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PHOTODEGRADATION OF 4-CHLOROPHENOL BY UV/PHOTOCATALYSTS: THE EFFECT OF THE INTERPARTICLE ELECTRON TRANSFER PROCESS

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Abstract

This study explores the photodegradation of 4-chlorophenol (4-CP). Coupled-photocatalyst systems are tested to determine whether the interparticle electron transfer (IPET) process improves the photodegradation efficiency. TiO_2, ZnO and SnO_2 are selected as photocatalysts. In the single-photocatalyst test, ZnO exhibits the highest catalytic activity. The pseudo first-order rate constant of the coupled-catalyst system, ZnO/SnO_2, is approximately 22% higher than that of ZnO; these rate constants are 0.95 and 0.78 h^{-1} at pH 11, respectively.

Keywords: Photodegradation, interparticle electron transfer process, TiO_2; ZnO, SnO_2

INTRODUCTION

The problem of pollutants, particularly the serious environmental impact of their residues and the low efficiency of current remediation processes, has led

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to several attempts to find more efficient degradation alternatives. Numerous pollutants are decomposed by Advanced Oxidation Processes (AOPs) [1-4]. Heterogeneous photocatalysis has emerged as an efficient approach for purifying water [2, 5]. TiO_2 and ZnO have been extensively investigated as heterogeneous photocatalysts, mainly because of their high capacity for degrading toxic and recalcitrant chemical species with fairly simple procedures. The applications of the photocatalytic process, mostly involving TiO_2, have been extensively documented [2-5]. However, their photodegradation efficiency is restricted mainly by the recombination of the photogenerated holes and electrons. Photocatalysis involves chemical oxidation *via* a photogenerated hole from the semiconductor, so every recombination event leads to the loss of a hole that might otherwise have promoted degradation. Hence, a major focus of current photocatalysis research is to enhance the separation characteristics, thus improving photocatalytic efficiency. Various methods of increasing photo-efficiency have been proposed, including: (1) promoting photochemical degradation by including transition metals [6, 7], and (2) exploiting the difference in the band gap between semiconductors with different energy potentials to retard the recombination of the generated photoelectrons and photoholes, thus increasing the hydroxyl radical production efficiency, in a process called IPET [2, 5, 8, 9]. The coupled semiconductors with different redox energy levels for their corresponding conduction and valence bands can be employed to improve the charge separation efficiency, raising the charge lifetime and the efficiency of the interfacial charge transfer to the adsorbed substrate. Ultimately, this process significantly improves the photocatalytic performance of the semiconductors. This study elucidates the IPET effect using TiO_2, ZnO and SnO_2 as model photocatalysts, and 4-CP as the parent compound.

MATERIALS AND METHOD

Three semiconductor powders, TiO_2 (Degussa P25), ZnO (Fluka) and SnO_2 (RDH), were used as photocatalysts. 4-CP (99%) was purchased from Aldrich and was utilized without further treatment. Water was deionized and doubly distilled by Milli-Q.

All photodegradation experiments were conducted in a batch reactor. The reaction mixtures were illuminated under a UV lamp (8W, Philips), and the temperature was controlled at 25°C during the experimental period. Prior to the photocatalytic experiment, the suspension was prepared by mixing the desired concentration of 4-CP (2×10^{-4} M) with various single and coupled photocatalysts, TiO_2, ZnO, SnO_2, TiO_2/ZnO, TiO_2/SnO_2, ZnO/SnO_2 and

$TiO_2/ZnO/SnO_2$ (1.2 g/L). The slurry was stirred magnetically for 30 min in the dark to achieve an adsorption equilibrium for the substrate on the photocatalytic system, and hydrochloric acid or sodium hydroxide was added to maintain the desired pH. The samples were centrifuged at 3000 rpm, and the supernatant was filtered through a 0.45 μm filter membrane (Millipore). The concentration of 4-CP was analyzed using an HPLC (Waters 600E system) equipped with an UV-detector set at 274 nm. UV-Vis (GBC Cintra 20) analyses were performed to obtain the light adsorption spectrum and band gap of each photocatalyst.

RESULTS AND DISCUSSION

Background experiments were conducted to confirm that 4-CP degradation was caused by the ambient environment or photodegradation. Hence, direct photolysis, evaporation and adsorption of 4-CP were tested, revealing that the disappearance of 4-CP was negligible under the background experimental conditions. Accordingly, 4-CP disappearance in the photocatalytic experiments could be attributed to complete photodegradation.

The specific surface areas of TiO_2, ZnO and SnO_2 powders were calculated as 54.2, 4.6 and 4.8 m^2/g, and the band gap energies were determined as 3.17, 2.92 and 4.13 eV, respectively. The main wavelength of the UV lamp was approximately 365 nm, decreasing the quantum efficiency of SnO_2 with a wider band gap owing to poor utilization of UV light. The quantities applied in the test system were 0.5, 0.8, 1.0, 1.3, 1.6, 1.9, 2.2, 3, 4, 6 and 8 g/L to optimize the concentration of catalyst required that maximizes the degradation rate. A genetic algorithm simulation on a software package (Evolve 5.0) was adopted to examine the effect of adding various quantities of catalyst on the photodegradation rate. Experiments were performed using various amounts of TiO_2 at fixed pH and initial concentration of 4-CP. The genetic algorithm software found that the optimal quantity of photocatalyst was 1.2 g/L. Therefore, the photocatalyst dosage was set to 1.2 g/L in all experiments.

Figures 1(a), (b) and (c) depict the photo-oxidation of 4-CP for each photocatalytic system in three aqueous media (pH 4, 7 and 11). Table 1 lists the kapp values of 4-CP using single, coupled and sandwiched photocatalysts at pH 4, 7 and 11. The reaction rates fit a first-order reaction model. Additionally, several investigations have demonstrated that the photodegradation rates can generally be approximated using first-order kinetics [10, 11]. Figure 1(a) indicates that ZnO is a poor photocatalyst in the oxidative degradation of 4-CP at pH 4, since it corrodes in aqueous acidic media, as also showed in a previous study [12]. However, at pH 7 and 11, ZnO exhibited better activity toward 4-

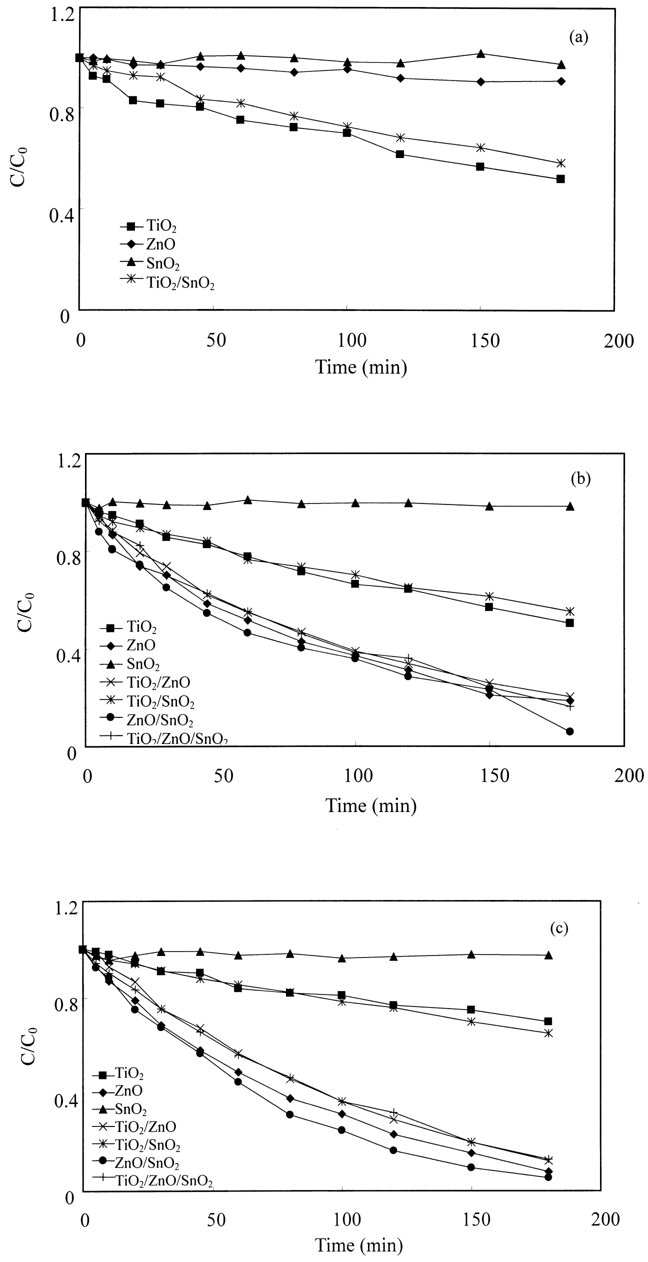

Fig. 1. Photodegradation of 4-CP with various photocatalytic systems at various pH values (a) pH 4, (b) pH 7 and (c) pH 11 (photocatalyst = 1.2 g/L, 4-CP = 2×10^{-4} M and 25°C)

CP than did TiO_2 by a factor of 3–7 for single-photocatalyst systems (Table 1). Also as expected, 4-CP did not degrade when SnO_2 was irradiated with 365 nm UV light, since the UV source has insufficient energy to photoactivate SnO_2. Meanwhile, the k_{app} values reveal that ZnO and ZnO/SnO_2 are the best catalytic systems at pH 7 and 11, respectively. Thus, ZnO is a good photocatalyst for degrading 4-CP in alkaline aqueous media, suggesting that ZnO is highly active for 4-CP degradation. The single, coupled and sandwiched photocatalyst test results in Figs 1(a), (b) and (c) demonstrate that the reaction rate at pH 11 is significantly higher than that at pH 7 or pH 4, except for the TiO_2 and TiO_2/SnO_2 systems. This observation is consistent with the results obtained at high concentrations of photogenerated OH radicals in highly alkaline aqueous media [2, 5, 9, 12].

Table 1

Apparent first-order kinetics ($k_{app.}$, h^{-1}) of the disappearance of 4-CP with various photocatalytic systems (photocatalyst = 1.2 g/L, 4-CP = 2×10^{-4} M and 25°C)

Systems	pH 4		pH 7		pH 11	
	k	r^2	k	r^2	k	r^2
TiO_2	0.20	0.974	0.22	0.996	0.12	0.970
ZnO	0.03	0.921	0.57	0.992	0.78	0.988
SnO_2	N.D.	--	N.D.	--	N.D.	--
TiO_2/ZnO	--	--	0.53	0.998	0.68	0.992
TiO_2/SnO_2	0.17	0.991	0.19	0.988	0.14	0.997
ZnO/SnO_2	--	--	0.56	0.900	0.95	0.994
TiO_2/ZnO/SnO_2	--	--	0.56	0.992	0.65	0.991

Significantly, the catalytic ability of TiO_2 was found to follow the order pH 7 > pH 4 > pH 11. For TiO_2 and TiO_2/SnO_2 systems at pH 4 and 7, the predominant species in the solution were the undissociated 4-CP molecules, rather than the corresponding anions, due to the pK_a of 4-CP (pK_a = 9.2). Meanwhile, positively charged TiO_2, owing to its surface acidity at pH 4 and 7, offers an appropriate prevailing condition for adsorption, under which the affinity between TiO_2 and 4-CP is high, making the reaction rate higher than that at pH 11. Hence, 4-CP disappeared more slowly at pH 11 than pH 7, despite the increase in number of OH radicals in TiO_2 surface, implying that the dominant role was the electrostatic repulsion between the negatively charged 4-CP and the negatively charged TiO_2 surface. Similar results were previously observed for the photodecomposition of 3-chlorophenol, since HO_2 radicals form at low pH, compensating for the decline in hydroxyl ion concentration [13].

The photodegradation rates of 4-CP at pH 11 for the TiO_2/ZnO, TiO_2/SnO_2, ZnO/SnO_2 and TiO_2/ZnO/SnO_2 systems were 0.68, 0.14, 0.95 and 0.65 h^{-1}, respectively. The k_{app} values for the TiO_2 and ZnO single systems were 0.12 and 0.78 h^{-1}. The experimental results indicate that the kinetics of the coupled-photocatalyst are superior to those of the single-photocatalyst systems, indirectly confirming the IPET effect. Galindo *et al.* [14] stated that OH radicals can be more easily generated in an alkaline solution by oxidizing more hydroxide ions on the surface of the photocatalyst, increasing the efficiency of the process. Moreover, scavenging electrons using a sacrificial electron-acceptor reduces charge recombination, and thus increases the photoactivity of the catalysts. Hence, IPET improved efficiency only under alkaline conditions. However, the details of this phenomenon remain unknown.

At pH 11, the experimental results agree with those in most works, showing highly alkaline media facilitate photocatalysis [2, 5, 9]. The kinetic results of the TiO_2/SnO_2 and ZnO/SnO_2 systems demonstrate even greater activity toward 4-CP than in the single photocatalyst systems, TiO_2 and ZnO, since the redox energy levels of TiO_2 and SnO_2 differ significantly, as do those of ZnO and SnO_2. The TiO_2/ZnO and TiO_2/ZnO/SnO_2 coupled and sandwiched photocatalyst systems at pH 7 and 11 exhibited no increase in kinetic energy over of single TiO_2 or ZnO. The absolute energy levels of the valence and conduction bands played the most important role for the excited particles, explaining the possible IPET effect. The TiO_2/SnO_2 and ZnO/SnO_2 tests were significantly different in redox energy levels, and so exhibit better results concerning the IPET effect, particularly for the ZnO/SnO_2 tests, in which the difference between the conduction and valence bands was found to be large. This event is associated with the small difference between the conduction and valence bands of TiO_2 and ZnO. Accordingly, TiO_2/ZnO tests may offer more opportunities for photo-electrons and photo-holes to recombine, reducing the IPET efficiency to below that in the TiO_2/SnO_2 and ZnO/SnO_2 tests.

In non-acidic aqueous media, ZnO was found to be a very efficient photocatalyst for the degradation of 4-CP, unlike TiO_2, which catalyzed degradation 3-7 times more slowly than ZnO. SnO_2 exhibited almost no photocatalytic activity. However, when TiO_2 or ZnO were coupled with SnO_2 at pH 11, 4-CP oxidation was 17 and 22% faster than that obtained from TiO_2 and ZnO systems, respectively. The experimental results reveal that SnO_2 particles in the coupled photocatalyst systems (TiO_2/SnO_2 and ZnO/SnO_2) are important for accepting the photogenerated electrons, and that the enhanced charge separation resulting from coupling two semiconductor systems with different energy levels improves the rate of photocatalytic degradation.

CONCLUSIONS

The efficiency of 4-CP degradation depends strongly on the pH value and the incorporation of the semiconductors. This study indicates that the chemical kinetics associated with the IPET process indicate a decline in electron-hole recombination. However, this work also found that IPET does not provide all of the anticipated benefits to photocatalysis. The disappearance rate of 4-CP is higher in the coupled photocatalyst system than in single-photocatalyst systems when catalytic system is complex with a large difference between the redox energy levels of the corresponding conduction and valence bands, as in ZnO/SnO_2. Furthermore, the IPET effect only improved the photodegration rate in pH 11. The IPET effect provides an attractive mechanism for increasing the charge separation efficiency, increasing the lifetime of the charge carriers and improving the efficiency of the interfacial charge transfer to adsorbed substrates.

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