

## Capability of coupled CdSe/TiO<sub>2</sub> for photocatalytic degradation of 4-chlorophenol

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### Abstract

The photocatalytic process using TiO<sub>2</sub> and coupled semiconductor in the photodegradation reaction of 4-chlorophenol (4-CP) was investigated. Nanosized titanium dioxide powder was synthesized via the sol–gel procedure and modified via the coupled photocatalysts. The microstructural and chemical properties of TiO<sub>2</sub> and coupled CdSe/TiO<sub>2</sub> were also examined. For CdSe/TiO<sub>2</sub> samples, the specific surface area was 7.0 m<sup>2</sup>/g and the deposition proportion of CdSe was approximately 27.6%. In the photocatalysis results, higher photodegradation efficiency of 4-CP was observed at higher pH values. In the UV 254 nm system, the degradation efficiency of 4-CP and TOC with sol–gel produced TiO<sub>2</sub> (TiO<sub>2</sub>(SG)) powder was higher than with commercial TiO<sub>2</sub>(RdH) powder. For the coupled semiconductor system (CdSe/TiO<sub>2</sub>), the apparent first-order rate constants were  $1.35 \times 10^{-2}$ ,  $4.33 \times 10^{-2}$ ,  $2.0 \times 10^{-3}$  and  $1.9 \times 10^{-3} \text{ min}^{-1}$  at the conditions of pH 7 (254 nm), pH 11 (254 nm), pH 7 (365 nm), and pH 11 (365 nm). The disappearance of 4-CP under CdSe/TiO<sub>2</sub>(RdH) photoreaction at pH 7 and 365 nm condition is better than that of TiO<sub>2</sub>(RdH) system, with 30% versus 22% 4-CP reduction in 180 min. In the same condition, CdSe/TiO<sub>2</sub>(RdH) provided more photomineralization efficiency than that of TiO<sub>2</sub>(RdH) in terms of TOC reduction. Both 4-CP and TOC reduction were significant for systems illuminated at 254 nm. Considering the direct photolysis effect at 254 nm where 4-CP reduction is near 100% and TOC removal is nil, CdSe/TiO<sub>2</sub>(RdH) exhibits a 50% photomineralization efficiency and a nearly four times faster reaction rate than the single TiO<sub>2</sub>(RdH) semiconductor.

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**Keywords:** Photocatalysis; TiO<sub>2</sub>; Coupled semiconductor; 4-CP

### 1. Introduction

In most of the industrial wastewater treatment works, adsorption by activated carbon, advanced chemical oxidation, and enhanced coagulation are commonly employed technologies for removal of refractory pollutants from industrial wastes. These treatment schemes provide fairly reliable effectiveness on pollutant removal. However, the chemicals and adsorbents used and the solid residues (sludge) generated are unavoidable disadvantages of these treatment practices. For decades, scientists and engineers are seeking innovative tech-

nologies that can be applied to degrade chlorine-containing refractory organic pollutants, particularly with low or no chemical usage and sludge generation. The advance of photochemical processes has made the decomposition of synthesized refractory organics sustainable, especially with the advent of semiconductor photocatalysts [1,2]. Several semiconductors have been developed to exhibit photocatalytic behavior. The most commonly referenced semiconductors for waste degradation are TiO<sub>2</sub>, ZnO, CdS, etc. [1]. Most studies on photoassisted decomposition of chlorinated organic compounds used TiO<sub>2</sub> as a model photocatalyst because of the photooxidation efficiency and stability of TiO<sub>2</sub> under illumination in aqueous environments [3–6]. A dosage of 2–5 g/L TiO<sub>2</sub> irradiated by near UV light with wavelength below near

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400 nm is able to decompose chlorophenol effectively to inorganic carbon in about 350 min without consuming chemicals and generating sludge [3,6].  $\text{TiO}_2$  has also been employed to investigate the photodegradation of various organic pollutants such as *p*-coumaric acid, 2-phenylphenol, humic acids, dyes, and 4-nitrophenol, etc. [7–9]; their results have shown a very promising application of  $\text{TiO}_2$  on photodecomposition of organic pollutants.

Upon irradiation, conduction band electrons and valance band holes will be created in a semiconductor. These electrons and holes in conjunction with dissolved oxygen and hydroxyl ions on the semiconductor surface will initiate complicated redox reactions in aqueous systems, resulting in oxidizing organic pollutants. However, the rapid recombination of photoproducted electrons and holes in semiconductors significantly diminishes the efficiency of photocatalytic reactions [10], therefore providing limited usefulness in practical applications. To enhance the photocatalytic efficiency of semiconductors, Serpone et al. [10] proposed an interparticle electron transfer process (IPET) by coupling two semiconductors with different redox energy levels to increase charge separation for the corresponding conduction and valance bands. By IPET, electrons are irreversibly transferred from the photoactivated semiconductor to the non-photoactivated semiconductor and holes are transferred from the non-photoactivated semiconductor to the photoactivated semiconductor [10]. Thus, the efficiency of photocatalytic reactions can be enhanced. Theoretically, CdS and ZnO are in the category of photoexcited semiconductors, which are typically coupled with non-photoexcited semiconductors of  $\text{TiO}_2$  and  $\text{SnO}_2$  to promote permanent charge separation via IPET [10]. In the past decade, composite semiconductors are attractive approaches to achieve better efficiency on photodegradation of refractory organics [10–14]. Serpone et al. [10] examined the kinetics of phenol disappearance with various combinations of composite semiconductors ( $\text{CdS}/\text{TiO}_2$ ,  $\text{CdS}/\text{Fe}_2\text{O}_3$ ,  $\text{CdS}/\text{SnO}_2$ ,  $\text{TiO}_2/\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}/\text{SnO}_2$ ,  $\text{ZnO}/\text{TiO}_2$ ,  $\text{ZnO}/\text{WO}_3$ ,  $\text{TiO}_2/\text{SnO}_2$  and  $\text{TiO}_2/\text{WO}_3$ ) to provide evidences of the IPET process. For example, it is apparent that  $\text{TiO}_2$  is sensitized by CdS illuminated at  $> 406$  nm via IPET, while there is no disappearance of phenol concentration at the same conditions with  $\text{TiO}_2$  alone. Kang et al. [13] compared the photodecomposition of 4-CP with  $\text{TiO}_2$  and  $\text{CdS}/\text{TiO}_2$  suspensions. They concluded that the apparent rate constants and adsorption constants of 4-CP on  $\text{CdS}/\text{TiO}_2$  are 2 and 1.5 times higher than those on  $\text{TiO}_2$ . Doong et al. [11] also reported that coupled  $\text{TiO}_2/\text{CdS}$  (0.5/0.5 g/L) exhibits better 2-chlorophenol degradation than  $\text{TiO}_2$  (0.5 g/L) and CdS (0.5 g/L) alone.

Sensitization of  $\text{TiO}_2$  by CdS is frequently addressed in research on coupled semiconductors. With lower band gap energy and higher energy level, CdS is an ideal semiconductor to couple with  $\text{TiO}_2$  for promoting the IPET process and enhance the efficiency of photodegrading refractory organic pollutants. Among the various semiconductors, we found that CdSe with even lower band gap energy (1.7 eV compared to

CdS of 2.4 eV) is another potential material to form composite semiconductors with  $\text{TiO}_2$ . The photocatalytic properties of coupled  $\text{CdSe}/\text{TiO}_2$  have not been investigated extensively. Therefore, it is the purpose of this study to examine the photodegradation efficiency of coupled  $\text{CdSe}/\text{TiO}_2$  using 4-CP as a test substrate. In addition, the effects of UV light wavelength and solution pH on photodegradation efficiency in single- and coupled-photocatalyst systems were also evaluated.

## 2. Materials and methods

The experimental work consists of preparation of  $\text{TiO}_2$  and coupled  $\text{CdSe}/\text{TiO}_2$ , characterization of coupled  $\text{CdSe}/\text{TiO}_2$  and photodegradation of 4-CP with  $\text{TiO}_2$  alone and coupled  $\text{CdSe}/\text{TiO}_2$ .

### 2.1. Preparation of semiconductors

Two types of  $\text{TiO}_2$  were used in this study.  $\text{TiO}_2(\text{SG})$  was prepared using a sol–gel method [15].  $\text{TiO}_2(\text{RdH})$  was obtained from Riedel-de Haen Co. (Sleeze, Germany). In the preparation of  $\text{TiO}_2(\text{SG})$ , 10 mL of  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  (Aldrich) was mixed with 5 mL propanol (J. T. Baker), and further mixed with a solution of propanol/deionized water (10 mL propanol in 120 mL deionized water). Then 0.4 mL of nitric acid (65%, Ferak) was added and the whole batch stirred at 800 rpm for 24 h. After the formation of semi-transparency gels, the batch was conditioned at  $50^\circ\text{C}$  for dehydration. The dehydrated gels were then ground and calcined at  $500^\circ\text{C}$  for 2 h to obtain  $\text{TiO}_2(\text{SG})$  particles.

Coupled  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  was prepared by liquid phase deposition.  $\text{TiO}_2(\text{RdH})$  was used to serve as a medium platform to chemically couple CdSe precipitates. The steps were: (1) preparation of sodium selenosulfite ( $\text{Na}_2\text{SeSO}_3$ ) solution by dissolving 5 g selenium powder (Nacalai Tesque) and 10 g  $\text{Na}_2\text{SO}_3$  (Nacalai Tesque) in 150 mL deionized water (the solution was continuously stirred at  $70^\circ\text{C}$  for 6 h), (2) preparation Cd cocktail solution consisting of 10 mL 0.5 M  $\text{Cd}(\text{CH}_3\text{COO})_2$  (Ferak), 10 mL  $\text{NH}_4\text{OH}$  (28%, Nacalai Tesque) and 15 mL triethanolamine ( $> 99\%$ , Ferak), (3) addition of 20 mL  $\text{Na}_2\text{SeSO}_3$  solution to the Cd cocktail solution and stirring for 6 h at  $45^\circ\text{C}$ , while controlling solution pH between 10 and 10.5 with  $\text{NH}_4\text{OH}$ , and (4) use of deionized water to wash the composite product and then dehydrating at  $110^\circ\text{C}$  for 24 h to obtain  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  particles.

### 2.2. Characterization of semiconductors

Prepared semiconductors were subjected to differential thermal analysis (DTA) with a Dupont TA 1600 and X-ray diffractometry (XRD) with a Scintag X1 for morphology, electron spectroscopy for chemical analysis (ESCA) with a VG Scientific ESCALAB 250 spectrometer for surface distribution of elemental composition, and scanning electron

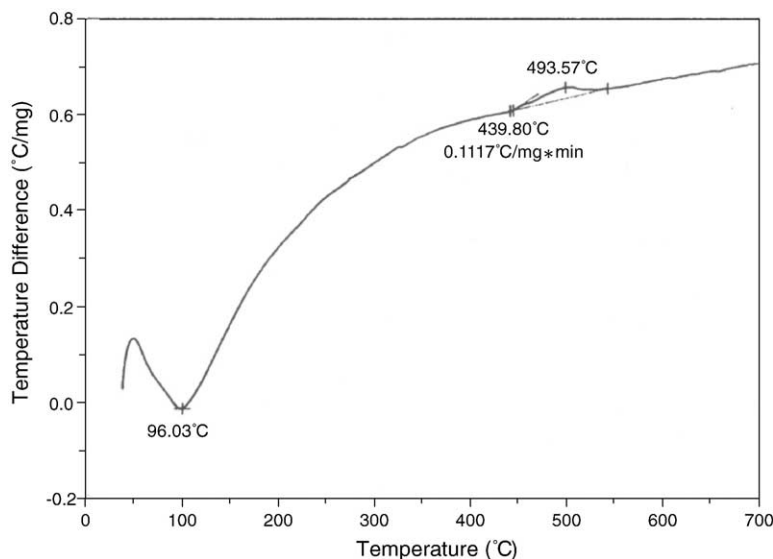


Fig. 1. The DTA result of  $\text{TiO}_2$  (SG).

microscopy (SEM) with a LEO 1530. Specific surface areas of the semiconductors were measured by the BET method with a Micromeritics ASAP2010. UV–vis spectroscopy was used to profile the absorbance spectrum of the semiconductors from wavelength 190–1000 nm at a rate of 500 nm/min with a GBR Cintar 20. The UV–vis spectrum results were used to calculate semiconductor band gap energy.

### 2.3. Photodegradation of 4-CP

All chemicals used in the experiments were of analytical grade. 4-CP was obtained from Avocado Co. with an analytical purity of > 99%. Water used was deionized and double distilled with a MINIQ. Photocatalytic experiments were carried out in a 3 L hollow cylindrical glass reactor. The reactor was cooled with circulating water to maintain reaction temperature at a constant  $298 \pm 2$  K. The inner hollow tube is made of quartz and an 8 W UV-lamp (Philips) was placed inside the hollow tube as an irradiation source. Three UV-light wavelengths of 254, 365 and 420 nm were utilized. The bandwidth of the 254, 365 and 420 nm UV-lights ranged from 230 to 320 nm, 300 to 460 nm and 400 to 520 nm, respectively. The photocatalyst concentration was 1.2 g/L and the 4-CP concentration was  $2 \pm 10^{-4}$  M in all experiments. The reaction system was continuously stirred at 300 rpm and the solution pH was controlled at 7 and/or 11 by an automatic titrator.

An aliquot of 20 mL sample was withdrawn from the photoreactor at a pre-determined time interval. The photocatalyst suspension was separated by centrifugation at 3000 rpm or 15 min, then filtered by a  $0.22 \mu\text{m}$  filter. Mineralization of 4-CP was defined by reduction in total organic carbon (TOC), which was analyzed with a O.I. 1010 TOC analyzer. Photodegradation of 4-CP was detected by high performance liquid chromatography (HPLC) using a Millipore

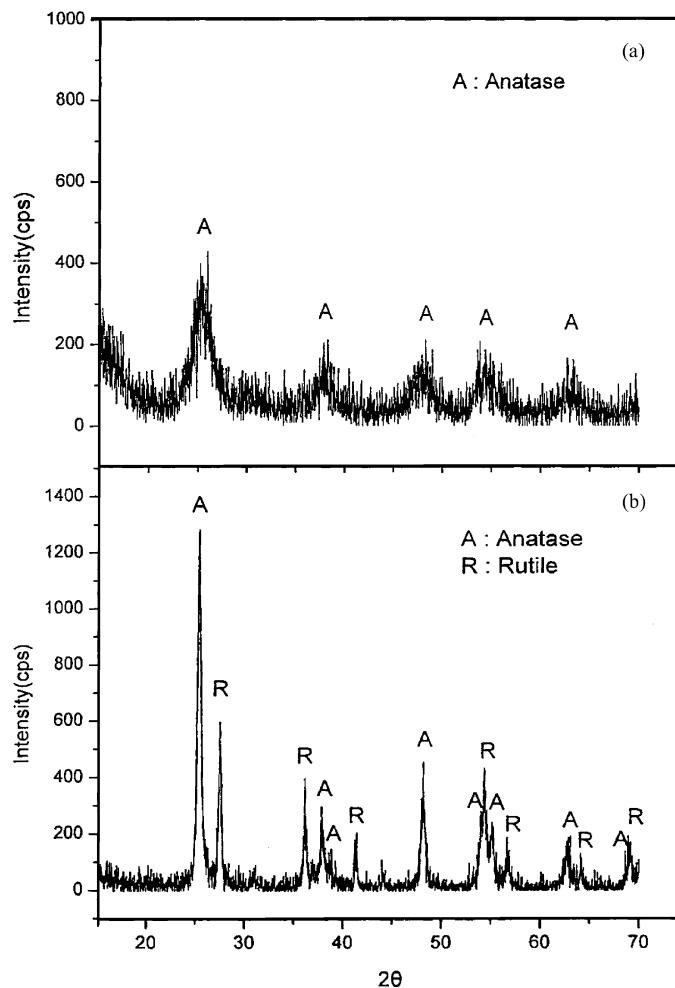


Fig. 2. The XRD patterns of  $\text{TiO}_2$  (SG): (a) before  $500^\circ\text{C}$  calcinations; (b) after  $500^\circ\text{C}$  calcination.

Waters 600E with a Waters 486 detector. A MetaChem Polaris C18-A5  $\mu$  column ( $250 \pm 4.6$  mm) and a detection wavelength of 224 nm were used in HPLC operation with  $\text{CH}_3\text{CN}:\text{H}_2\text{O}:\text{CH}_3\text{COOH}$  (50:50:0.1) mobile phase. In addition, chloride concentration was detected by a Dionex model DX-120 ionic chromatograph (IC) to determine the photodechlorination efficiency.

### 3. Results and discussion

#### 3.1. Characterization of $\text{TiO}_2$ particles

Anatase, rutile and brookite are the three phases of  $\text{TiO}_2$  crystals. Anatase and rutile exhibit better photocatalytic activity than brookite [16]. Theoretically, the phase transformation occurs at  $500^\circ\text{C}$  where anatase is gradually shifted to the rutile phase, which is less photoactive than anatase [16]. In DTA analysis (Fig. 1), an exothermic peak was detected around  $500^\circ\text{C}$ . It is likely that this peak is due to phase transformation from anatase to rutile. Indeed, examination of  $\text{TiO}_2(\text{SG})$  before  $500^\circ\text{C}$  calcination by XRD has shown only the anatase phase, while the XRD pattern of  $\text{TiO}_2(\text{SG})$  after  $500^\circ\text{C}$  calcination reveals the formation of both anatase and rutile (Fig. 2). The BET specific surface areas of the commer-

cial  $\text{TiO}_2(\text{RdH})$ ,  $\text{TiO}_2(\text{SG})$  (dehydrated at  $50^\circ\text{C}$ ),  $\text{TiO}_2(\text{SG})$  (dehydrated at  $500^\circ\text{C}$ ) and composite  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  are 8.8, 158.5, 23.5, and  $7.0\text{ m}^2/\text{g}$ , respectively. It is clear that the specific surface area of  $\text{TiO}_2(\text{SG})$  is significantly reduced (from 158.5 to 23.5) after calcination and this lower specific surface area certainly will affect the catalytic activity of the photo-semiconductors. However, calcination is a necessary process to enhance the chemical and physical stability of  $\text{TiO}_2$ . Bacsá and Kiwi [7] noted that nanocrystalline titania catalysts have specific surface areas of  $68\text{--}100\text{ m}^2/\text{g}$  and the reaction activity of titania catalyst is greatly affected by specific surface area. Fig. 3(a) and (b) show the UV-vis spectrum of  $\text{TiO}_2(\text{SG})$  and  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  particles. It can be seen from the figures that  $\text{TiO}_2(\text{SG})$  absorbs UV light at wavelength less than 400 nm and  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  absorbs light at wavelength less than 620 nm. Substituting the critical wavelengths of  $\text{TiO}_2(\text{RdH}) = 396$  nm (figure not shown),  $\text{TiO}_2(\text{SG}) = 412$  nm (Fig. 3(a)) and  $\text{CdSe}/\text{TiO}_2(\text{RdH}) = 620$  nm (Fig. 3(b)) into the Planck equation ( $E = h\nu$ ), the band gap energies of  $\text{TiO}_2(\text{RdH})$ ,  $\text{TiO}_2(\text{SG})$  and  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  are 3.1, 3.0, and 2.0 eV, respectively, which are fairly close to literature values of 3.2 eV (anatase  $\text{TiO}_2$ ), 3.0 eV (rutile  $\text{TiO}_2$ ) and 1.7 eV (CdSe) [1]. The morphologies of  $\text{TiO}_2(\text{RdH})$ ,  $\text{TiO}_2(\text{SG})$ , and  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  are presented by the SEM microphotographs in Fig. 4(a–c), respectively. The particle

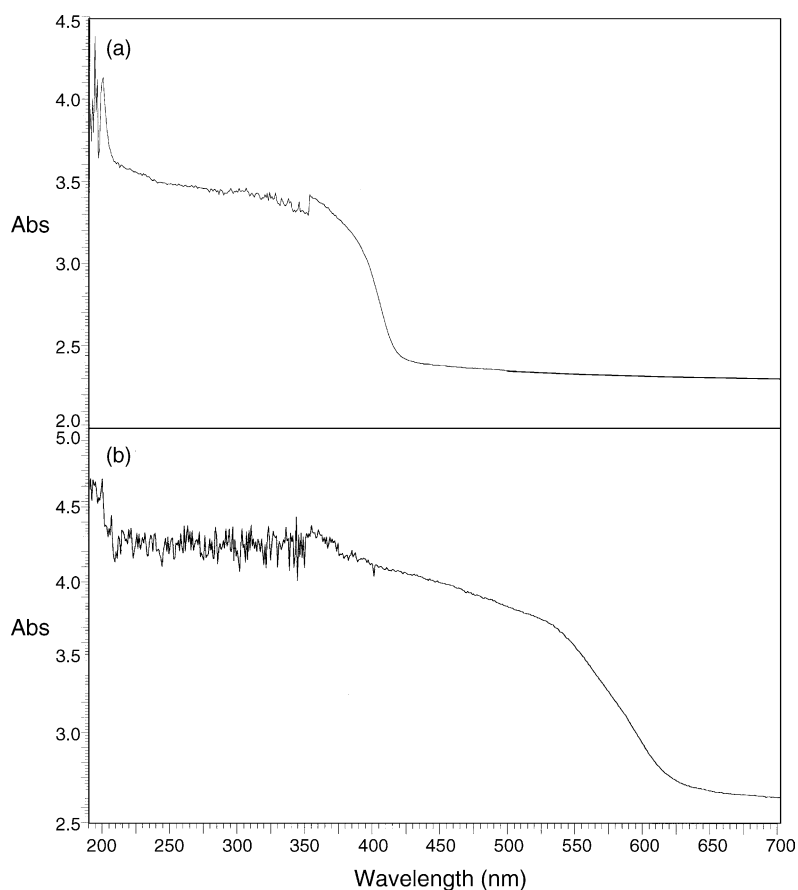


Fig. 3. The UV-vis spectrum of different catalyst: (a)  $\text{TiO}_2(\text{SG})$ ; (b)  $\text{CdSe}/\text{TiO}_2(\text{RdH})$ .

sizes of  $\text{TiO}_2(\text{RdH})$  and  $\text{TiO}_2(\text{SG})$  as shown in the SEM photographs are in the range of 100–500 and 15–30 nm, respectively. The observed particle size of  $\text{TiO}_2(\text{SG})$  is comparable to the average particle size of 18–24 nm calculated by the Scherrer equation [14]. The SEM micrograph of  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  particles reveals significant morphological differences from that of  $\text{TiO}_2(\text{RdH})$ . As can be shown

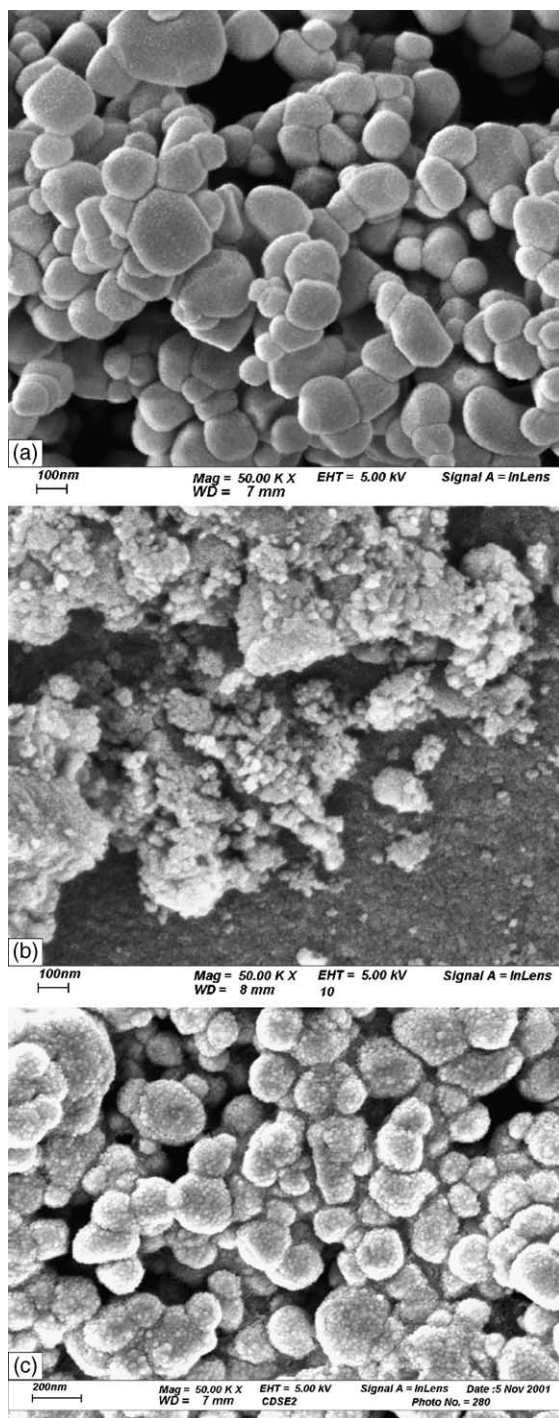


Fig. 4. The SEM microphotograph of different catalysts: (a)  $\text{TiO}_2$  (RdH); (b)  $\text{TiO}_2$  (SG); (c)  $\text{CdSe}/\text{TiO}_2$  (RdH).

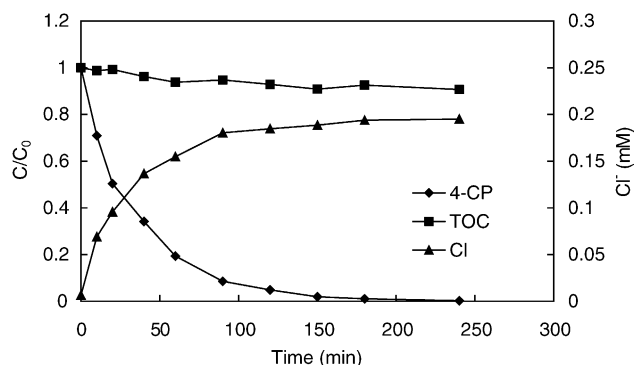


Fig. 5. The direct photolysis of 4-CP at UV 254 nm at pH 7.

in Fig. 4(c), the  $\text{CdSe}$  particles precipitate on the surface of  $\text{TiO}_2(\text{RdH})$  by the liquid phase deposition process.

The elemental composition of the composite  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  by ESCA shows that the atomic percentages of  $\text{Cd}(3d)$  and  $\text{Ti}(2p)$  are 27.6% and 72.4%, respectively.

### 3.2. Photodegradation of 4-CP

Before heterogeneous photocatalytic experiments were performed, volatilization of 4-CP, direct photolysis of 4-CP without semiconductors and adsorption of 4-CP on semiconductors were carried out to examine their effects on disappearance/degradation of 4-CP. Volatilization, adsorption experiments and direct photolysis with 365 and 420 nm reveal no detectable change of 4-CP. However, the direct UV photolysis at 254 nm does cause a significant photocatalysis (reduction in 4-CP) but not photomineralization (reduction in TOC) of 4-CP as shown in Fig. 5. Therefore, it is assured that any variation in 4-CP concentration can be attributed to heterogeneous photocatalytic reactions except under 254 nm irradiation conditions. The degradation profiles of 4-CP in the  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  system aerated and irradiated at wavelength 420 nm are illustrated in Fig. 6. The rationale of using 420 nm wavelength is to prevent direct photolysis and to inactivate photocatalysis by  $\text{TiO}_2$ , which is photoactivated

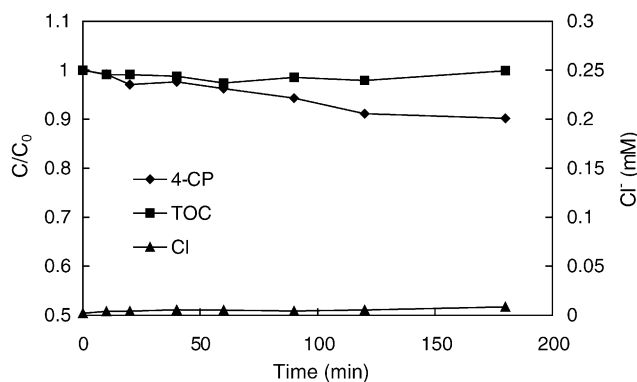


Fig. 6. The photodegradation of 4-CP in  $\text{CdSe}/\text{TiO}_2(\text{RdH})$  system with 420 nm UV at pH 7.



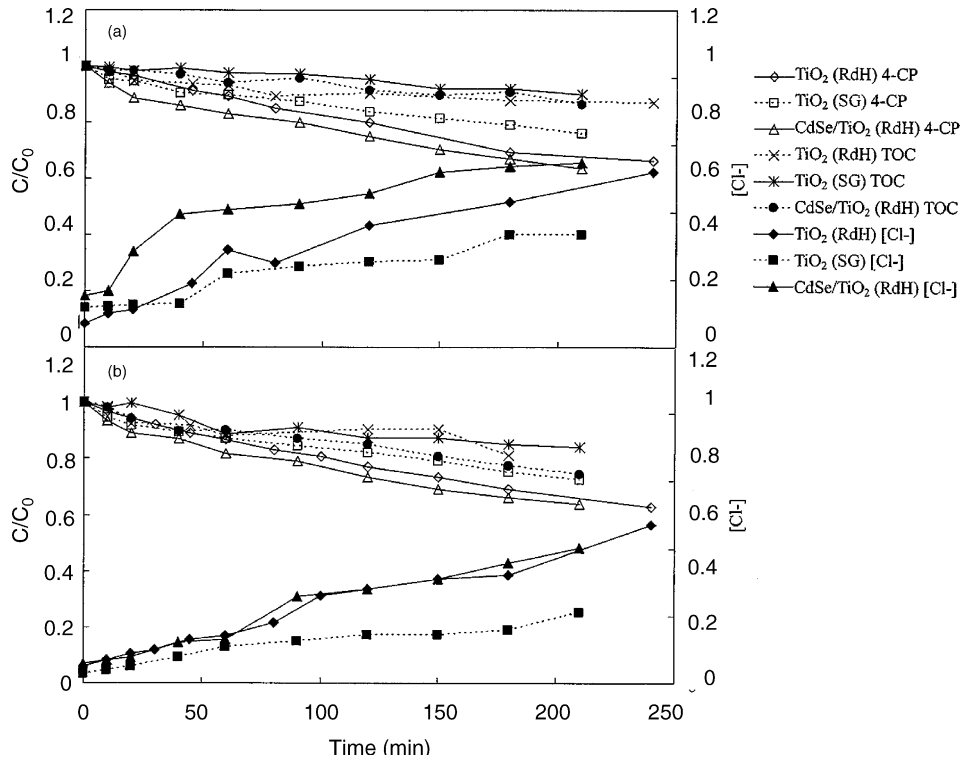


Fig. 7. The photodegradation and photomineralization of 4-CP by various semiconductors irradiated with 365 nm UV under different pH: (a) pH = 7; (b) pH = 11.

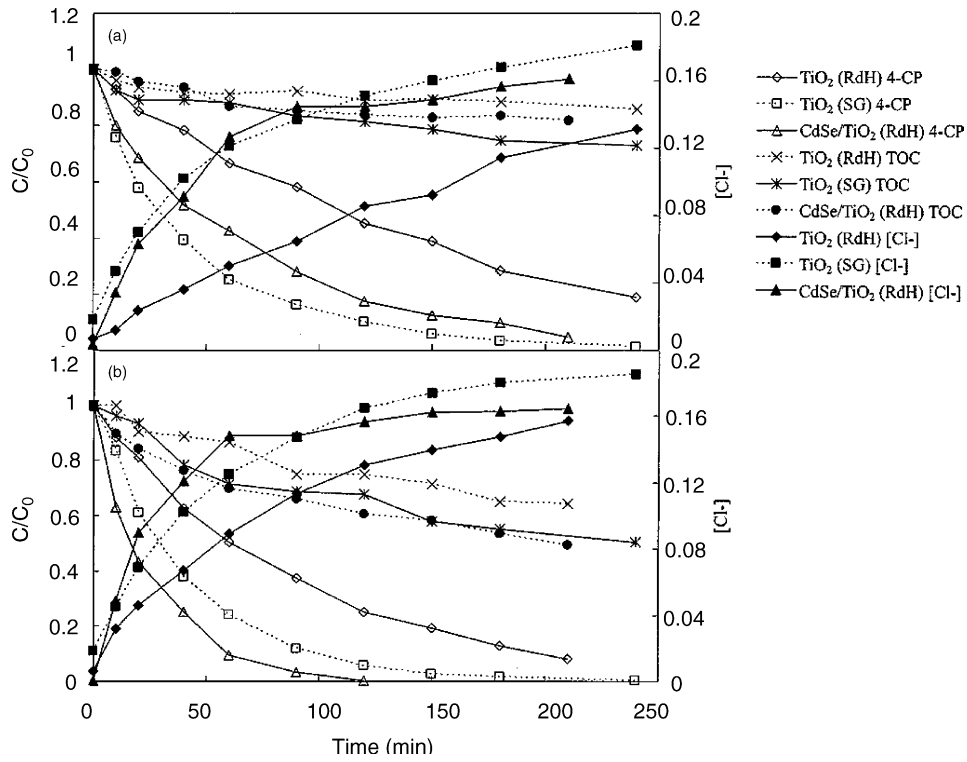


Fig. 8. The photodegradation and photomineralization of 4-CP by various semiconductors irradiated with 254 nm UV under different pH: (a) pH = 7; (b) pH = 11.

below the critical wavelength of 380 nm. Only 10% of 4-CP photodegradation is observed in about 180 min with the pseudo first-order rate constant about  $6 \times 10^{-4} \text{ min}^{-1}$ . This degradation rate constant is far less than that of the coupled CdS/TiO<sub>2</sub> system with phenol, where the rate constant is  $5.3 \times 10^{-3} \text{ min}^{-1}$  at pH 12.2 and 402 nm [10]. The photomineralization of 4-CP is also ineffective in terms of TOC change. The inefficiency of the coupled CdSe/TiO<sub>2</sub>(RdH) irradiated with 420 nm on photodegradation of 4-CP might probably be due to insufficient amounts of CdSe on TiO<sub>2</sub>(RdH) and the equal conduction band energy of CdSe and TiO<sub>2</sub>. The latter makes it adverse for the sensitization of photoactivated electrons to TiO<sub>2</sub>, based on the IPET proposed by Serpone et al. [10].

The efficiency of the coupled CdSe/TiO<sub>2</sub>(RdH) was further tested using wavelengths of 254 and 365 nm under two pH conditions, and the results were compared with those of TiO<sub>2</sub>(SG) and TiO<sub>2</sub>(RdH). Fig. 7 elucidates the photodegradation and photomineralization of 4-CP in various semiconductor systems irradiated with 365 nm UV. For the comparison of TiO<sub>2</sub>(SG) and TiO<sub>2</sub>(RdH), TiO<sub>2</sub>(RdH) exhibits a better photodegradation of 4-CP than TiO<sub>2</sub>(SG), or 30% versus 22% 4-CP reduction in 180 min at pH 7 (Fig. 7(a)). In both cases, the TOC reduction and chloride production are not effective; less than 10% 4-CP is destroyed to CO<sub>2</sub>. At pH 11, the efficiencies of both TiO<sub>2</sub>(SG) and TiO<sub>2</sub>(RdH) (Fig. 7(b)) are fairly identical to those under pH 7 condition, indicating an insignificant role of pH under 365 nm UV photocatalysis.

The photocatalytic disappearance of 4-CP in the CdSe/TiO<sub>2</sub>(RdH) system as illustrated in Fig. 7 is better than that in TiO<sub>2</sub> systems, albeit with a slight difference. Specifically the reductions of 4-CP in the coupled CdSe/TiO<sub>2</sub>(RdH) system are 33 and 34% at pH 7 and pH 11, respectively. It is noted that a 20% TOC reduction was observed in coupled CdSe/TiO<sub>2</sub>(RdH) at pH 11. In general, the coupled CdSe/TiO<sub>2</sub>(RdH) exhibits a better photocatalytic effect than TiO<sub>2</sub> alone.

The photodegradation efficiency is much better at 254 nm wavelength (Fig. 8). Within an 80 min reaction period, 72 and 97% of 4-CP were degraded in the TiO<sub>2</sub>(RdH) and TiO<sub>2</sub>(SG) system at pH 7, respectively; with a corresponding TOC reduction of 11 and 25%, respectively. Although the efficiency of 4-CP photodegradation in the TiO<sub>2</sub>(SG) system is not much different between pH 7 and 11, the efficiency is enhanced in the TiO<sub>2</sub>(RdH) system at pH 11. It is also detected that the generation of chloride concentration is faster in the TiO<sub>2</sub>(SG) system than in the TiO<sub>2</sub>(RdH) system. In heterogeneous system, the 4-CP degradation occurs through, at least, two pathways. In fact for all the runs the disappearance of 4-CP is not balanced by the appearance of chloride ions. This is a clear indication that in heterogeneous system the 4-CP degradation occurs by a mechanism responsible for releasing chloride ions to the solution and a mechanism in which that release does not occur. By observing the results of Figs. 7 and 8 it may be noted that these pathways are affected by the pH and by the type of photocatalyst.

As for the coupled CdSe/TiO<sub>2</sub>(RdH) system, degradation of 4-CP is about 90% with 17% TOC removal (180 min, pH 7 in Fig. 8(a)). Again, the efficiency is enhanced significantly at pH 11, in which 99% (4-CP) and 46% TOC removals were achieved (Fig. 8(b)). The degradation rate of 4-CP reacted with various photoexcited semiconductors was simulated using pseudo first-order reaction kinetics. These rate constants (Table 1) represent an index for how fast 4-CP can be converted to intermediates but not necessarily to ultimately CO<sub>2</sub>. Apparently, solution pH, wavelength and type of semiconductor used all play a role on the reaction rate. By ignoring the effect of direct photolysis (365 nm), the reaction rates of three different semiconductors at the same pH conditions are almost comparable. However, there is a significant discrepancy between coupled and single semiconductors under 254 nm conditions; the rate constants of CdSe/TiO<sub>2</sub>(RdH) systems are nearly double than those in the TiO<sub>2</sub>(RdH) systems. Nevertheless, this discrepancy is confounded by direct photolysis and the possible IPET effect. The rate constant of direct photolysis (254 nm) is  $2.65 \times 10^{-2} \text{ min}^{-1}$ . The rate constants of direct photolysis exceeded those of heterogeneous systems at pH 7 under 254 nm UV irradiation. This is explained as follows: a significant quantity of UV light may be absorbed by the photocatalyst particles, thus reducing degradation efficiency; that is a UV-screening effect of photocatalyst particles. Restated, the path length of photons entering the solution decreased with the increasing photocatalyst particle concentration.

The purpose of coupling semiconductors is to improve separation of photoexcited electrons to further enhance photodegradation. In this work, experimental pH does not affect the photodegradation efficiency, except for those at 254 nm. Photomineralization efficiency of 4-CP was not attainable, though disappearance of 4-CP is quite apparent. Sensitization of TiO<sub>2</sub> with CdSe only provided dramatic photocatalytic effects on 4-CP degradation at 254 nm. In the previous studies by Serpone et al. [10], at 1.6 g/L CdS/TiO<sub>2</sub> with  $\lambda > 406 \text{ nm}$ , at least 50% of phenol reduction in 120 min was reported in comparison to nearly no photocatalytic effect for TiO<sub>2</sub> alone. In this combination, the energy gap of CdS (2.4 eV) is lower than that of TiO<sub>2</sub> (3.2 eV) and the conduction energy level of CdS is higher than that of TiO<sub>2</sub>. It is believed that these are requirements to render IPET workable composite semiconductors. These prerequisites, however, cannot explain the inactivity of TiO<sub>2</sub>/SnO<sub>2</sub> under other conditions (pH 3,  $\lambda >$

Table 1  
Rate constants of 4-CP photodegradation in various systems

	Wavelength					
	254 nm		365 nm		420 nm	
	pH 7	pH 11	pH 7	pH 11	pH 7	pH 11
TiO <sub>2</sub> (SG)	1.78	2.49	0.12	0.14	<0.01	<0.01
TiO <sub>2</sub> (RdH)	0.68	1.16	0.18	0.19	<0.01	<0.01
CdSe/TiO <sub>2</sub> (RdH)	1.35	4.33	0.20	0.19	0.06	0.07

The rate constant is expressed as  $10^{-2} \text{ min}^{-1}$ .

355 nm, and phenol  $\sim 204$  mM), since the reaction rate constants of single  $\text{TiO}_2$  and the composite are the same ( $14 \times 10^{-3} \text{ min}^{-1}$ ). Thus, there must be other factors affecting the sensitized IPET efficiency.

Use of CdS to couple with  $\text{TiO}_2$  seems to be the most favorable practice in photosensitization related studies. Doong et al. [11] and Kang et al. [13] conducted similar work using coupled CdS/ $\text{TiO}_2$  for photodegradation of chlorophenol compounds. Kang et al. [13] pointed out that the apparent rate constant of CdS/ $\text{TiO}_2$  is 90% larger than that of single  $\text{TiO}_2$  ( $1.9 \times 10^{-3}$  versus  $1.0 \times 10^{-3} \text{ min}^{-1}$ ). However, the experiments were carried out under 255 nm UV, thus the results might be confounded with direct photolysis. In the work of Doong et al. [11], CdS/ $\text{TiO}_2$  was reported to exhibit better photocatalytic degradation of 2-CP than single CdS and  $\text{TiO}_2$ . However, it is noticed that the comparison was under different semiconductor concentrations: 0.5 g/L  $\text{TiO}_2$ , 0.5 g/L CdS and 1.0 g/L CdS/ $\text{TiO}_2$ . Besides, the quantum efficiency of coupled CdS/ $\text{TiO}_2$  is less than that of CdS.

The usefulness of sensitizing physically and chemically stable semiconductors has been studied extensively to prove its success. Theoretically, one can couple two semiconductors with different band gap energy and conduction band energy levels. However, there are also factors affecting the photocatalysis efficiency. In this work, we tested the idea that coupled CdSe/ $\text{TiO}_2$ (RdH) exhibits better photoactivity than single  $\text{TiO}_2$ ; however its performance is still less superior to the more often mentioned CdS/ $\text{TiO}_2$ .

#### 4. Conclusions

Coupled CdSe/ $\text{TiO}_2$ (RdH) was prepared to investigate the photodecomposition of 4-CP via the interparticle electron transfer process. The prepared CdSe/ $\text{TiO}_2$ (RdH) had a specific surface area of  $7 \text{ m}^2/\text{g}$  and an elemental composition of Cd(3d) and Ti(2p) of 27.6 and 72.4%. In a system irradiated at 420 nm where photocatalysis of  $\text{TiO}_2$  is inactivated, nearly 10% of 4-CP photodegradation was obtained with CdSe/ $\text{TiO}_2$ (RdH), indicating the effectiveness of IPET. However, this insignificant efficiency of 4-CP decomposition might be due to insufficient amounts of CdSe on the  $\text{TiO}_2$ . The disappearance of 4-CP under a CdSe/ $\text{TiO}_2$ (RdH) photoreaction at pH 7 and 365 nm condition is better than that of the  $\text{TiO}_2$ (RdH) system, with 30% versus 22% 4-CP reduction in 180 min. At the same condition, CdSe/ $\text{TiO}_2$ (RdH) yielded more photomineralization efficiency than that of  $\text{TiO}_2$ (RdH) in terms of TOC reduction. Both 4-CP and TOC reduction were noteworthy for systems photoilluminated at 254 nm. By considering the direct photolysis effect at 254 nm where 4-CP reduction is nearly 100% and TOC removal is nil, CdSe/ $\text{TiO}_2$ (RdH) exhibits a 50% photomineralization efficiency and an almost four times greater reaction rate than the  $\text{TiO}_2$ (RdH) semiconductor alone.

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