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Enhanced photodecomposition of 4-chlorophenol in aqueous solution by deposition of CdS on TiO_2

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Abstract

The photocatalyzed degradation of 4-chlorophenol (4-CP) in water is comparatively examined with TiO_2 powder, TiO_2/CdS powder, TiO_2 thin film electrodes and TiO_2/CdS thin film electrodes in the initial stages of the reaction. The apparent intermediates of 4-CP photodegradation with TiO_2 and TiO_2/CdS powders in suspensions are found to be 1,4-benzoquinone (BQ) and hydroquinone (HQ), with HQ rapidly converting into BQ with TiO_2 and TiO_2/CdS electrodes at an applied anodic potential of 0.6 V vs Ag/AgCl. The apparent reaction rate constants using the Langmuir–Hinshelwood equation with TiO_2/CdS powder and the TiO_2/CdS electrode are obtained to be about 90% and 33% larger than with TiO_2 powder and the TiO_2 electrode, respectively, indicating that the TiO_2/CdS catalysts have more photocatalytic activities than the TiO_2 catalysts in the initial stages. The adsorption coefficient (K) of 4-CP on TiO_2/CdS powder is one and a half times larger than that on TiO_2 powder. With the electrode catalysts at 0.6 V, the value of K increases several times with respect to the corresponding powder catalysts and shows essentially no difference between the TiO_2/CdS electrode and the TiO_2 electrode. Thus, the value of K may strongly depend on the electrostatic interaction between 4-CP and the electrode surface, but not very much on the type of electrode surface.

Keywords: Benzoquinone; CdS; 4-Chlorophenol; Hydroquinone; Photodegradation; TiO_2

1. Introduction

Phenolic compounds are common pollutants in industrial waste water that may originate from petroleum refining, coal conversion and fiberboard production. More specifically, 4-chlorophenol (4-CP) is used for the production of dyes, drugs and fungicides. In recent years, the photocatalytic degradation of 4-CP using semiconductors under UV light has attracted considerable attention for application to environmental problems [1–10].

Irradiation with light of an energy higher than the bandgap of a semiconductor generates photoinduced conduction band electrons and valence band holes in the semiconductor. The photodegradation of 4-CP is initiated by the attack of the photogenerated holes or subsequently produced hydroxyl radicals ($OH^{\bullet}$) on the surface of the semiconductor particles [7–11,14,21,22]. Many studies [11–20] suggest that highly oxidizing hydroxyl radicals are produced in two ways: the oxidation of hydroxyl ions or water molecules adsorbed on the surface of semiconductor particles by photogenerated holes, and a series of redox reactions from the trapping of photogenerated electrons by oxygen.

The photocatalytic degradation has been investigated with nanocrystalline semiconductor suspensions and particulated semiconductor thin films immobilized on an optically transparent electrode. In suspension, a semiconductor particle behaves as a short-circuited microelectrode and promotes oxidation and reduction on the same particle by the photogenerated holes and electrons. One of the disadvantages of using a semiconductor in suspension is the easy recombination between holes and electrons, while in the case of a particulate semiconductor thin film [7,9,23,24], the efficiency of charge separation can be greatly improved by driving the photogenerated electrons via the external circuit to the counter electrode under an externally applied anodic bias.

Among the semiconductors being studied, TiO_2 is one of the most efficient photocatalysts because of its affordability and photochemical stability against photocorrosion. But its large bandgap ($E_g \cong 3.2$ eV) reduces enormously the fraction of solar radiation that can be utilized. Recently, to overcome the limited spectral range of TiO_2, the use of semiconductor particles of nanometer size that have small bandgap (e.g., CdS$\cong$2.5 eV, PbS$\cong$0.4 eV) has received attention as sensitizers [25–27]. The photophysics and photochemistry of

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nanoparticles, however, are still poorly understood and most of the knowledge is empirically based.

To enhance the photodecomposition of 4-CP, we have performed a comparative investigation utilizing CdS nanoparticles coated on TiO_2. Since the bottom of the conduction band of CdS lies lower than that of TiO_2 by about 0.5 eV [28], it is possible to use CdS as a photosensitizer for TiO_2 by directly injecting the conduction band electrons from CdS to TiO_2 and by reducing recombination of the charge carriers following photoexcitation of CdS [29]. The photodecomposition was catalyzed with TiO_2 and CdS-coated TiO_2 both in suspensions and in the form of electrodes. In some photocatalytic studies of 4-CP, hydroquinone (HQ) [7–10], benzoquinone (BQ) [10,11], and 4-chlorocatechol (4-CC) [8,9] have been found to be the predominant intermediates. The photodegradation, however, has not been investigated by combining CdS with TiO_2. The irradiated solution of 4-CP was analyzed by using UV absorption spectroscopy complemented by GC/MS. The kinetics of 4-CP photodegradation was followed by the Langmuir–Hinshelwood equation [10].

2. Experimental

2.1. Preparation for the catalysts

For preparing a TiO_2 film electrode, the method reported by Grätzel and coworkers was utilized [30]. 1 g of commercial TiO_2 (58 m^2/g, P-25, Degussa AG) was ground to a viscous paste in a mortar with 350 μl of water containing 10% (v/v) acetylacetone. The paste was diluted by the addition of 2.5 ml of water followed by 2.5 μl of Triton X-100. After each addition, the paste was ground. About 100 μl TiO_2 suspension was spread on In_2O_3–SnO_2 coated Corning glass (ITO glass, Samsung) at 3000 rpm. After air drying, the TiO_2 film electrode on ITO was fired at 500°C in air for 30 min. A film about 1.0 μm thick was obtained per coating. The thickness of a film formed by multiple applications in the above procedure was determined with a Tencor Alpha Step 200 profilometer. Typical film thickness was ∼6 μm.

CdS particles of nanometer size were deposited on the nanocrystalline TiO_2 film or on TiO_2 powder for 7 min from a 100 ml solution of 2 mM $CdCl_2$, 5 mM NH_4Cl, 4% NH_3 and 0.02 M thiourea with stirring at 83°C [31]. The CdS-coated TiO_2 (TiO_2/CdS) was washed with 1.0 M HCl and distilled water, and baked for 1 h at 160°C in an oven. A Physical Electronics PHI-680 Auger nanoprobe, a Hitachi S-4200 SEM, and a Perkin–Elmer plasma 40(ICP) were used to characterize the surfaces and the chemical composition.

2.2. Photodegradation

Stock solutions containing the desired concentrations of 4-CP, HQ, BQ (Aldrich) and 4-CC (Kasei Chemical, Japan) were prepared with Milli-Q water without further purification. A photochemical reactor equipped with a water circulating jacket and three openings for electrodes was made of Pyrex glass with a plain quartz window. For the photodegradation experiments in suspensions, the reactor contained 60 ml of the stock solution and 1.0 g/l catalyst, while for the photodegradation with an electrode, the electrode with the geometric area of typically about 1.7 cm^2 was inserted into the 60 ml stock solution containing 1.0 M NaCl. EG and G Princeton Applied Research 366A or model 273 potentiostats were used to apply a potential and to obtain cyclic voltammograms. These measurements were carried out with the standard three electrodes consisting of a semiconductor working electrode, a Pt counter electrode, and a Ag/AgCl electrode as a reference. All potentials were cited against the reference electrode. Irradiation was carried out with a Xe lamp (Ilctec, 3115FS-12TE-B30). After the irradiation, the semiconductor particles were filtered at 3500 rpm with a Hanshin Medical HC-16A centrifuge. The degradation of 4-CP was monitored by measuring the absorption spectra of the irradiated solution using a Hewlett Packard 8453 diode array spectrophotometer. The degradation intermediates were identified with a Hewlett Packard 6890 gas chromatograph-5972 mass selective detector (GC/MSD). The column of GC/MSD was DB-5MS and the temperature of the oven was increased from 120°C (2 min) to 280°C (5 min) at a rate of 10°C/min. Owing to difficulties in taking GC/MSD measurements on aqueous solutions, an aliquot of 12 ml of the irradiated solution was treated with 3 ml of ether to extract the reaction intermediates for the measurements.

3. Results and discussion

3.1. Basic characteristics

SEM images (Fig. 1) were obtained to compare the top view of a TiO_2/CdS surface with that of a TiO_2 surface. No size difference is apparent, indicating CdS particles on TiO_2 are smaller than a few nm. The BET surface area of the prepared TiO_2/CdS particles, determined from N_2 adsorption data at 77 K, was 57.5 m^2/g. The weight ratio of Ti:Cd of the prepared TiO_2/CdS particles and electrodes was estimated to be 12:1 from an Auger spectrum. Since the TiO_2 film is porous, CdS particles can enter the pores of the film. Auger depth profile revealed that the Cd concentration monotonically decreased up to 35 nm with increase in the Ti concentration. Typically at a depth of 25 nm, the Cd concentration was 20% of the value at zero sputtering time. Fig. 2 shows the absorption spectra of TiO_2 and TiO_2/CdS films. The absorption edge is extended to about 500 nm by the deposition of nanocrystalline CdS. Thus, the use of CdS particles with TiO_2 is expected to increase photogenerated charge carriers under the irradiation of visible light. In order to help investigate the photodegradation of 4-CP by UV absorption spectroscopy, the absorption spectra of 1.0×10^{-4} M authentic 4-CP, 4-CC, BQ and HQ in aqueous

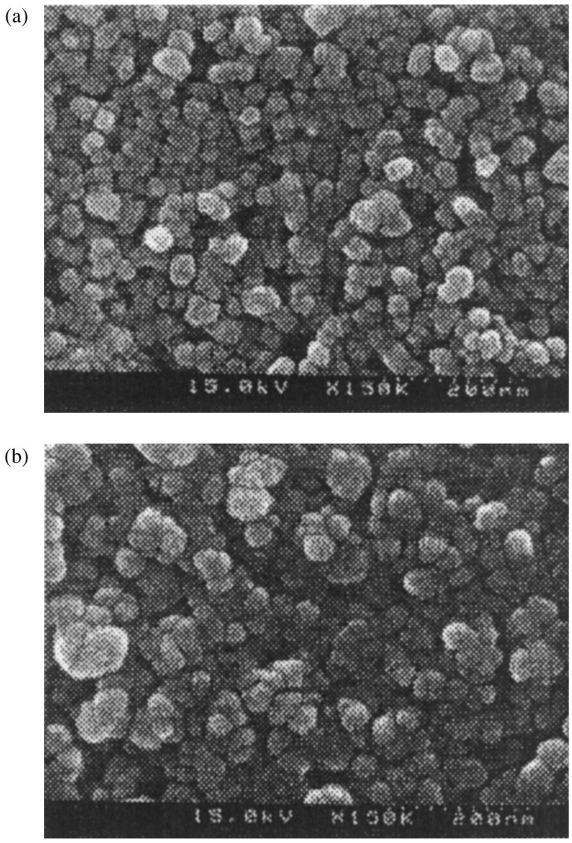

Fig. 1. SEM images of a TiO_2 film and a TiO_2/CdS film on ITO.

solution are taken for reference as shown in Fig. 3. The last three compounds are known to be stable reaction intermediates produced from the photodecomposition of 4-CP [7–11]. Broad absorption peaks appear at 225 and 280 nm for 4-CP, at 221 and 284 nm for 4-CC, at 246 nm for BQ, and at 221 and 290 nm for HQ.

3.2. Photodegradation of 4-CP with powders in suspension

Irradiation of a solution containing 4-CP with a Xe lamp yields time-dependent absorption spectra of the solution in the presence of suspended TiO_2 or TiO_2/CdS as shown in Fig. 4(a) and (b), respectively. The absorbance changes at 225, 246 and 290 nm from Fig. 4 are plotted as a function of the irradiation time in Fig. 5. The monotonic decreases in the absorbance at 225 nm clearly reveal that the decomposition of 4-CP is faster with TiO_2/CdS. As shown in Fig. 3, the predominant intermediate corresponding to the absorption peak at 246 nm is apparently BQ, which is in good agreement with Ren and coworkers [11]. It is surprising that the appearance of an absorption peak near 290 nm has not been considered extensively. The broad absorption peak near 290 nm in Fig. 4 may possibly consist of the combination from 4-CP and some intermediates such as HQ and 4-CC (see Fig. 3). Intermediate 4-CC, however, has almost no absorption at wavelengths longer than 300 nm. In addition, an analysis by GC/MS of the irradiated solution did not detect the presence of 4-CC. Therefore, it is possible at earlier stages of the reaction to rule out 4-CC as an apparent reaction intermediate responsible for the absorption peak near 290 nm.

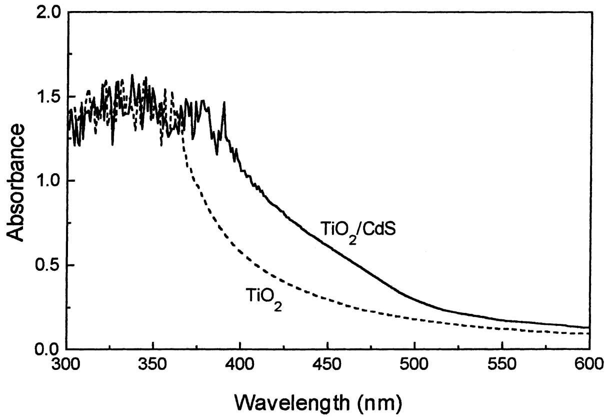

Fig. 2. Absorption spectra of a TiO_2 film and a TiO_2/CdS film on ITO.

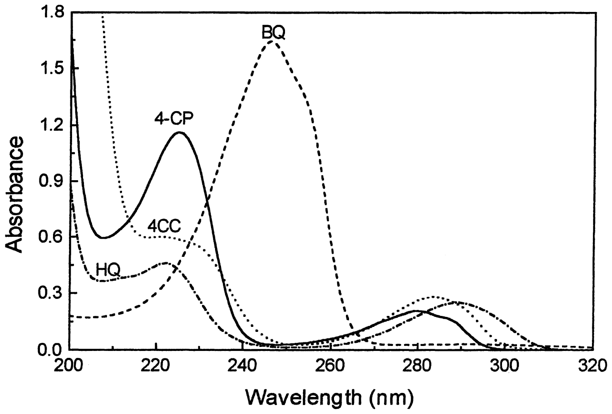

Fig. 3. Absorption spectra of 1×10^{-4} M aqueous solution of 4-CP, 4-CC, HQ, and BQ.

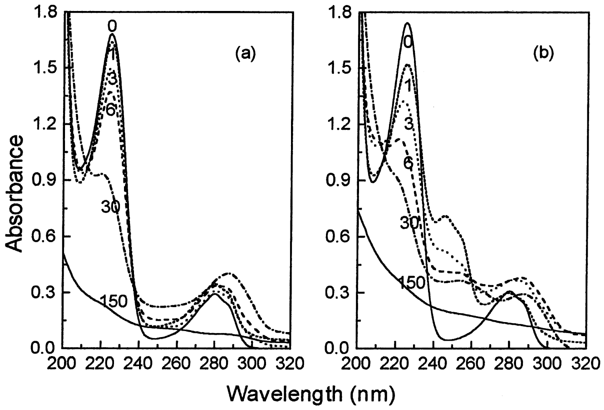

Fig. 4. Irradiation time-dependence of absorption spectra of 1.5×10^{-4} M 4-CP aqueous solution using (a) TiO_2 and (b) TiO_2/CdS powders in suspension. The numbers indicate the time of irradiation in minutes.

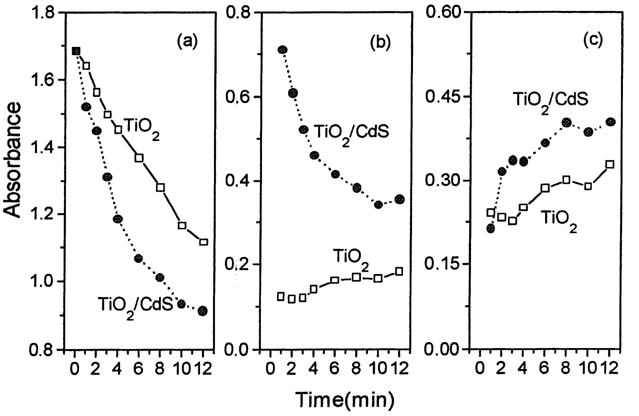

Fig. 5. Changes in the absorbances of 1.5×10^{-4} M 4-CP aqueous solution at (a) 225 nm, (b) 246 nm, and (c) 290 nm vs irradiation time with TiO_2 and TiO_2/CdS powders in suspension.

The absorbance at 290 nm (Fig. 5(c)) rises faster with TiO_2/CdS except for the initial 1 min of the irradiation, which is largely consistent with the data in Fig. 5(a), considering that 4-CP first decomposes into HQ by the reaction with $OH^{\bullet}$. The absorbances at 246 nm, however, behave somewhat differently (Fig. 5(b)). That is, the initial concentration of BQ is much larger with TiO_2/CdS than with TiO_2. Apparently, a large concentration of BQ with TiO_2/CdS powder is produced very rapidly and decays faster than with TiO_2 powder. Known mechanisms suggest that BQ is produced by an oxidation of HQ [9–11]. The large concentration of BQ can be explained in terms of rapid oxidation of HQ to BQ most likely by the reaction with the increased amount of photogenerated holes in the presence of CdS. In addition, by assuming BQ is predominantly oxidized also by those holes to produce minor intermediates such as 2-hydroxybenzoquinone (2-HBQ) [10], the faster decay rate of BQ with TiO_2/CdS in Fig. 5(b) can be explained. Thus, it is concluded that HQ and BQ are the main initial intermediates of 4-CP photocatalytic degradation with TiO_2 and TiO_2/CdS in suspensions, and the rate of the photodegradation with TiO_2/CdS powder is faster than with TiO_2 powder. Experiments to monitor 2-HBQ were performed using BQ and HQ as substrates in place of 4-CP. In the early stage of the photoreactions no significant amount of 2-HBQ in the absorption spectra and gas chromatograms are detected.

3.3. Photodegradation of 4-CP with electrodes

For the photodegradation of 4-CP with catalysts in the form of electrodes, a potential was applied to enhance the separation of photogenerated charge carriers. A potential was chosen at which no oxidation of 4-CP occurs. Fig. 6(a) and (b) show the cyclic voltammograms of TiO_2 and TiO_2/CdS electrodes in 0.01 M 4-CP and 1 M NaCl solution, respectively, measured at a scan rate of 20 mV/s from +1.2 to −0.5 V. It is noted that no oxidation or reduction peaks of 4-CP are observed in the range of +0.8 to −0.1 V. At an applied anodic potential of 0.6 V, the cyclic voltammograms show that the photocurrent with a TiO_2/CdS electrode is about 10 times larger than with a TiO_2 electrode. This considerably large current with a TiO_2/CdS electrode originates from the increased spectral response (Fig. 2), and consequently the rate of photocatalytic degradation of 4-CP is expected to increase with the TiO_2/CdS electrode.

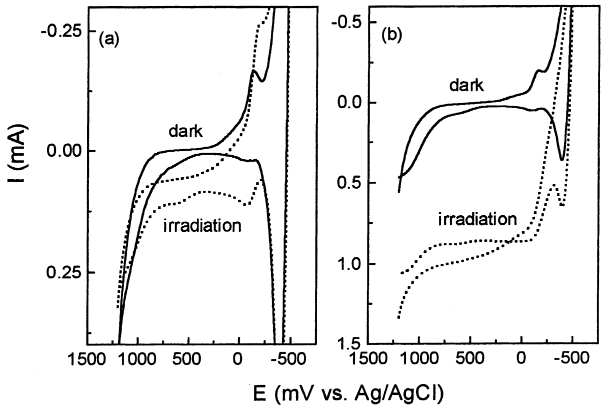

Fig. 6. Cyclic voltammograms of 1.0×10^{-2} M 4-CP aqueous solution with (a) TiO_2 and (b) TiO_2/CdS electrodes at a scan rate of 20 mV/s.

Fig. 7(a) and (b) show the variation of the absorption spectra of 4-CP aqueous solution recorded at various times of irradiation with the TiO_2 and TiO_2/CdS electrodes at 0.6 V, respectively. The absorbance near 246 nm conspicuously increases for the first few minutes of irradiation. During the same period of irradiation, contrary to the absorption spectra obtained with powder catalysts (Fig. 4), it is surprising to see both absorption spectra show that the absorption characteristics in the region over 275–290 nm do not change very much, and clearly no new absorption peaks emerge. There appears to be a little contribution from HQ to absorbances in the spectral range. Thus, we may conclude that only BQ is the predominant intermediate of 4-CP photodegradation with catalysts in the form of electrodes. This difference in the formation of the

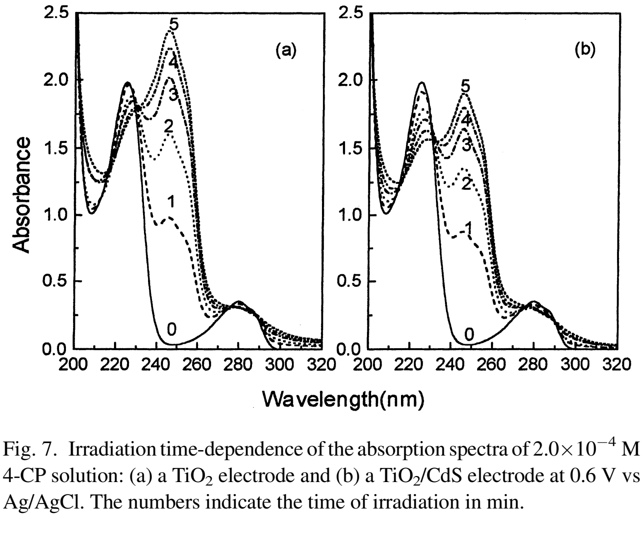

Fig. 7. Irradiation time-dependence of the absorption spectra of 2.0×10^{-4} M 4-CP solution: (a) a TiO_2 electrode and (b) a TiO_2/CdS electrode at 0.6 V vs Ag/AgCl. The numbers indicate the time of irradiation in min.

predominant intermediates in comparison with the powder catalysts may arise from the applied anodic potential on the electrode, based on the following analysis. The relevant redox reaction is given by [32]

$$BQ + 2H^+ + 2e^- \rightleftarrows HQ \quad E^\circ = 0.700\,V. \tag{1}$$

At V_{app}=0.6 V, the potential of the working electrode should be E_w=0.6+0.2=+0.8 V. By assuming that a rapid equilibrium is established, the Nernst equation at room temperature

$$E_w = E^o - 0.05916/n \log\{[HQ]/\{[BQ][H^+]^2\}\} \tag{2}$$

leads the ratio of [HQ]/[BQ] to be 10^{-11}–10^{-12} at pH 4. That was the pH of the solution measured during the photocatalytic degradation of 4-CP. Eq. (2) calculates that the concentration of HQ is negligible compared with that of BQ, indicating that HQ is almost completely converted into BQ by the applied anodic potential on the electrodes. Thus Eq. (2) explains why the peak of HQ at 290 nm in the absorption spectra of the irradiated 4-CP solution is not observed with the electrode catalysts in comparison with powder catalysts.

Changes in the absorbance at 246 nm and in the relative absorbance at 225 nm from the spectra in Fig. 7 are plotted in Fig. 8. It is obvious that the rate of 4-CP photodegradation with the TiO_2/CdS electrode appears to be faster than that with the TiO_2 electrode, judging from the rate of decrease in the absorbance at 225 nm. Therefore, it is expected that with the TiO_2/CdS electrode the concentration of BQ is larger than with the TiO_2 electrode for the initial few minutes of irradiation. Contrary to this expectation, however, the concentration of BQ with the TiO_2 electrode is found to be larger than with the TiO_2/CdS electrode (Fig. 8). This apparently means that the use of the TiO_2/CdS electrode can enhance the rate of the photodecomposition of 4-CP as well as its intermediate, BQ, over the TiO_2 electrode. This enhanced disappearance rate of BQ with the TiO_2/CdS electrode is consistent with the changes in the absorbances at 246 nm of 4-CP in the presence of TiO_2/CdS powder (Fig. 5(b)). The result can be again attributed to the increased number of photogenerated holes and consequently hydroxyl radicals as a result of the increase in the spectral response upon coating CdS on TiO_2.

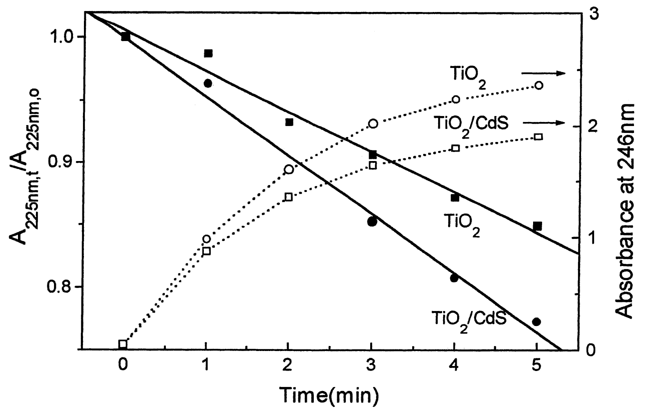

Fig. 8. Time-courses of the absorbance at 246 nm (broken lines) and the absorbance ratio at 225 nm (solid lines) of 4-CP solution using TiO_2 and TiO_2/CdS electrodes.

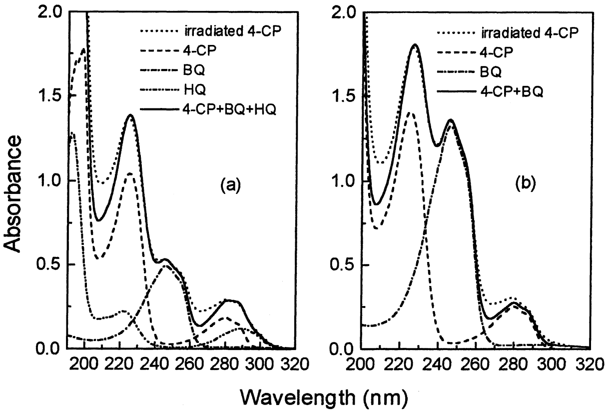

Fig. 9. Resolution of the absorption spectra of the irradiated 4-CP solution for (a) 3 min with TiO_2/CdS powder in suspension and (b) 2 min with a TiO_2/CdS electrode into the component absorption spectra.

Fig. 9 compares the absorption spectra of the irradiated 4-CP solutions with the combined spectra of the resolved intermediates. The 4-CP solutions were irradiated for 3 min with TiO_2/CdS in suspension (Fig. 9(a) and 2 min with a TiO_2/CdS electrode (Fig. 9(b). Based on the above results, the measured absorption spectra have been resolved into 4-CP, HQ, and BQ for powder, and 4-CP and BQ for the TiO_2/CdS electrode. In the latter, HQ was excluded for the reasons discussed above. The resolutions appear to be reasonably good, although some discrepancies are noticed in the wavelength regions near 210 and 270 nm. The discrepancies can be attributed to the contributions from the background absorption, which consists of the absorbances of minor decomposed products, inevitably present in the irradiated solution. The background absorption has no characteristic peaks and increases towards shorter wavelengths as can be seen from the spectra obtained after a quite lengthy period of irradiation, e.g., 150 min, in Fig. 5. Higher background absorbance in the shorter wavelength region explains a larger discrepancy near 210 nm than near 270 nm. A quantitative kinetic analysis follows.

3.4. Kinetics of 4-CP photodegradation

The rate of the photocatalytic degradation of 4-CP is a function of the initial concentration of 4-CP. This rate can be evaluated with the apparent reaction rate constant (k_a), adsorption coefficient (K), and initial concentration of 4-CP by the inverse of Langmuir–Hinshelwood equation,

$$-dt/d[4\text{-}CP] = 1/k_a + 1/\{k_a K[4\text{-}CP]\} \tag{3}$$

A plot of the inverse of the initial rate of 4-CP photodegradation obtained as a function of the reciprocal initial 4-

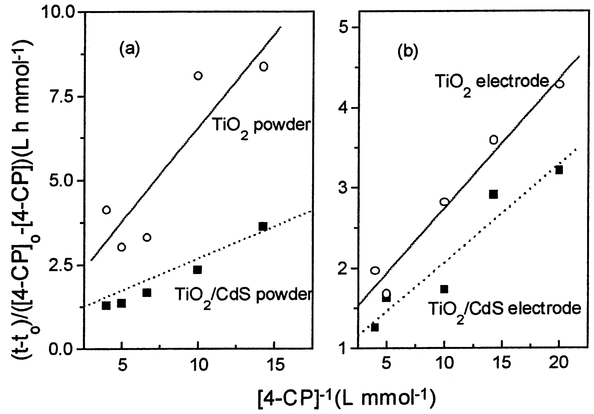

Fig. 10. Plot of the inverse of the initial rate of 4-CP disappearance vs the reciprocal of the initial 4-CP concentration using (a) TiO_2 and TiO_2/CdS in suspensions and (b) TiO_2 and TiO_2/CdS electrodes.

CP concentration is shown in Fig. 10. k_a and K can be derived from the intercept and the slope of these straight lines. The results are summarized in Table 1. The apparent reaction rate constants with TiO_2/CdS powder and the TiO_2/CdS electrode are found to be about 90% and 33% larger than those with TiO_2 powder and the TiO_2 electrode, respectively. That is, both in the form of electrode and powder, a CdS-coated TiO_2 catalyst has a better photocatalytic activity than TiO_2 at the initial stages of 4-CP photodegradation. These kinetic data confirm the qualitative results obtained from the decreases in the absorbance of the irradiated 4-CP solution at 225 nm with the time of irradiation shown in Figs. 5 and 8.

Although the photocurrent of a TiO_2/CdS electrode is about 10 times larger than that of a TiO_2 electrode at 0.6 V as estimated from the first scan of cyclic voltammograms (Fig. 6), the apparent reaction rate constant of 4-CP photodegradation with a TiO_2/CdS electrode is larger only by 33% in comparison with a TiO_2 electrode. It was also observed by cyclic voltammetry that the photocurrent with a TiO_2/CdS electrode rapidly decreased. The photogenerated holes can proceed a competing reaction with CdS and promote dissolution of CdS on the electrode surface, which is evidenced by that an ICP analysis showed a ppb level of cadmium ion present in the irradiated 4-CP solution with a TiO_2/CdS electrode. It can be concluded that the use of CdS with TiO_2 definitely improves the photocatalytic activity with respect to TiO_2 at the initial stages due to the increased number of photogenerated holes and $OH^{\bullet}$, but the advantages of CdS rapidly disappear possibly due to the photocorrosion of CdS with the increasing irradiation time. To see if CdS does not function as only a sacrificial electron donor, photocatalytic turnover number (PTN) was evaluated according to the equation provided by Serpone et al. [33]. The PTN of a TiO_2/CdS catalyst is found to be 3.5 times larger than a TiO_2 catalyst.

Table 1
Apparent reaction rate constants and adsorption constants

	Suspension		Electrode[a]	
	TiO_2	TiO_2/CdS	TiO_2	TiO_2/CdS
k_a (10^{-3} mol/h)	1.0	1.9	0.9	1.2
K (10^3 l/mol)	1.8	2.8	7.1	6.7

[a] At an applied potential of 0.6 V.

Table 1 shows that an apparent reaction rate constant can vary depending on the experimental conditions. In the table, we notice that the apparent reaction rate constant of TiO_2/CdS in suspension is significantly larger than that of the TiO_2/CdS electrode. The difference possibly arises for two reasons: firstly, it is reported [34] that chloride ions present in the electrolyte solution are rapidly adsorbed on CdS particles and consume the photogenerated holes, which in turn reduces photodegradation rates of the organic compounds. A preliminary experiment revealed that the photodecomposition of 4-CP in the absence of the catalysts proceeded slower when NaCl was added to the solution, which supports the role of chloride ions. Secondly, the area of the electrode and thus the amount of catalyst in the electrode are somewhat smaller compared with the catalyst in suspension.

The adsorption of 4-CP on a semiconductor catalyst is a crucial factor in the kinetics of heterogeneous photodegradation. The adsorption coefficient, K, of 4-CP on the suspended TiO_2 was reported as $K=2.4\times10^4$ l/mol, previously [10]. The adsorption coefficient, however, should be corrected from the reported value to 2.4×10^3 l/mol because of an error involved in the calculation of the slope. The corrected value is similar to the present result obtained with TiO_2 powder in suspension, 1.8×10^3 l/mol. The value of K of 4-CP on TiO_2/CdS in suspension is one and a half times larger than that on TiO_2 in suspension (Table 1). It means that 4-CP adsorbs more on CdS than on TiO_2. This improved adsorption explains the enhanced rate of 4-CP decomposition with the TiO_2/CdS catalysts. At the applied anodic potential of 0.6 V, the K of 4-CP on the electrodes increased several times compared with the corresponding catalysts in suspension. The difference in the K between the TiO_2/CdS electrode and the TiO_2 electrode is not large. Apparently, the electrostatic interaction between the electrodes and 4-CP increases upon the application of an anodic potential on the electrodes and overwhelms the difference in the surface characteristics between TiO_2 and TiO_2/CdS.

4. Conclusion

We have comparatively investigated the photodecomposition of 4-CP with TiO_2 and TiO_2/CdS in the form of suspensions and electrodes. BQ and HQ are the predominant intermediates of the 4-CP photodegradation with the powders in suspension. With the electrodes at an applied anodic potential of 0.6 V, however, only BQ is found to be the predominant intermediate and HQ is rapidly converted into

BQ. The Langmuir–Hinshelwood equation shows that the apparent reaction rate constants of the 4-CP photodegradation with TiO_2/CdS powder and the TiO_2/CdS electrode are 90% and 33% larger than with TiO_2 powder and the TiO_2 electrode, respectively, indicating that the TiO_2/CdS catalysts have more photocatalytic activities than the TiO_2 catalysts. The enhanced photocatalytic activities can be ascribed to the increased number of photogenerated holes in CdS due to the improved spectral response. In addition, the K of 4-CP on TiO_2/CdS powder is one and a half times larger than that on TiO_2 powder. At an applied anodic potential of 0.6 V, the value of K of the electrode catalysts increases several times with respect to the corresponding powder catalysts and shows essentially no difference between the TiO_2/CdS electrode and the TiO_2 electrode. Thus, the value of K may strongly depend on the electrostatic interaction between 4-CP and the surface of the electrode, but not very much on the type of electrode surface.

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