

A “Sense and Shoot” Approach for Photocatalytic Degradation of Organic Contaminants in Water

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A “sense and shoot” approach has been developed for the photocatalytic degradation of organic contaminants from aqueous solutions. The presence of aromatic compounds such as chlorinated phenols is readily detected from the quenching of visible emission of ZnO semiconductor film. The emission quenching is quantitative and can be analyzed on the basis of adsorption equilibrium between ZnO and organic molecules. High apparent association constant values ($K_a = (1-5) \times 10^4 \text{ M}^{-1}$) make possible the detection of these organic molecules at very low concentration levels. For example, 1 ppm of 4-chlorocatechol in water results in a 15% decrease of ZnO emission. Interestingly, the same ZnO film is capable of degrading aromatic compounds present in water under UV irradiation. The concept of adopting a strategy of simultaneous sensing and degradation in photocatalysis is illustrated in this paper.

Introduction

Chlorinated phenols and other organochlorines have become a major environmental concern in recent years.^{1,2} These contaminants enter the environment as emissions from its manufacture, incineration, use as a wood and leather preservative and biocide. Significant amounts also result from the chlorination of phenol-containing wastewater. Many of the chemicals used in the pulp mill and wood treatment processes primarily include chlorinated phenols such as Cresote and finds their way into soil, sludges and sediments.^{3,4} When the company closes down, these chemicals are often left untreated. The poor containment practices of these companies result in migration of chemicals as ground-water plumes offsite. These chlorinated phenols already have found their way into drinking water. Detection of increased levels of chlorophenols in urine has established the human intake of such toxins via oral, dermal, or respiratory tracks.^{5,6}

The photocatalytic properties of semiconductor nanoparticles are useful in the remediation of chemical contaminants such as chlorinated phenols from air and water.^{7–15} Under band gap excitation semiconductor nanoparticles undergo charge separation and initiate oxidation of the organics at the interface. TiO_2 , a large band gap semiconductor, is a widely explored system. While TiO_2 is a useful photocatalyst, it is not effective to sense the presence of organic molecules present in its immediate vicinity. Details on the photocatalytic degradation of organic compounds can be found in several review articles.^{1,16–21}

ZnO is another important large band gap semiconductor that has wide applications in electronic, display and catalytic devices. Its band gap and band energies are very similar to those of TiO_2 ($E_g = 3.2 \text{ eV}$; $E_{CB} = -0.5 \text{ V}$ versus NHE). While the photocatalytic activity of colloidal suspension has been explored in early work, its effectiveness in environmental remediation is yet to be explored fully. The studies that exist in the literature merely compare the photocatalytic performance of ZnO to that of TiO_2 .^{22–25} Nanostructured ZnO films cast on electrodes have been employed as photosensitive electrodes.^{26–30} This semi-

conductor has an added advantage that it emits quite strongly in the visible region. Size-dependent emission properties of ZnO colloids have been explored in earlier photochemical studies.^{31–33} The visible emission of ZnO, which usually arises from anionic vacancies, is very sensitive to hole scavengers. The emission is quantitatively quenched by hole scavengers such as iodide ions.³⁴ The obvious question is whether one can sense organic compounds in water by monitoring the ZnO emission.

Recently attention has been drawn toward sensing of nerve gas agents³⁵ hydrocarbons³⁶ and nitroorganics^{37,38} using porous silicon. By making use of detection based on the electrical conductivity,³⁹ photoluminescence,^{35,37} or the interferometer³⁵ principle, the researchers have achieved sensitivity in the range of ppb–ppm levels. Although the thermal conductivity property is often used to sense organic vapors and gases,⁴⁰ to the best of our knowledge no effort has been made to utilize the visible emission of ZnO for sensing trace organic chemicals present in aqueous system.

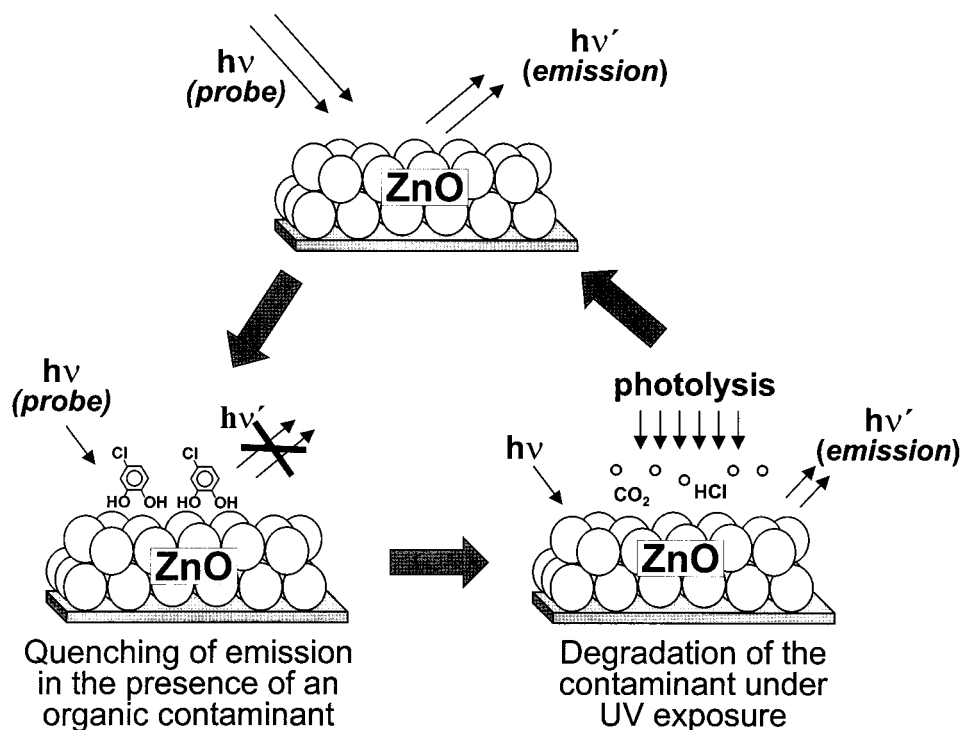
A desirable feature for the detoxification of air and water is to develop a catalyst system that can simultaneously sense and destroy toxic chemicals. Such a catalyst system is especially useful to trigger the photocatalytic operation on demand, i.e., photocatalysis becomes operational only when the system senses the presence of a aromatic compound in the immediate surrounding. ZnO promises to be an ideal candidate for such specialized environmental applications (Scheme 1). We present here a unique approach of sensing and destruction of organic compound using a metal oxide semiconductor. By using 4-chlorocatechol (4-CC) as a model compound, we demonstrate here the dual role of ZnO semiconductor film as a sensor and as a photocatalyst.

Experimental Section

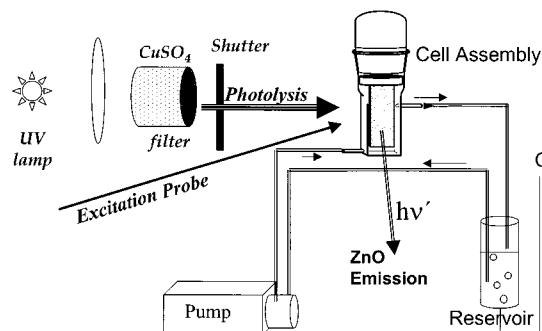
Materials. Optically transparent electrodes (OTE) (5 cm × 0.9 cm) were cut from an indium tin oxide coated glass plate (1.3 mm thick, 20 Ω /square) obtained from Pelkington. (Ordinary glass plates should also serve the purpose of casting films.) High purity ZnO was obtained from ASER; 4-chlorocatechol and other organic compounds were obtained from Aldrich and used without further purification.

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SCHEME 1: Schematic Diagram Illustrating the Principle of "Senses and Shoot" Approach in Photocatalysis



SCHEME 2: Flow Cell Set up Employed in the Emission and Photocatalysis Experiments



Casting of ZnO Films. One gram of ZnO powder was suspended in 25 mL of water containing 0.1 mL of glacial acetic acid. The solution was vigorously stirred in a water bath at 80 °C and transferred to a thick-walled glass cell and sealed. The ZnO suspension was autoclaved by keeping it in an oven at 523 K for 12 h. Both the cell design and autoclaving conditions should be carefully handled for this procedure. The cooled suspension was sonicated and used for casting films on conducting or plain glass plates. A small aliquot (usually 250–500 μ L) was spread over an area of 2 cm² and air-dried. The semiconductor coated glass plates were then annealed in the oven at 673 K for 1 h. The immobilized semiconductor was inserted in a specially designed flow cell (Scheme 2) that can be accommodated in a spectrofluorimeter or on the optical bench of the photolysis set up.

Photocatalysis Experiments. All the photocatalysis experiments were carried out by circulating 15 mL of the aqueous solution using a peristaltic pump (flow rate 0.8 mL/s). Care was taken to use Teflon tubing for circulating the solution. (Commonly employed Tygon tubing is unsatisfactory for flow measurements since significant amounts of aromatic compounds are adsorbed by the polymeric material of the tubing.). The ZnO film was illuminated continuously with collimated light

from a 150 W xenon lamp filtered through CuSO₄ solution ($\lambda > 300$ nm). Samples were drawn periodically from the reservoir for the analysis. At any given time, 4 mL of the solution resided in the cell while the rest remained in the tubing and reservoir. For recording the emission measurements another identical cell assembly was mounted in the cell chamber of the SLM 8000 spectrofluorimeter. Since the front face emission measurements are sensitive to the positioning of the electrode, we kept the cell and the ZnO film undisturbed while the desired solution was circulated continuously during the measurements.

Result and Discussion

Morphology and Emission Properties of Nanostructured ZnO Films. ZnO particulate films cast on a glass slide or optically transparent electrode (OTE) are opaque and remain firm during our flow cell operation. The onset of absorption which is around 400 nm corresponds to its band gap of 3.2 eV. Since the ZnO film essentially is a three-dimensional assembly of nanoparticles, we expect a nanostructured morphology for the catalyst system. Similar nanostructured films of SnO₂,⁴¹ TiO₂,^{42,43} and ZnO²⁶ semiconductor have been characterized in earlier studies.

The AFM images recorded (Figure 1A,B) using a tapping mode show that the ZnO particles assembled in the film have a diameter in the range of 20–40 nm. The depth profile analyzed in Figure 1B shows a diameter of 27 nm for a representative ZnO nanoparticle. Overall the film exhibits a high porosity in the nanometric dimensions, thus providing a large surface area for the molecules to interact. Such a morphology of the catalyst film is important for the organic contaminants to adsorb on the semiconductor surface during photocatalytic operation.

ZnO film exhibits a strong emission in the visible with a maximum around 500 nm (Figure 2). The emission band is relatively broad and is similar to the one observed for small ZnO particles³³ and membranes.⁴⁴ A quantum size-dependent emission property of ZnO colloids has been discussed in our

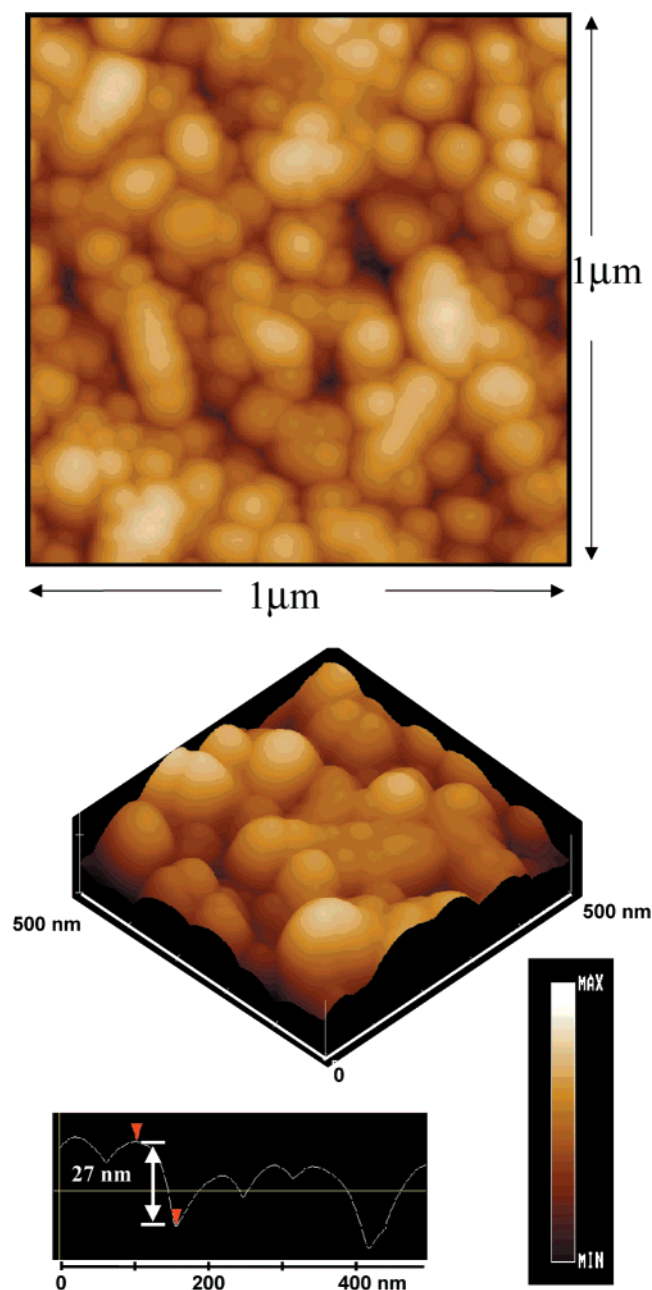


Figure 1. AFM images of ZnO film cast on an OTE plate.

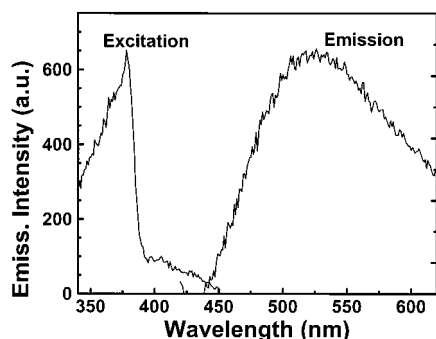


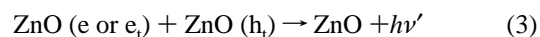
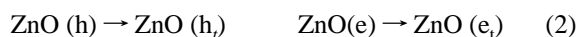
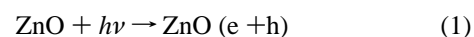
Figure 2. Excitation (emission wavelength 520 nm) and emission (excitation wavelength 325 nm) spectra of ZnO film.

earlier studies.^{31,33} The excitation spectrum recorded by monitoring the visible emission (550 nm) shows an onset at ~ 400 nm. The emission intensity rises sharply at excitations below

400 nm. ZnO absorbs strongly in this region as the incident light is able to induce band gap excitation of the semiconductor. The decrease in intensity at lower wavelengths essentially arises from the inhomogeneous absorption of the incident light as these films exhibit very strong absorption in the UV.

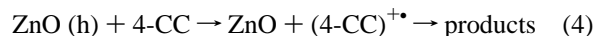
As has been characterized in earlier studies with ZnO colloids^{33,45} and nanostructured films,^{26,44} the visible emission in ZnO arises from the anionic vacancies. In alkaline solutions, however, Zn^{2+} vacancies also contribute to the visible emission.³² Surface binding of acetate ions is known to enhance the emission yield as they create vacancies that promote the visible emission.⁴⁴

Photoinduced charge separation in ZnO nanoparticles is followed by charge trapping and charge recombination via radiative and nonradiative processes (reactions 1–3). A fraction of the charge recombination that results in emission, thus becomes a direct probe of the reactivity of photogenerated charge carriers.



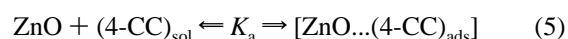
Emission Quenching as a Probe to Sense Organic Molecules in Solution. The ZnO emission seen at room temperature is usually insensitive to oxygen and other electron scavengers. However, hole scavengers such as iodide ions have been shown to quench the emission of ZnO quite efficiently.³³ To see whether the ZnO emission is sensitive to the presence of the chlorinated aromatic molecules, we monitored the ZnO emission at different concentration of 4-CC. To maintain the accuracy in electrode positioning during the emission measurements, we kept the cell assembly fixed in the compartment of the spectrofluorimeter. The solution was continuously circulated through the cell assembly during the emission measurements. When necessary, the solution in the reservoir was changed to another concentration of 4-CC. This flow cell arrangement (See Scheme 2) provided good reproducibility for emission quenching experiments. Figure 3A shows the emission spectra of ZnO film at different concentrations of 4-CC in aqueous solution. The emission yield decreased with increasing concentration of 4-CC. More than 50% emission was quenched at concentration levels of 0.5 mM 4-CC.

As the 4-CC from aqueous solution came in contact with the semiconductor surface it effectively scavenged the holes (reaction 4), thus competing with the charge recombination process (reaction 3) responsible for emission of ZnO nanoparticles,



A major criterion for such a charge transfer at the semiconductor interface is effective adsorption of organic molecules. The surface concentration of the adsorbed species and the energetics determine the rate and efficiency of hole transfer at the semiconductor interface.

We further analyzed the emission quenching data by considering an adsorption equilibrium between ZnO and 4-CC illustrated below.



The observed emission yield $\Phi_f(\text{obs})$ can then be related to the emission yields of ZnO colloids that are unassociated (Φ_f^0) and

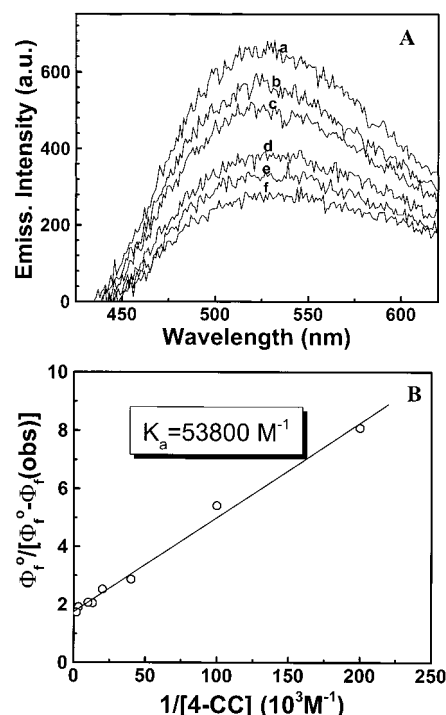


Figure 3. A. Emission spectra of ZnO film at different 4-CC concentrations (excitation wavelength 325 nm). The aqueous solution containing different amounts of 4-CC was circulated through the flow cell during the emission measurement. (a) no 4-CC, (b) 0.005 mM 4-CC, (c) 0.01 mM, (d) 0.05 mM, (e) 0.1 mM, and (f) 0.5 mM. Excitation wavelength was 325 nm. B. Plot of $\Phi_f^0/(\Phi_f^0 - \Phi_f(\text{obs}))$ versus $1/[4\text{-CC}]$.

associated (Φ_f') with 4-CC, by the expression 6,³³

$$\Phi_f^0/(\Phi_f^0 - \Phi_f(\text{obs})) = \Phi_f^0/(\Phi_f^0 - \Phi_f') + \Phi_f^0/K_a(\Phi_f^0 - \Phi_f')[4\text{-CC}] \quad (6)$$

If the observed emission quenching is influenced by an adsorption equilibrium, the expression 6 would then demand a linear relationship between $\Phi_f^0/(\Phi_f^0 - \Phi_f(\text{obs}))$ and $1/[4\text{-CC}]$. Indeed, the straight line fit of the double reciprocal plot shown in Figure 3B confirms the validity of this argument. From the intercept and slope of the straight-line plot we obtain an apparent equilibrium constant of 53800 M^{-1} . Such a high value of K_a is essential if one is interested in sensing low concentrations of organic molecules present in aqueous solution. In the present experiments, we can put a sensitivity limit of the order of ~ 1 ppm 4-CC as the detection limit using ZnO film. (Approximately 15% quenching is seen at 1 ppm of 4-CC.)

Response of ZnO Emission to the Presence of Various Organics in Solution. To check the generality of the ZnO emission to probe the organics present in the solution, we tested several representative organic compounds. Emission measurements were made by flowing aqueous solution of 4-chlorophenol, 4-chlorocatechol, and catechol at different concentrations. Figure 4 shows the dependence of emission intensity at 500 nm versus the concentration of organics in solution. The varying degree of quenching arises from the difference in adsorption and the rate with which photogenerated holes are scavenged from the ZnO surface. The degree of adsorption is influenced by the substituent groups on the aromatic ring. As established earlier,⁴⁶ molecules possessing donor groups with the highest ionic contribution to bonding adsorb to the greatest extent on oxide surfaces. The apparent equilibrium constants obtained

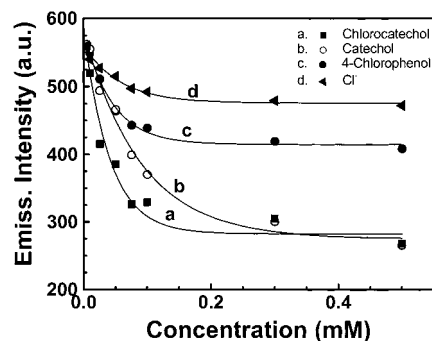


Figure 4. Effect of different chemical species on the relative emission intensity (monitored at 500 nm with excitation wavelength set at 325 nm) of ZnO. (a) 4-chlorocatechol, (b) catechol, (c) 4-chlorophenol, and (d) Cl^- .

TABLE 1: Apparent Association Constant (K_a) for the Adsorption on ZnO Surface^a

chemical species	apparent association constant $K_a (\text{M}^{-1})^b$
4-chlorocatechol	53800
catechol	29700
4-chlorophenol	13300
chloride ion	8700

^a K_a values were measured by monitoring emission intensity at 500 nm and using expression 6. ^b Within the experimental error of $\pm 5\%$.

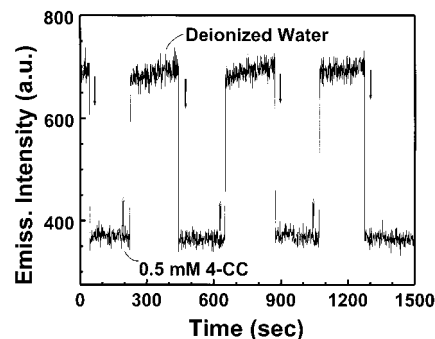


Figure 5. Response of ZnO emission (excitation wavelength 325 nm) to the presence of 4-CC (0.5 mM) in solution.

from the double reciprocal plot are summarized in Table 1. The values of K_a for all the organic compounds tested in this study are relatively high suggesting stronger interaction with the semiconductor surface even at low concentration levels. These results further support the choice of ZnO film as a smart nanomaterial for sensing organic molecules in aqueous solutions.

Reproducibility of Sensing Response. During the course of our experimental study we have found that the emission response of ZnO is very reproducible. This property becomes important if one has to consider such systems for sensor applications. In the case of porous Si, it is often necessary to regenerate the passivated surface during the detection of the organic molecules. Since the emission quenching is dependent on the adsorption equilibrium, it should directly reflect the concentration of organic molecules present in aqueous solution.

We checked the reproducibility of the ZnO emission response to the presence of 4-CC in solution by alternating the solution between deionized water and 0.5 M solution of 4-CC circulated through the cell assembly. The results are presented in Figure 5. As soon as the 4-CC entered the cell, the ZnO emission was quenched, confirming thereby the presence of organics in the solution. The response time to observe quenching is less than a minute. When the solution was switched to deionized water,

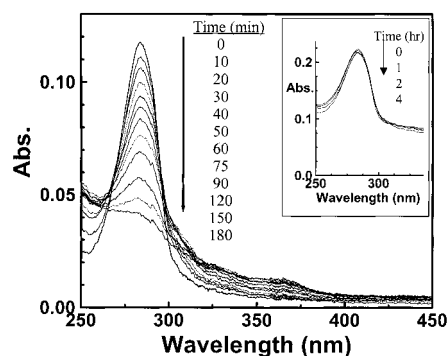


Figure 6. Photocatalytic degradation of 4-CC (0.05 mM) at an UV-irradiated ZnO film. The aqueous solution was continuously circulated through the cell during UV irradiation. The inset shows the changes in 4-CC absorption following UV irradiation in the absence of ZnO photocatalyst.

the emission intensity increased as 4-CC was swept away from the surface of ZnO. The original emission intensity was restored following the exposure of the film to deionized water. This shows that the interaction between the ZnO and 4-CC is physisorption and not chemisorption as observed in the case of TiO_2 -catechol system.^{47,48} The emission traces recorded in Figure 5 highlight the ability of ZnO film to sense the organics from aqueous solution in a reproducible way.

Photocatalytic Degradation of 4-CC at a ZnO Electrode.

In earlier studies the photocatalytic activity of semiconducting metal oxides such as TiO_2 has been explored in great detail. (See, for example, refs 1, 19, 21, and 49–51.) Its usefulness in mineralizing organic contaminants has attracted attention from scientists and engineers from various disciplines. Since ZnO has energetics similar to that of TiO_2 ($E_g \sim 3.2$ eV; $E_{VB} \sim +2.5$ V vs NHE) we expect it to be photocatalytically active under UV irradiation. In the present study we tested the feasibility of employing immobilized ZnO film for the degradation of 4-CC in the present experiments by irradiating it with UV-light ($\lambda > 300$ nm) while the 4-CC solution was continuously circulated through the cell. (The experimental design was same as the one employed for emission measurements. The only difference is that the ZnO film was subjected to high-intensity UV-light).

Figure 6 shows the absorption spectrum of 4-CC recorded at different time intervals of UV irradiation. Note that the sample was drawn at regular intervals to record the absorption spectrum. The solution was transferred back into the reservoir after completing the measurements. 4-CC has an absorption maximum at 280 nm. At shorter irradiation times, the absorption band of 4-CC decreases while the absorption in the 300–400 nm region increases. We attribute these changes to the oxidative transformation of 4-CC to generate several aromatic intermediates. HPLC analysis of the analyte has indicated the presence of catechol, hydroquinone, and oxalic acid as possible reaction intermediates. Identification of similar reaction intermediates has also been made in earlier photocatalytic degradation of chlorinated phenols and catechols in UV-irradiated TiO_2 slurries.^{14,52–54}

At longer irradiation times the overall absorption decreases as the aromaticity of the intermediates disappears and nonabsorbing species such as carboxylic acids are produced. Continued irradiation can further lead to the mineralization of the organics in the solution. Comparison of the photocatalytic performance between ZnO and TiO_2 films was made by monitoring the initial disappearance of the 4-CC absorption at 280 nm. It is evident from Figure 7 that the degradation of 4-CC at ZnO surface

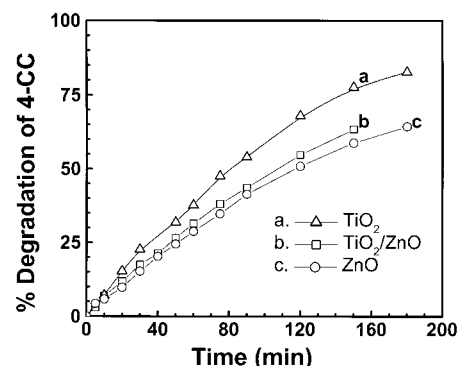


Figure 7. Comparison of the performance of ZnO, ZnO/ TiO_2 (1:1), and TiO_2 of photocatalytic degradation of 0.05 mM 4-CC in oxygenated aqueous solution. The disappearance of the absorption at 280 nm was considered for determining the initial degradation of 4-CC.

occurs at a slightly slower rate than that at TiO_2 films. The time required for 50% disappearance of 4-CC was 120 and 80 min for ZnO and TiO_2 respectively. Although the energetics of the two semiconductors are similar the difference in morphology, surface interactions and charge-transfer dynamics can influence the overall degradation rate. We also attempted to improve the photocatalytic performance of ZnO film by mixing with TiO_2 . Semiconductor films cast with equal weight of ZnO and TiO_2 showed slightly better performance (trace b in Figure 7). The time required for 50% degradation of 4-CC was 105 minutes. Although the improvement in the degradation rate observed with the mixed semiconductor system over that of pristine ZnO film was small, it opens up an avenue to imbed ZnO nanoparticles as sensing probes in an efficient catalyst system (e.g., TiO_2). Mixed semiconductor systems such as $\text{SnO}_2/\text{TiO}_2$ have been shown to be beneficial for enhancing the photocatalytic degradation rate since they improve net charge separation following band gap excitation.^{55,56} In the present experiments we see only additive effects. Since the band energies of two semiconductors (ZnO and TiO_2) are isoenergetic we do not expect to observe any charge rectification effects in these systems.

Recovery of ZnO Emission. The sensing and photocatalytic experiments discussed in earlier sections demonstrate a unique property of ZnO semiconductor system to sense and degrade organic compounds. This dual role of the photocatalyst can facilitate design of a photocatalytic reactor that can sense and decontaminate the water simultaneously. The obvious question that arises from these experiments is whether one could observe regeneration of ZnO emission as the organic compounds are photocatalytically decomposed in aqueous solution. We employed a 0.05 mM catechol solution for these measurements.

Figure 8 shows an increase in the 500 nm emission from the ZnO film following the photocatalysis for a long period of time. Since the concentration and composition of the organic intermediates change during the course of photocatalytic reaction, we expect to see their effect on the emission of another ZnO film mounted separately in the spectrofluorimeter. Note that the emission and photocatalytic experiments were carried out in two separate experimental set ups. We periodically transferred the solution in the reservoir from the photocatalysis experiment to the second cell assembly mounted in the spectrofluorimeter to monitor the emission from ZnO film. After completing the emission measurement the solution was transferred back to the photocatalysis set up.

In the initial stages of photocatalysis we do not see any noticeable increase in the ZnO emission. The breakdown of the target compound (catechol) produces a variety of aromatic

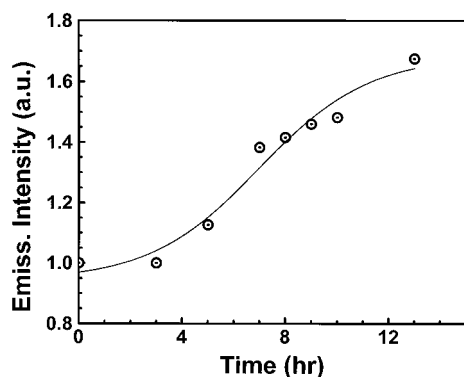


Figure 8. Recovery of fluorescence of ZnO film during a photocatalytic degradation process. Catechol (0.05 mM) was subjected to photocatalytic degradation at an UV-irradiated ZnO film. The effect of this solution on the ZnO emission intensity at 500 nm (excitation wavelength 325 nm) was checked at different time intervals.

intermediates such as phenols, quinone, and hydroquinone. Accordingly, the absorption spectrum recorded at the end of 3 h in Figure 6 shows residual absorption below 350 nm. These aromatic intermediates formed in this early stage of photocatalysis continue to quench the emission since they scavenge away photogenerated holes from semiconductor surface. These reaction intermediates eventually break down into carboxylic acids and other carbonaceous species in aqueous solutions. Following the photolysis at time intervals greater than 4 h we observe a rise in the ZnO emission. The rise in emission intensity during the next few hours is steep and finally attains saturation at longer time intervals. More than 80% of the emission was recovered during the 13 h of photocatalysis. The presence of carbonaceous species is likely to contribute to the remaining 20% emission which is yet to recover. Ion conductivity and HPLC analysis of the solution at the end of photocatalysis experiment have confirmed the presence of carboxylic derivatives such as oxalic acid. It is important to note, however, that we did not detect any aromatic intermediates in the samples analyzed at the end of the photocatalysis experiment.

The experiment illustrating the emission increase during photocatalytic degradation shows that this emission recovery parallels the degradation of aromatic intermediates from the aqueous solution. Thus, ZnO films can be used to monitor the course of a photocatalytic reaction. Though not selective, ZnO emission quenching serves as a probe to sense the presence of aromatic intermediates in water. ZnO film-based nanosensors should be useful in applications such as checking the quality of drinking water, or assessing the contamination in undergroundwater. Design and development of fiber optic probes can miniaturize the sensor design for environmental applications.

Conclusions

The feasibility of employing nanostructured ZnO films for simultaneous sensing and degradation of organic contaminants has been demonstrated. The ZnO emission is very sensitive to the presence of aromatic compounds such as chlorinated phenols in water. The observed emission quenching is quantitative as the extent of quenching by the organics is determined by the adsorption equilibria. A detection sensitivity of the order of 1 ppm can be achieved in these systems. A major feature of the ZnO semiconductor system is its ability to degrade the organic contaminant under high-intensity UV-illumination. Alternatively, the ZnO film-based sensors are also useful to monitor the course of a decontamination process as the emission intensity corresponds to the presence of aromatic species in water. The use of

nanostructured ZnO films in these studies highlights the possibility of designing nanosensors for monitoring the quality of drinking and undergroundwater.

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