdS NPs and the olefin molecules. Photocatalytic activity is reduced in the case that CdS NPs are encapsulated in mesoporous silica nanopores.

**Key words:** CdS, nanoparticles, photocatalysis, olefin, mesoporous

## INTRODUCTION

Photocatalysis of organic molecules with semiconductors has been attracted a great deal of interests for the last

several decades [1-5]. The photocatalytic reactions using inorganic semiconductors have much been reported for the bulk particles of which band-gap energies ( $E_g$ ) were well known and fixed. When light is

irradiated, organic molecules on a semiconductor surface can be photochemically oxidized or reduced in high chemical yields.

Previously, the carbonylization of an olefin, 1,1-diphenylethylene (DPE), had been studied with bulk titania semiconductor in the presence of oxygen and light ( $\lambda < 380$  nm) [6,7]. The proposed mechanism of such photocatalytic molecular conversion includes the process of photo-excited carriers transfer from the semiconductor to DPE and molecular oxygen in reaction solution. The photo-induced intermediate species, olefin cation radicals and oxygen radicals, are coupled each other, and consequently result in benzophenone (BP) [4]. Therefore, the efficient energetic coupling between the electronic energy bands of semiconductors and the respective redox potential states of organic reactants is a crucial factor for the high chemical yield of photocatalytic reactions [8,9].

Since organic compounds have finite oxidation and reduction potential energies, variable electronic band energy of a semiconductor, which can be simply controlled by decreasing nanoparticle diameter, can modify the photocatalytic efficiency. Because of the characteristics of heterogeneous photocatalytic reaction, the surface condition of a semiconductor is an additional factor for a photo-induced chemical reaction [5]. In this study, we report controllable photocatalytic activities on the olefin conversion with the CdS semiconductor particles depending on different diameters and surface conditions.

## MATERIALS AND METHODS

The photocatalytic reactions were performed on the CdS semiconductor of different diameters and surface conditions: Bulk, colloid, and encapsulated form in MCM-41 mesoporous materials. Bulk CdS (purchased from Aldrich) microparticles were used in photocatalytic reaction without further purification. Nanosized colloidal CdS particles were prepared as following procedures. 25 ml of 0.1 M Cd(NO<sub>3</sub>)<sub>2</sub> aqueous solution was added to 25 ml of 0.1 M Na<sub>2</sub>S solution. Mixing both the ionic solutions yielded colloidal CdS NPs

through rapid precipitation, and the resulting colloidal CdS nanoparticles (NPs) were separated from the solution and purified by repetitive centrifugations. The encapsulated CdS NPs in mesoporous MCM-41 were prepared by introducing reverse micelles including CdS NPs into the pores of the MCM-41, and then calcined at 500 °C, as described in our previous report [10]. Hereafter, we denote it as CdS@MCM.

For the heterogeneous photocatalytic reaction, the respective CdS catalysts (bulk, colloidal NPs, and CdS@MCM-41) of powder type (5 mg) were suspended in respective solutions (3 ml) of 0.01M DPE in dry acetonitrile/trifluoroethanol (20:1 v/v), and then the heterogeneous solutions were irradiated with the light ( $\lambda > 350$  nm) for 6 hours with Xe lamp under oxygen atmosphere at room temperature. After irradiation, the mixtures were filtered with a 0.2  $\mu$ m membrane to remove suspended CdS catalysts from the solutions. The separated homogeneous solutions were further applied to spectroscopic measurements to evaluate photocatalytic efficiency.

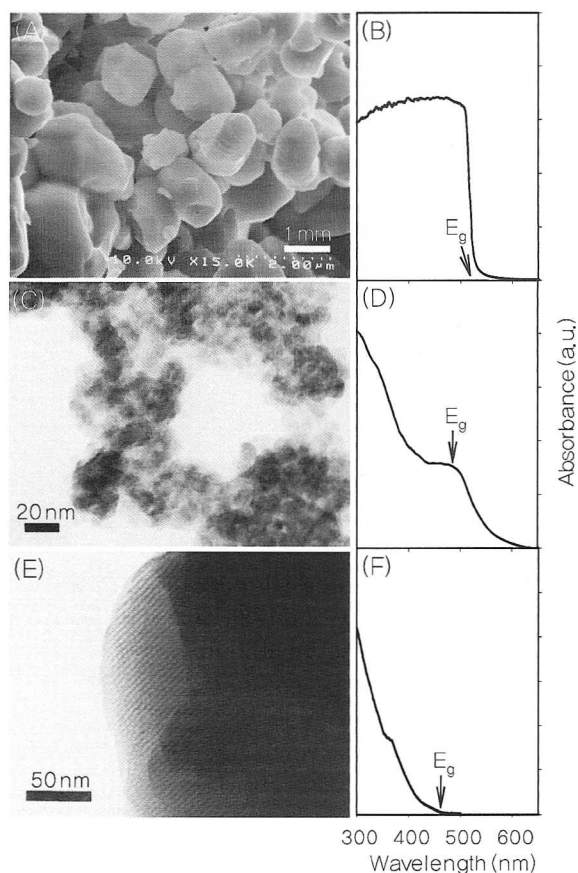
A field-emission scanning electron microscope (FE-SEM, JEOL, JEM-6700F) and a transmittance electron microscope (TEM, JEOL, 3011) were utilized to analyze the size and morphology of the utilized CdS catalysts. Absorption spectra were measured using a spectrophotometer (Jasco, V-550) equipped with an integrating sphere (Jasco, ISV-469). Fourier-transformed infrared (FT-IR) spectra were obtained using a spectrometer (Nicolet, Impact 400).

## RESULTS AND DISCUSSION

Figure 1 shows the electron microscopic images for the bulk, the colloidal, and the encapsulated form of CdS. The bulk CdS has a particle size of  $1.4 \pm 0.5 \mu$ m (Figure 1A). The colloidal CdS shows small crystallites with an average particle diameter of  $6 \pm 2$  nm (Figure 1C). The encapsulated CdS in the MCM-41 has an effective crystallite diameter of  $\sim 1.6$  nm (Figure 1E), which is proven in our previous report [10].

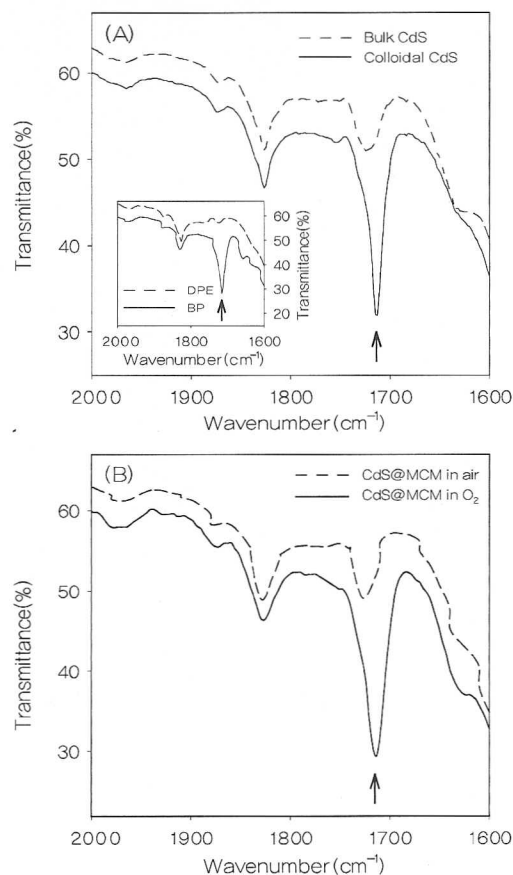
The observed absorption spectra show unique





**Figure 1.** Electron microscopic images of (A) the bulk, (C) the colloid, and (E) the encapsulated form of CdS in the mesoporous MCM-41. Absorption spectra of (B) the bulk, (D) the colloid, and (F) the encapsulated form of CdS in the MCM-41 are also presented.

confinement properties depending on the diameter of CdS. The absorption spectrum of the bulk CdS exhibits the characteristic bulk band-gap energy of  $\sim 2.4$  eV ( $\sim 520$  nm), as shown in Figure 1B. As the particle size reduces to  $\sim 6$  nm for the colloidal NPs, an excitonic absorption peak is observed, which appears in the blue-shifted spectral region of  $\sim 490$  nm (Figure 1D). When CdS NPs are confined in the mesoporous MCM-41, the observed spectrum shows an absorption onset at  $\sim 465$  nm that is further blue-shifted from the band-gap energy of the colloidal CdS NPs. Such absorption characteristics of the size-dependent blue-shift is due to quantum size effects [11].



**Figure 2.** FT-IR spectra for the olefin solution after photocatalytic reaction with the different catalysts: (A) the bulk (dashed line) and the colloidal (solid line) CdS, and (B) the CdS@MCM in ambient (dashed line) and oxygen gas bubbled conditions (solid line). Inset is the FT-IR spectra for pure DPE and BP molecules.

With the CdS particles of different diameters and surface conditions, here we have conducted the well-known photocatalytic conversion of olefine, i.e., DPE to BP. Figure 2 shows the infrared vibrational spectra for the solutions before and after the photocatalytic conversion reactions. Photocatalytic conversion efficiency could be easily estimated from vibrational spectra. Since the photo-oxidized product of benzophenone has a carbonyl group, it provides a strong absorption band in the characteristic region of  $\sim 1,720\text{cm}^{-1}$  (indicated by arrows) that is responsible for the symmetric C=O stretching mode of the carbonyl group. This vibrational mode is clearly discriminated

from DPE molecule without the carbonyl group (inset of Figure 2A). Therefore, the intensity change of this characteristic vibrational band directly informs the efficiency of the photocatalytic conversion from DPE to BP. Figure 2 shows the intensity change of the characteristic C=O stretching mode after photocatalytic conversion as the different catalysts used. With the bulk CdS, the characteristic carbonyl stretching band is a little increased, while it is greatly enhanced when the colloidal NPs were used as a catalyst (Figure 2A).

It is well-known that the excitation of semiconductor catalyst with the light of higher energy than its band-gap energy generates charge carriers (i.e., electrons and holes) in the catalyst, which leads to oxidation or reduction reaction of an involved organic molecule [12]. In the photocatalytic system with bulk CdS, the holes that are generated in the valence band ( $E_v = +1.6$  V vs. saturated calomel electrode (SCE)) of the catalyst with light excitation ( $\lambda_{\text{ex}} > 350$  nm) are utilized for the oxidation of DPE ( $E_{\text{ox}} = +1.8$  V vs. SCE) whereas the photo-excited electrons in the conduction band ( $E_c = -0.85$  V vs. SCE) are transferred to reduce the molecular oxygen ( $E_{\text{red}} = -0.78$  V vs. SCE), which generate the radical oxygens [13-15]. For the bulk CdS, the photocatalytic conversion yield is proven to be low in this study, as similarly with the previous report [16], which is plausibly due to a low surface area of bulk particles and weak energetic couplings between the bulk CdS and the organic molecules that were participated in the photo-redox processes. However, in the photocatalytic reaction with the colloidal CdS NPs, it is notable that a considerable quantity of the photo-oxidized product of BP is produced (Figure 2A). Such the result is expected from the quantum size effect of the CdS NPs. The  $E_g$  of CdS increases by  $\sim 0.15$  eV as the particle size decreases from the bulk to the particle diameter of  $\sim 6.0$  nm, which is estimated from Figure 1C and D. Therefore, the valence band potential (+1.6 V) of the bulk CdS approaches toward the oxidation potential (+1.8 V) of DPE as particle size decreases, which consequently enlarges the energetic coupling between the two energy states. Meanwhile, the conduction band potential (-0.85 V) also increases as the particle size decreases, which departs from the reduction potential (-0.78 V) of the molecular oxygen

for the radical oxygen generation. On the other hand, surface electronic states, which abundantly exist below the conduction band of CdS NPs, have a larger chance to overlap with the reduction potential of the oxygen. Previously, it was suggested that an indirect electronic transition might be possible through the surface defect states [17]. Such an indirect electronic transition is shown for the CdS NPs in this study as the extended absorption at the longer wavelength region below the bulk band-gap energy of  $\sim 520$  nm, which is energetically lower than the interband transition at  $\sim 490$  nm (Figure 1D). This extended absorption is not prominent in the bulk CdS (Figure 1B). Therefore, these intermediate trap states are conceived to mediate photo-excited electrons transfer to the molecular oxygen more efficiently, and then, subsequently, producing the radical oxygen species more.

In order to estimate the role of the intermediate trap states, we have accomplished the photocatalytic conversion using the catalyst of CdS@MCM composite, with which it is generally expected a high yield of photocatalysis due to the increased band-gap energy (Figure 1F). On contrary, the observed photocatalytic efficiency is not so prominent in ambient condition with the CdS@MCM composite catalyst (Figure 2B). It was spectroscopically proved that the intermediate trap states on the surface of the encapsulated CdS NPs are largely eliminated through strong chemical coupling between CdS NPs and surrounding silica wall framework [10,18]. Therefore, we believe that this low photocatalytic conversion yield is mainly attributed to the reduced population of surface electronic states in the case of the CdS@MCM. Interestingly, the photocatalytic conversion is recovered in the reaction solution that is priority oxygen gas bubbled, which implies that the less efficient reaction pathway due to the reduced density of surface electronic states can be recovered through the additional introduction of oxygen concentration.

## CONCLUSIONS

In conclusion, the energetic couplings between the valence and conduction bands with the oxidation and

reduction potential states of reactant molecules is not large enough for the photocatalytic reaction of olefin using bulk CdS catalyst. In the case of CdS NPs, however, the increased band-gap energy and the large fraction of the surface electronic states enable the efficient energetic coupling to the organic reactant molecules (olefin and oxygen), which consequently result in the considerable photocatalytic activity. However, the encapsulated form of CdS NPs in the MCM-41 nanopores show reduced photocatalytic activity compared to the colloidal CdS NPs.

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