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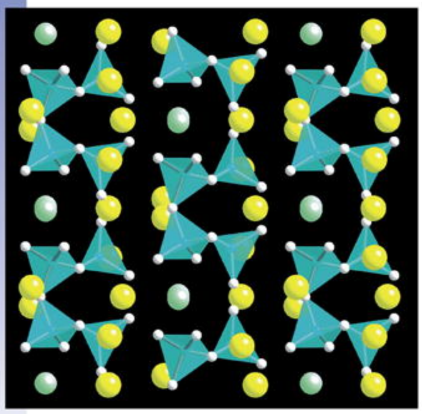

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Dye-effect in TiO_2 catalyzed contaminant photo-degradation: Sensitization vs. charge-transfer formalism

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Abstract

Anatase TiO_2 surfaces have been treated with 2,4,6-triphenylpyrilium hydrogen sulfate (TPPHS) dye to yield the modified TiO_2/TPPHS surface. The modified TiO_2/TPPHS surface was then supported onto activated carbon (AC) surfaces to yield a *new* class of catalytic system AC/TiO_2/TPPHS. The catalytic activities of naked TiO_2, TPPHS solution, TiO_2/TPPHS and AC/TiO_2/TPPHS systems were examined in photo-degradation of phenol and benzoic acid in water, using both UV and visible regions. All studied systems showed low catalytic activity when used in the visible region. In UV, the AC/TiO_2/TPPHS showed highest activity, whereas the naked TiO_2 and TPPHS solutions were the least active systems. The dye role, in enhancing activity of modified surfaces in UV degradation of contaminants, is understandable by a charge-transfer catalytic effect rather than a sensitizing effect. AC role is explainable by its ability to adsorb contaminant molecules and bringing them closer to catalytic sites.

Keywords: TiO_2; 2,4,6-Triphenylpyrilium hydrogen sulfate; Photo-degradation; Phenol; Benzoic acid; Sensitization

1. Introduction

Mono-crystalline and nano-crystalline semi-conducting materials are especially useful in photo-electrochemical applications [1–21]. Nano-crystalline TiO_2 has been widely used to catalyze the photo-degradation of water contaminants such as chlorinated hydrocarbons, phenols, benzoic acid and others [8–17]. Despite the many known advantages of using TiO_2, it suffers the shortcoming of having a large band gap ($\sim$3.2 eV) which restricts its use to the UV region. Such radiations are not highly abundant in the solar radiations that reach the earth, which limits the use of TiO_2 in solar energy utilization. Therefore, research has been directed to sensitize TiO_2 surfaces in order to function in the visible region. Dye sensitized TiO_2 surfaces have therefore been successfully experimented in photo-electrochemical devices to produce electricity from visible light [18–21]. Literature described the use of dye sensitized TiO_2 surfaces in photo-degradation of contaminants in the visible region [8,22–24]. In addition to TiO_2, other systems sensitized by low gap dyes, are also known. Incomplete degradation of fungicides has been reported using 2,4,6-triphenylpyrilium tetrafluroborates sensitized triadimenol, to yield other organic products [25]. Up to 70% partial oxidation has been reached within 50 h of continued visible illumination. In addition to visible sensitization, dye sensitized systems have also been described in UV degradation processes [24,25].

Strictly speaking, sensitization involves *activation of the TiO_2 surface under wavelengths longer than those corresponding to its band gap*. In such a process, the dye is excited by the visible light, Scheme 1. An electron is then excited to the dye conduction band. The electron travels across the TiO_2 conduction band, and then reduces contaminants with suitable reduction potentials (more positive than TiO_2 conduction band edge). At the other side, a hole is created in the dye valence band. The hole may then oxidize easy-to-degrade

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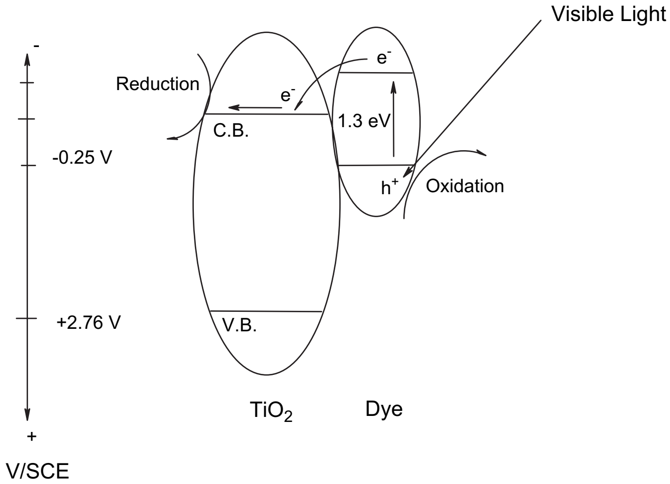


Scheme 1. Schematic TiO_2 sensitization to visible light with TPPHS.

contaminants only, which demand oxidizing potentials less positive than the dye valence band edge. As such, the holes may not oxidize contaminants that demand more positive potentials. Therefore, dye sensitized TiO_2 surfaces have two characteristic features: they are sensitized to longer wavelengths (e.g. visible), and they oxidize contaminants demanding oxidation potentials less positive than the dye valence band edge only. If dye modification enhances TiO_2 catalytic activity in UV regions or nearby, the process may not then be a sensitization process. Therefore, sensitization formalism need not be claimed in all cases and should be limited to cases where real sensitization occurs. If the dye modification enhances TiO_2 surface catalytic efficiency in UV regions, other formalism needs to be adopted.

For this purpose, TiO_2 surfaces have been modified here with TPPHS. The dye-modified TiO_2 surfaces were then examined to photo-degrade phenol and benzoic acid in water. Both species are water contaminants that are difficult to degrade. Both visible and UV radiations have been used in this study. In order to further enhance its catalytic activity, the dye-modified TiO_2 has been supported onto activated carbon (AC). Very few reports, if any, described supporting dye-modified TiO_2 onto activated carbon, and to our knowledge this is the first study that employs AC surface to support TPPHS-modified TiO_2 and uses the supported modified system in photo-degradation of phenol and benzoic acid. AC support has the added value of increasing catalytic activity of TiO_2 by adsorbing contaminant molecules and bringing them into close proximity to the catalytic sites, provided that the adsorption is not strong enough to inhibit their immigration to the catalytically active sites. The use of AC in supporting naked TiO_2 and enhancing its activity has been described in literature [9,23,26,27]. Due to its hydrophobic nature, AC has the additional technical advantage of making supported TiO_2 system easier to isolate after reaction completion [26,28]. Results of this study are presented, together with an understanding of the mode of action of both the dye and the AC support.

2. Experimental

2.1. Chemicals

Nano-crystalline TiO_2 (Anatase), AC, 2,4,6-triphenylpyrilium hydrogen sulfate, phenol, benzoic acid, and other common chemicals have been purchased from Aldrich, Ltd., in a pure form. AC and TiO_2 surface areas were measured according to literature [29–31] using the acetic acid adsorption isotherms and were 850 and 125 m^2/g, respectively.

The dye-modified TiO_2 surface was prepared as previously described for supporting naked TiO_2 systems onto AC [8]. TiO_2 solid was suspended and stirred with aqueous solutions of TPPHS (0.003 g in 10.00 mL, 3.4×10^{-4} M) for 4 h in the dark. The solid was then separated, by suction filtration through a sintered glass funnel, washed with water and dried at room temperature. Using different dye concentrations gave same dye/TiO_2 ratio, as saturation was obtained with low dye uptake even with low TPPHS concentrations used. The yellow TPPHS dye absorbs at around 435 nm. Solid state IR spectra confirmed the presence of TPPHS onto the TiO_2 surfaces. IR bands, due to adsorbed TPPHS, were unchanged for TiO_2/TPPHS system after use in UV degradation experiments.

The AC supported dye-modified TiO_2 system, AC/TiO_2/TPPHS, was prepared by stirring a suspension of AC (0.1 g) with TiO_2/TPPHS (0.5 g) in water for 5 h. The solid was then separated and washed with water before drying.

Contaminant phenol concentrations were spectrophotometrically analyzed using known literature methods [32]. Absorbance vs. concentration calibration curves were constructed in order to measure remaining contaminant concentrations in aliquots that were syringed out from reaction mixtures at different times. Benzoic acid concentrations were measured using HPLC.

GC–MS was used to analyze degradation reaction products. Apart from remaining unreacted phenol or benzoic acid, no other organic products were detected. This indicated that CO_2 and water were the only resulting products from phenol and benzoic acid photo-degradation. This is consistent with earlier literature [27].

2.2. Equipment

A Shimadzu UV-1601 spectrophotometer was used for absorbance measurements. Gas Chromatography/Mass Spectrometery analysis was conducted on a Shimadzu GCMS-QP 5000. The GC was equipped with an auto-injector (AOC-17), a Class 5000 software and a 30 m J&W SCIENTIFIC long and 0.25 mm I.D. capillary column DB-SMS (5% – phenyl) Methylopolysiloxane 0.25 μm thick film. The injector was set up at 250 °C, GC–MS interface at 280 °C, helium carrier gas at a flow rate of 0.80 mL/min at 25 °C. The sample (2 μl) was injected in the splitless injection mode. The oven temperature was programmed starting at 100 °C for 1 min, raised to 320 °C (5 °C/min), and held at 320 °C for 10 min. Aqueous aliquots were first extracted with organic solvents, and then the organic phase was injected for GC–MS analysis.

HPLC analysis was conducted on a Waters 2695/Separation Module equipped with a Photodiode Array detector, functioning at 254 nm. Analysis was performed on a 250×4 mm I.D. Merck Lichrospher 100 RP-18 (5 μm) column fitted with guard column. The injected volume was 20 μl. Elution was conducted using 20% acetic acid solution, pH = 3, as mobile phase.

Thermal gravimetric analysis (TGA) was thankfully conducted at the SCA-CNKS laboratory, Service Central d'Analysis, France, using a 2950HR V5-3 TA. Under-air heating was started at room temperature and ended at 1000 °C, with temperature increase rate of 5 °C/min. Solid state FT-IR spectra were recorded for TiO_2, TiO_2/TPPHS, and AC/TiO_2/TPPHS as KBr pellets, on a Shimadzu FTIR-8201PC.

UV irradiation was conducted using an Oriel 500 W Hg/Xe lamp equipped with a Model 66901 Universal Arc Lamp Housing, and a fiber optical bundle. The lamp was run at a 150 W working power. To maximize exposure of reaction mixture to irradiation, and to minimize radiation loss, the bundle terminus was directly inserted inside the reactor through a glass tube. The glass tube was in turn dipped inside the reaction mixture. Visible illumination was conducted using a model 45064 − 50 W Xe lamp (Leybold Didactic Ltd.) equipped with a housing and a concentrating lens. Lamp specifications are described in special manuals [31–34]. In each case, the reaction vessel that contained reactants, solvent and catalyst, was wrapped out with aluminum foil to reflect any lost radiations back to reaction mixture. The reaction mixture was thermostated by dipping the reaction vessel inside a water bath. The reaction mixture was magnetically stirred.

2.3. Photo-degradation experiments

A typical degradation experiment was conducted as follows: different catalytic systems were placed inside a thermostated three-necked glass flask reactor. Water samples, contaminated with known concentrations of phenol or benzoic acid, were added to the reactor. The pH was measured as 6.0 and 2.7 in phenol and benzoic acid solutions, respectively. Illumination was conducted either by UV or visible lamps, as described above. Aliquots were syringed out of the reaction vessel at different reaction times, and spectrophotometrically analyzed as described earlier.

To ensure that contaminant loss was due to photo-degradation, control experiments were conducted. Experiments were run using different catalytic systems in the dark. Illumination experiments were also conducted in the absence of catalysts. Additional control experiments were conducted using AC surface only, to see if contaminant loss may occur due to adsorption rather than degradation. Only up to 3% contaminant loss was observed due to contaminant adsorption onto AC surface, as relatively high contaminant concentrations were used in degradation experiments here.

3. Results and discussion

Experiments conducted in the dark, with or without catalytic systems, showed no significant phenol or benzoic acid loss. Control experiments conducted under illumination (UV or vis), in the absence of TiO_2 or TiO_2/TPPHS showed no significant loss in contaminant concentrations.

In visible light experiments, conducted using different catalytic systems (naked TiO_2, TiO_2/TPPHS and AC/TiO_2/TPPHS), no significant contaminant loss was observed under experimental conditions described here. On the other hand, UV illumination caused significant contaminant loss depending on the nature of the catalytic system used. Therefore, unless otherwise stated, all results shown hereafter were observed using UV illumination.

3.1. Naked TiO_2, TPPHS and TiO_2/TPPHS catalytic systems

When naked TiO_2 was used in UV degradation of phenol or benzoic acid, only up to 8% and 4% contaminant losses were observed, respectively, within 120 min. Despite the thermodynamic feasibility of degradation in TiO_2 catalyzed process, the reaction demands kinetic enhancement, in such a way to speed up the charge transfer. When the TiO_2 was replaced with TPPHS solution, only low contaminant loss was observed. This is presumably due to the dye valence band edge being not positive enough to degrade phenol or benzoic acid molecules, vide infra.

When modified TiO_2/TPPHS surface was used in UV, up to 30% and 35% loss, in phenol and benzoic acid concentrations, was observed, respectively, within 120 min. Maximum contaminant loss was observed in an open reactor. When the reactor was closed to oxygen, lower contaminant losses were observed. Moreover, when air stream was used, contaminant loss was lower than that observed in an open reactor only. Such results are consistent with earlier reports, where oxygen is needed in degradation experiments, but higher oxygen pressures inhibit the degradation reaction [9,35–42]. Therefore, unless otherwise stated, all oncoming experiments were conducted in an open-to-air reactor with no air streams. Turnover number values, showing the effect of the dye on the TiO_2 activity, were calculated as shown in Table 1.

3.2. AC/TiO_2/TPPHS catalytic system

In UV illumination, the supported modified catalyst AC/TiO_2/TPPHS showed higher catalytic activity than its unsupported counterpart. About 65% and 57% losses in phenol and benzoic acid concentrations, respectively, were observed when the AC/TiO_2/TPPHS catalytic system was used, within 120 min. In the visible light processes, only little contaminant degradation was observed.

Values of turnover number for different catalytic systems used in UV degradation of phenol and benzoic acid degradation are shown in Table 1. The table shows that in either phenol or benzoic acid, the catalytic activities for different catalytic systems vary in the order: AC/TiO_2/TPPHS > TiO_2/TPPHS > naked TiO_2 ∼ TPPHS.

Temperature effect on catalytic activity of AC/TiO_2/TPPHS was studied in UV degradation of phenol and benzoic acid.

Table 1
Values of turnover numbers for different catalytic systems, measured for degradation of phenol and benzoic acid in water, using UV illumination

Catalyst	TiO_2 amount (g)	Nominal TPPHS amount g (mol)	Turnover number (moles reacted contaminant per mole dye, after 120 min)	
			Phenol degradation	Benzoic acid degradation
Naked TiO_2	0.5	0	33[a]	49.4[a]
Dye only	0	0.006 (1.476×10^{-5})	27	50.4
TiO_2/TPPHS	0.5	0.006 (1.467×10^{-5})	270	316.0
AC/TiO_2/TPPHS	0.5	0.006 (1.476×10^{-5})	372	454.9

[a] Calculations were made assuming the presence of 0.006 g (1.476×10^{-5} mol) TPPHS.

The temperature showed no significant effect on catalyst efficiency, and slightly higher activity was observed at lower temperatures. The results are consistent with earlier literature [27,43], which showed that photo-catalytic degradation rates are not much affected by changes in temperature. The degradation rate independence of temperature is reflected by the low activation energy (a few kJ/mol) compared to ordinary thermal reactions [27]. Moreover, at higher temperatures, oxygen concentrations in the reaction solution are lowered by increasing the temperature. This explains why at 20 °C the rate was slightly higher than at higher temperatures here. The reaction rate was also independent of initial contaminant concentration, and the rate was slightly higher when using lower concentrations. This is in accordance with literature [27] where organic contaminant photo-degradation is independent of the contaminant concentration, and in some cases, the rate is lowered with increased initial concentration. Different explanations are proposed, all of which rely on the adsorption of contaminant molecules on the solid surface in a Langmuir–Hinshelwood model. One acceptable explanation is the fact that at higher contaminant concentration, the contaminant molecules may compete with the adsorbed intermediates and inhibit degradation [27].

TGA, measured for AC/TiO_2/TPPHS before and after use in photo-degradation experiments, showed no difference in carbon content during the process. Samples of AC/TiO_2/TPPHS, recovered after pre-use in photo-degradation experiments showed 20% carbon loss on heating in the range 550 and 600 °C during TGA. This matched other fresh AC/TiO_2/TPPHS unused samples in degradation experiments, Fig. 1. The findings indicate that AC is robust enough to survive photo-degradation experimental conditions. This, together with its catalytic enhancement of TiO_2/TPPHS system, makes AC an advantageous support for photo-degradation catalysts. Another advantage in using AC support is its hydrophobic nature. Nano-sized TiO_2 particles form colloid-like mixtures with water which makes them difficult to isolate after use. Using the hydrophobic AC support makes it easier to isolate the AC/TiO_2/TPPHS catalytic system by simple filtration.

3.3. The role of the dye

Phenol and benzoic acid are examples of difficult-to-oxidize contaminants. In this work, the TPPHS dye failed to sensitize the TiO_2 in visible degradation of these contaminants. Despite its relatively high band gap, 435 nm, and its ability to degrade other contaminants such as methyl parathion [35], its valence band edge position may not be low enough to oxidize phenol and benzoic acid in the visible region. This was evident by the inability of TPPHS solutions to degrade phenol and benzoic acid using visible and UV. Therefore, a sensitization mechanism of TiO_2 by TPPHS, as shown in Scheme 1, to degrade phenol and benzoic acid in the visible light should be ruled out. Phenol and benzoic acid demand positive oxidation potentials more positive than 1.2 and 1.0 V/SCE, respectively, as calculated from

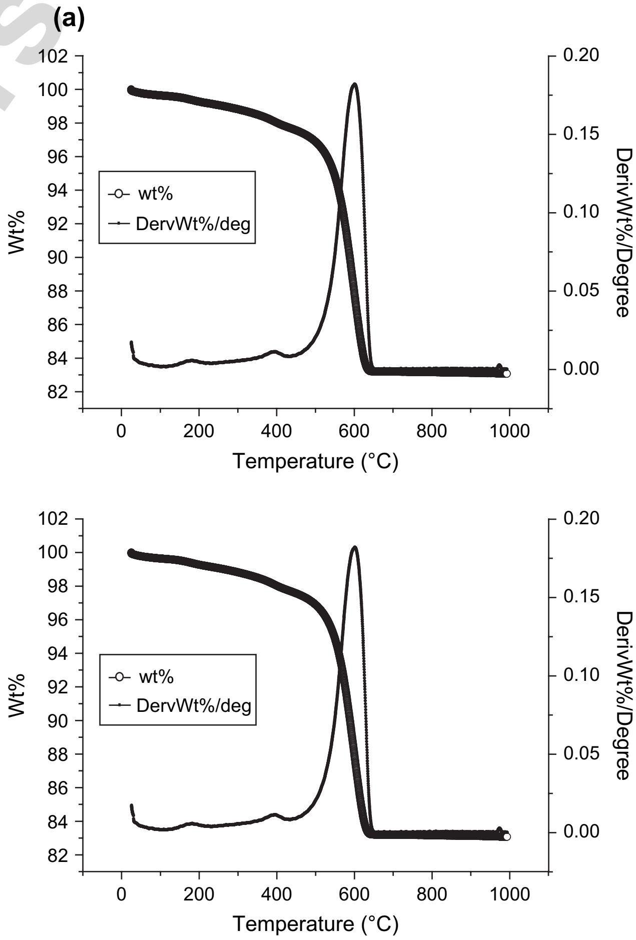
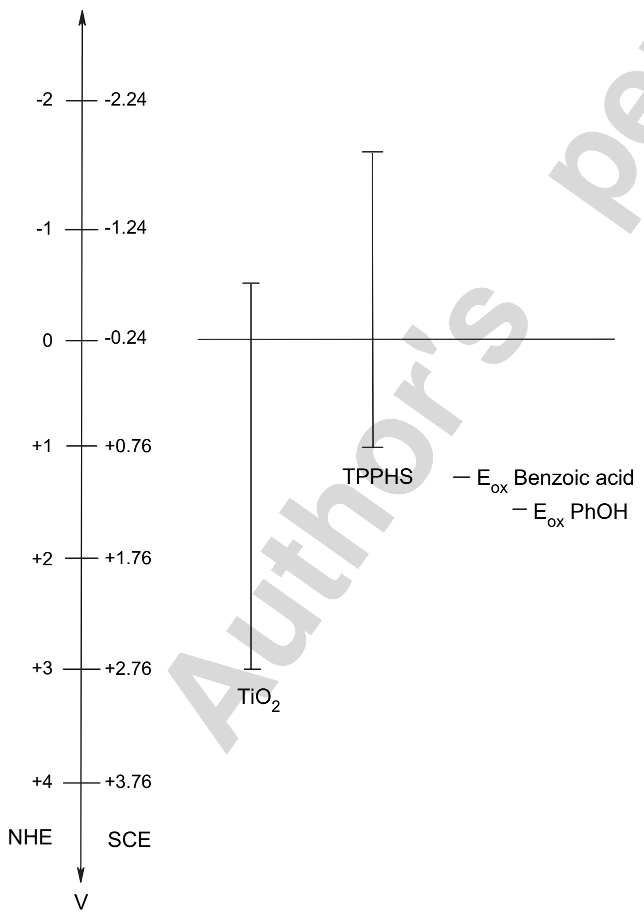


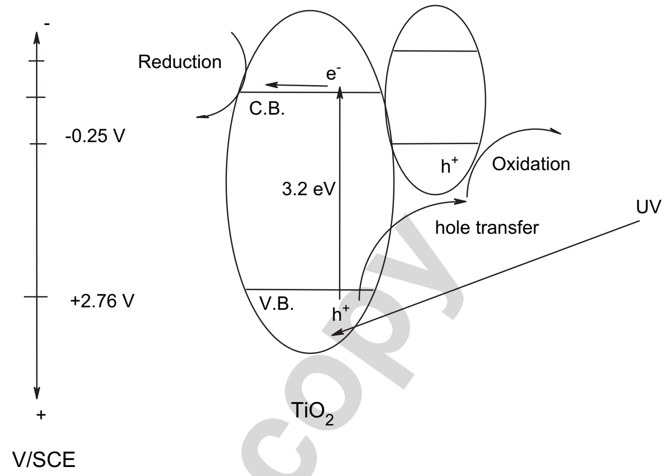
Fig. 1. TGA data measured for AC/TiO_2/TPPHS: (a) fresh sample and (b) recovered sample after pre-use in degradation.

thermodynamic data. Over-potentials are needed for contaminant degradation, and more positive potentials than these values should be available for degradation to occur. The needed potentials are more positive than that of the dye valence band, ∼+0.76 V/SCE, Scheme 2. This explains the failure of naked TPPHS to catalyze degradation in the visible and UV regions. This also explains the failure of AC/TiO_2/TPPHS system to degrade stable organic contaminants in the visible region.

In the UV region, TPPHS modification enhanced the catalytic activity of TiO_2. In this region, the TiO_2 is itself excited. Therefore, the ability of TiO_2/TPPHS to degrade phenol and benzoic acid in the UV region is not a sensitization process. Alternatively, the dye molecules enhance the catalytic activity of TiO_2 by other processes. One possible mechanism is that the dye molecules, attached here to TiO_2 surface as cations, may facilitate the charge transfer between the TiO_2 valence band and the contaminant molecules. The dye ions may adsorb the contaminant molecules and encourage the charge-transfer process. Thus, the holes, created in the TiO_2 valence band, immigrate faster toward the contaminant molecules through the dye. The role of the dye molecule in TiO_2 catalytic activity enhancement, here, is therefore understandable in charge-transfer formalism (Scheme 3) rather than sensitization formalism. Attempts to replace TPPHS with other low energy-band gap dyes, such as tetraphenylporphyrinato-manganese(III) ions, failed to enhance the catalytic activity of TiO_2 in UV and visible degradation of phenol and benzoic acid here.



Scheme 2. Schematic oxidation potential levels, for phenol and benzoic acid, relative to band edge positions of TiO_2 and TPPHS.



Scheme 3. Schematic charge-transfer formalism.

In the suggested formalism, the overall degradation process (which involves hole transfer from TiO_2 valence band to contaminant molecules) is thermodynamically feasible. On the other hand, the kinetics are enhanced by the dye molecules.

The results are consistent with literature in this aspect. TiO_2 surfaces, modified with TPPHS and other dyes, showed higher catalytic activity in UV degradation of contaminants than naked TiO_2 counterparts [9,44,45]. In some cases it has been stated that TiO_2 is sensitized by the dye, in the UV [41]. In other reports humic acid dyes inhibited the catalytic activity of TiO_2 in degrading *p*,*p*-DDT contaminants by UV [46]. The inhibition effect is understandable by the ease of degradation of humic acid in UV which competes with *p*,*p*-DDT degradation onto TiO_2 sites.

The fact that AC enhanced the catalytic activity of TiO_2/TPPHS, in UV degradation of stable contaminants, here, is other evidence in favor of charge-transfer formalism. Numerous reports described AC as support for TiO_2 [9,23,26,27,47,48]. Literature also indicated that AC supported TiO_2 showed higher activity in UV degradation of stable contaminants with no added dyes [26,27], and the AC and TiO_2 showed synergistic effects [49]. AC adsorbs water contaminants and brings them into closer proximity to the catalytic sites at the TiO_2 surface. Such formalism is acceptable, as AC has no reason to play as a TiO_2 sensitizer. AC may also have another role, as by adsorption of intermediates it brings them into close proximity to active sites and enables their complete degradation to yield complete contaminant degradation. This is consistent with other earlier reports [27]. The fact that the reaction rate was independent of reactant concentration is consistent with the discussion presented here, vide supra. Other supports, such as molecular sieves, may play more significant roles in enhancing catalytic activities of TiO_2 systems. Catalytic activity of 4-chlorophenol photo-degradation, by TiO_2/Cr in the visible region, has been significantly enhanced by molecular sieve supports, and the molecular sieves seem to play a role in the sensitization process itself [50].

4. Conclusions

The catalytic activity of TiO_2 surface, in UV degradation of phenol and benzoic acid, may be enhanced by surface modification with dyes such as TPPHS. Further enhancement could be achieved by supporting the TiO_2/TPPHS onto AC. The enhanced activity of the modified TiO_2 surfaces in UV may be due to a charge-transfer enhancement mechanism, rather than sensitization formalism.

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References

[1] A. Bansal, J.A. Turner, Suppression of band edge migration at the *p*-$GaInP_2/H_2O$ interface under illumination via catalysis, J. Phys. Chem. B 104 (2000) 6591–6598.
[2] S.S. Kocha, J.A. Turner, Displacement of the bandedges of $GaInP_2$ in aqueous electrolytes induced by surface modification, J. Electrochem. Soc. 142 (1995) 2625–2630.
[3] S.S. Kocha, J.A. Turner, Impedance analysis of surface modified $Ga_{0.5}In_{0.5}P$—aqueous electrolyte interface, Electrochim. Acta. 41 (1996) 1295.
[4] H.S. Hilal, M. Masoud, S. Shakhshir, N. Jisrawi, Metalloporphyrin/polysiloxane modified *n*-GaAs surfaces: effect on photoelectrochemical efficiency and surface stability, J. Electroanal. Chem. 527 (2002) 47–55.
[5] H.S. Hilal, M. Masoud, S. Shakhshir, N. Jisrawi, *n*-GaAs band-edge repositioning by modification with metalloporphyrin/polysiloxane matrices, Active Passive Elec. Comp. 26 (2002) 11.
[6] H.S. Hilal, W.M. Ateereh, T. Al-Tel, R. Shubaitah, I. Saadeddin, G. Campet, Enhancement of *n*-GaAs characteristics by combined heating, cooling rate and metalloporphyrin modification techniques, Solid State Sci. 6 (2004) 139.
[7] H.S. Hilal, J.A. Turner, Controlling charge-transfer processes at semiconductor/liquid junctions, J. Electrochim. Acta. 51 (2006) 6487–6497.
[8] D. Chatterjee, A. Mahata, Photo-assisted detoxification of organic pollutants on the surface modified TiO_2 semiconductor particulate system, Catal. Commun. 2 (2001) 1–3.
[9] J. Matos, J. Laine, J. Herrmann, Synergy effect in the photocatalytic degradation of phenol on a suspended mixture titania and activated carbon, Appl. Catal. B: Environmen. 18 (1998) 281–291.
[10] D.D. Dionysion, A.P. Khodadoust, A.M. Kern, M.T. Suidan, I. Baudin, J.-M. Laine, Continuous-mode photocatalytic degradation of chlorinated phenols and pesticides in water using a bench-scale TiO_2 rotating disc reactor, Appl. Catal. B: Environmen. 24 (2000) 139.
[11] D. Vione, C. Minero, V. Maurino, M.E. Carlotti, T. Picatonotto, E. Pelizzetti, Degradation of phenol and benzoic acid in the presence of a TiO_2-based heterogeneous photocatalyst, Appl. Catal. B: Environmen. 58 (2005) 79–88.
[12] A. Ajmera, S. Pangarka, Beenakers, Solar-assisted photo-catalytic degradation of benzoic acid using TiO_2 as a photo-catalyst, Chem. Eng. Technol. 25 (2) (2002) 180–186.
[13] R. Single, M. Ashokkkurnar, F. Grieser, The mechanism of the sonochemical degradation of benzoic acid in aqueous solutions, Res. Chem. Intermed. 30 (2004) 723–734.
[14] V. Brezová, M. Čeppan, E. Brandšteterová, M. Breza, L. Lapčík, Photocatalytic hydroxylation of benzoic acid in aqueous titanium dioxide suspension, J. Photochem. Photobiol. A: Chem. 59 (1991) 385–391.
[15] R.W. Matthews, Purification of water with near-UV illuminated suspensions of titanium dioxide, Water Res. 24 (1990) 653–660.
[16] K. Mehrotra, G.S. Yablonsky, A.K. Ray, Macro kinetic studies for photocatalytic degradation of benzoic acid in immobilized systems, Chemosphere 60 (2005) 1427–1436.
[17] D. Ossi, A. Mokrini, E. Chamarro, S. Esplugas, Photo-degradation of benzoic acid in aqueous solutions, Environmen. Technol. 19 (1998) 955–960.
[18] C. Karapire, C. Zafer, S. İçli, Studies on photophysical and electrochemical properties of synthesized hydroxy perylenediimides in nanostructured titania thin films, Synth. Met. 145 (2004) 51–60.
[19] Md. K. Nazeeruddin, S.M. Zakeeruddin, J.-J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Graetzel, Stepwise assembly of amphiphilic ruthenium sensitizers and their applications in dye-sensitized solar cell, Coord. Chem. Rev. 248 (2004) 1317–1328.
[20] B. O'Regan, M. Grätzel, A low cost, high-senitized colloidal TiO_2 films, Nature 353 (1991) 737–740.
[21] Md. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, Conversion of light to electricity by cis-X2Bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthium(II) charge-transfer sensitizers ($X = Cl^-$, Br^-, I, CN, and SCN) on nanocrystalline TiO_2 electrodes, J. Am. Chem. Soc. 115 (1993) 6382–6390.
[22] G. Granados O., C.A. Páez M., F. Martínez O., E.A. Páez-Mozo, Photocatalytic degradation of phenol on TiO_2 and TiO_2/Pt sensitized with metallophthalocyanines, Catal. Today 107/108 (2005) 589.
[23] D. Chatterjee, S. Dasgupta, N.N. Rao, Visible light assisted photodegradation of halocarbons on the dye modified TiO_2 surface using visible light, Solar Energy Mater. Solar Cells 90 (2006) 1013–1020.
[24] T.L. Villarreal, P. Bogdanoff, P. Salvador, N.N. Alonso-Vante, Photocatalytic oxidation on nanostructured chalcogenide modified titanium dioxide, Solar Energy Mater. Solar Cells 83 (2004) 347–362.
[25] M.R. Iesce, M.L. Graziano, F. Cermola, S. Montella, L. di Gioa, C. Stasio, Effects of sensitizers on the photodegradation of the systemic fungicide triadimenol, Chemosphere 51 (2003) 163.
[26] C.H. Ao, S.C. Lee, Combination effect of activated carbon with TiO_2 for the photodegradation of binary pollutants at typical indoor air level, J. Photochem. Photobiol. A: Chem. 161 (2004) 131–140.
[27] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, Prog. Solid State Chem. 32 (2004) 33.
[28] J. Araña, J.M. Doña-Rodríguez, E.T. Rendón, C. Garriga i Cabo, O. González-Díaz, J.A. Herrera-Melián, J. Pérez-Peña, G. Colón, J.A. Navío, TiO_2 activation by using activated carbon as a support, Part I. Surface characterisation and decantability study, Appl. Catal. B: Environ. 44 (2003) 161–172.
[29] F. Ahnert, H. Arafat, N. Pinto, A study of the influence of hydrophobicity of activated carbon on the adsorption equilibrium of aromatics in non-aqueous media, Adsorption 9 (2003) 311–319.
[30] S. Glasstone, D. Lewis, Elements of Physical Chemistry, 2nd edition, The Macmillan Press Ltd., New Delhi, 1983 p. 566.
[31] D. Shoemaker, C. Garland, J. Nibler, Experiments in Physical Chemistry, 5th edition, Mc Graw-Hill, Inc., N.Y., 1989.
[32] For phenol analysis, see AOAC Official Method 979.13, copyright 1998, AOAC International.
[33] The Book of Photon Tools, Oriel Instruments, Stratford, CT, USA, pp. 44, 50 (Manual).
[34] Thermo Oriel: 500 W Xenon/Mercury (Xenon) ARC Lamp Power Supply Model 68911 (Manual).
[35] A. Sanjuàn, G. Aguirre, M. Alvaro, H. García, 2,4,6-Triphenylpyrylium ion encapsulated within *y*-zeolite as photocatalyst for the degradation of methyl parathion, Water Res. 34 (2000) 320–326.
[36] J.A. Byrne, B.R. Eggins, N.M.D. Brown, B. McKinney, M. Rouse, Immobilization of TiO_2 powder for the treatment of polluted water, Appl. Catal. B: Environ. 17 (1998) 25–36.
[37] H.M. Coleman, B.R. Eggins, J.A. Byrne, F.L. Palmer, E. King, Photocatalytic degradation of 17-β-oestradiol on immobilized TiO_2, Appl. Catal. B: Environ. 24 (2000) L1–L5.

[38] J.A. Byrne, B.R. Eggins, W. Byers, N.M.D. Brown, Photoelectrochemical cell for the combined photocatalytic oxidation of organic pollutants and the recovery of metals from waste waters, Appl. Cat. B: Environmen. 20 (1999) L85–L89.

[39] S. Zhang, N. Fujii, Y. Nosaka, The dispersion effect of TiO_2 loaded over ZSM-5 zeolite, J. Mol. Catal. 129 (1998) 219–224.

[40] K.-H. Wang, H.-H. Tsai, Y.-H. Hsieh, The kinetics of photocatalytic degradation of trichloroethylene in gas phase over TiO_2 supported on glass bead, Appl. Catal. B: Environ. 17 (1998) 313–320.

[41] Y. Wang, C.-S. Hong, TiO_2-mediated photomineralization of 2-chlorobiphenyl: the role of O_2, Water Res. 34 (2000) 2791–2797.

[42] G. Heit, A.M. Braun, VUV-photolysis of aqueous systems: spatial differentiation between volumes of primary and secondary reactions, Water Sci. Technol. 35 (4) (1997) 25–30.

[43] M.A. Fox, M.T. Dulay, Marye Anne Fox, Maria T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341–357.

[44] X. Zhao, X. Quan, H. Zhao, S. Chen, Y. Zhao, J. Chen, Different effects of humic substances on photodegradation of *p*,*p*-DDT, on soil surfaces, in the presence of TiO_2 under UV and visible light, J. Photochem. Photobiol. A: Chem. 167 (2004) 177–183.

[45] A.A. Nada, M.H. Barakat, H.A. Hamed, N.R. Mohamed, T.N. Veziroglu, Studies on the photocatalytic hydrogen production using suspended modified TiO_2 photocatalysts, Int. J. Hydrogen Energy 30 (2005) 687–691.

[46] F. Haque, E. Vaisman, C.H. Langford, A. Kantzas, Preparation and performance of integrated photocatalyst adsorbent (IPCA) employed to degrade model organic compounds in synthetic wastewater, J. Photochem. Photobiol. A: Chem. 169 (2005) 21–27.

[47] J. Araña, J.M. Doña-Rodríguez, C. Garriga i Cabo, O. González-Díaz, J.A. Herrera-Melián, J. Pérez-Peña, FTIR study of gas-phase alcohols photocatalytic degradation with TiO_2 and AC-TiO_2, Appl. Catal. B: Environ. 53 (2004) 221–232.

[48] A.H. El-Sheikh, A.P. Newman, H. Al-Daffaee, S. Phull, N. Cresswell, S. York, Deposition of anatase on the surface of activated carbon, Surf. Coat. Technol. 187 (2004) 284.

[49] J. Matos, J. Laine, J.-M. Herrmann, D. Uzcategui, J.L. Brito, Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photodegradation, Appl. Catal. B: Environ., in press.

[50] B. Sun, E.P. Reddy, P.G. Smirniotis, TiO_2-loaded Cr-modified molecular sieves for 4-chlorophenol photodegradation under visible light, J. Catal. 237 (2006) 314–321.