Enhanced photocatalytic degradation of π-donor organic compounds by N,N'-dialkyl-4,4'-bipyridinium-modified TiO2 particles

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Abstract

TiO2 powders (Degussa P-25) were modified by a bipyridinium V^{2+} monolayer. The resulting modified V^{2+}-TiO2 photocatalyst reveals enhanced activities for the light-induced degradation of the series of organic compounds, 1,4-dimethoxybenzene (1), 1,2-dimethoxybenzene (veratrole) (2), indole (3) and eosin (4), exhibiting electron donor properties. Photodegradation of p-chlorobenzaldehyde (5) which lacks electron donor properties is inhibited in the presence of the modified photocatalyst V^{2+}-TiO2, whereas it degrades in the presence of unmodified TiO2. The enhanced photodegradation of the series of electron-rich compounds is attributed to the formation of a supramolecular donor-acceptor complex with the bipyridinium units at the semiconductor surface. Concentration of the organic materials at the s.c. surface leads to effective utilization of photogenerated $O_2^{\cdot-}$ and effective mineralization.
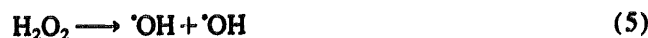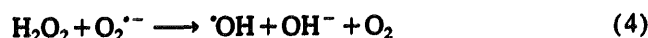
1. Introduction

Heterogeneous photocatalysis using semiconductors has attracted considerable interest during the last decade as a means for solar energy conversion and fuel generation, and particularly with respect to the degradation (mineralization) of organic and inorganic pollutants [1-5]. Among the various semiconductors studied, titanium dioxide (TiO2) has been extensively studied because of its non-toxicity and high stability under irradiation. Photocatalytic degradation of organic pollutants over TiO2 in the gas phase and solution was reported in several commercial applications [6-8]. Photoexcitation of semiconductors leads to the formation of electron-hole pairs. In the absence of suitable electron acceptors or hole scavengers, electron-hole recombination represents the energy dissipation route. For effective trapping of the photogenerated electron-hole the electron acceptor and electron donor should be confined to the semiconductor-air or semiconductor-solution interface. Various methods to control interfacial-electron transfer at the semiconductor-solution interface have been developed. These include the localization of electron acceptors at the semiconductor surface by electrostatic attraction [9], by association of the electron acceptor to receptor-modified semiconductors (i.e. cyclodextrin-modified TiO2) [10], by hydrophobic associ-

ation of organic materials to modified semiconductors [11] and by the adsorption of redox polymers on the semiconductor photocatalyst [12,13].

The photocatalytic degradation of organic materials in aqueous media by TiO2 particles, in the presence of oxygen, originates from the generation of superoxide and hydroxide radicals and their reaction products (Eqs. (1)–(5)):

$$O_2 + e_{cb}^- \longrightarrow O_2^{\cdot-} \tag{1}$$

$$H_2O + h^+ \longrightarrow OH^{\cdot} + H^+ \tag{2}$$

$$OH^{\cdot} + OH^{\cdot} \longrightarrow H_2O_2 \tag{3}$$

$$H_2O_2 + O_2^{\cdot-} \longrightarrow {}^{\cdot}OH + OH^- + O_2 \tag{4}$$

$$H_2O_2 \longrightarrow {}^{\cdot}OH + {}^{\cdot}OH \tag{5}$$

A variety of organic materials such as trichloroethylene [14], halogenated alkanes [15] and herbicides [16] were photochemically degraded or mineralized by TiO2. For effective degradation of organic pollutants, it is essential to utilize the photogenerated ·OH reactive intermediate effectively. Dimerization of this intermediate and subsequent reaction of the formed H2O2 with conduction band electrons adversely affect the photocatalytic degradation of organic pollutants. Thus, concentration or pre-adsorption of the pollutant at the semiconductor surface would enhance its photocatalytic degradation by efficient trapping of the reactive radical species.

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Donor–acceptor complexes between dialkoxybenzene, indole or xanthene dyes and N,N'-bipyridinium salts have been examined [17,18]. In this regard, cyclic bipyridinium salts and dialkoxybenzene cyclophanes were documented as potential building blocks for the self-assembly of catenanes and rotaxanes [19,20].

Here we wish to report the use of N,N'-dialkyl-4,4'-bipyridinium-modified TiO_2 as an improved photocatalyst for the light-induced degradation of organic compounds exhibiting electron donor properties. We demonstrate that the enhanced photocatalytic properties of the modified TiO_2 correlate with the effectiveness of adsorption of the organic substrate onto the modified TiO_2 surface by donor–acceptor interactions.

2. Experimental section

2.1. Modification of TiO_2 powders by N,N'-bipyridinium salts

0.5 g of TiO_2 (Degussa P-25) were refluxed in a dinitrogen atmosphere for 12 h in a 1% (v/v) solution of 3-bromopropyl trimethoxysilane in methanol [21]. The resulting powder was filtered and washed with methanol. The powder was further reacted by refluxing it in an acetonitrile solution of 0.2 g of N-methylpyridinium-4-pyridine, for 72 h under dinitrogen. The resulting powder was washed with acetonitrile and dried. Covalent attachment of the bipyridinium electron acceptor to the TiO_2 particles was confirmed by treatment of an aqueous suspension of the modified TiO_2 with $Na_2S_2O_4$ under nitrogen. The powder turned blue, characteristic of the bipyridinium radical cation.

Photochemical degradation of organic substrates was performed in a quartz cuvette which contained a solution of the respective substrate having concentrations $1.5 \times 10^{-5} - 8 \times 10^{-4}$ M, and 2.0–2.2 mg of the modified TiO_2. The suspension was irradiated by a 150 W Xe lamp (Oriel). Aliquots of the irradiated samples were collected at time intervals during the illumination. The samples were diluted with water, centrifuged and analyzed spectroscopically (Uvikon-860, Kontron spectrophotometer), for the organic content substrate. The light absorbed by the bare TiO_2 particles or modified TiO_2 powder was determined by placing a radiometer at the back side of the cuvette which contains the organic substrate solution alone or the same solution containing a similar amount of untreated TiO_2 respectively. The difference between the two recorded values was assumed to correspond to the absorbed light intensity. Since light scattering by the particles is neglected, the absorbed light intensities could be considered as upper limits.

Adsorption of the organic substrate onto TiO_2 was examined by stirring 4.0–5.0 mg of the catalyst in 5 ml of appropriate concentrations of the substrates in dark. After equilibration for 1 h, the catalyst was filtered and the concentration of the organic substrate was determined spectroscopically.
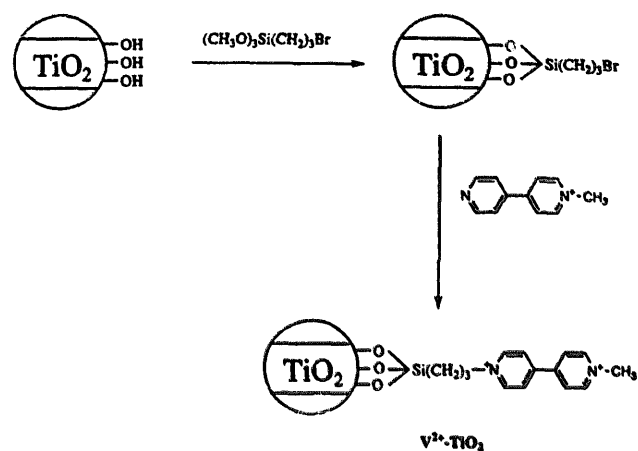
Scheme 1. Derivitazation of the TiO_2 powder by a bipyridinium monolayer.

3. Results and discussion

Modification of the TiO_2 powder was accomplished as outlined in Scheme 1. The surface hydroxyl groups associated with TiO_2 were silanated by 3-bromopropyl trimethoxysilane followed by reaction of the silanized powder with N-methylpyridinium-4-pyridine. The bipyridinium-modified TiO_2 powder could enhance the degradation of organic substrates by two different routes:

(a) Surface modification of the semiconductor by the bipyridinium salt could provide efficient traps for conduction band electrons. The resulting bipyridinium radical cation, reacting rapidly with molecular oxygen, could then effectively generate $O_2^{\bullet-}$, an active species in the mineralization of the organic material.

(b) The modified surface could act as an active interface for incorporation of electron-rich organic compounds via donor–acceptor interactions. Formation of such supramolecular complexes between the organic substrate and the modified surface is expected to concentrate the photodegradable organic material at the semiconductor surface and facilitates its mineralization.

In order to elucidate the photocatalytic properties of the bipyridinium-modified TiO_2, we studied the photocatalytic degradation of a series of electron donor substrates: 1,4-dimethoxybenzene (1), 1,2-dimethoxybenzene (veratrole) (2), indole (3) and eosin (4), in the presence of the modified TiO_2 and unmodified TiO_2. The photodegradation rates were correlated with the adsorption properties of the different organic substrates on the modified and unmodified TiO_2. We also examined the photodegradation of p-chlorobenzaldehyde (5), in the presence of the modified and unmodified TiO_2. The latter substrate does not exhibit electron donor properties and thus its rate of degradation by the two photocatalysts could reveal the importance of supramolecular complex formation at modified semiconductor interfaces in enhancing photocatalyzed degradation of certain classes of organic materials. Photodegradation of alkoxybenzene derivatives has some important practical implications. Tetrachlo-
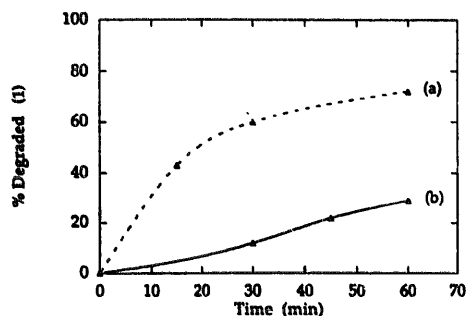
Fig. 1. Degradation of 1,4-dimethoxybenzene (8×10^{-4} M) over photocatalyst (2.1 mg) (curve (a), V^{2+}-TiO_2; curve (b), Degussa P-25) at various time intervals of irradiation. Curves are corrected for the light absorbed by the respective photocatalysts.
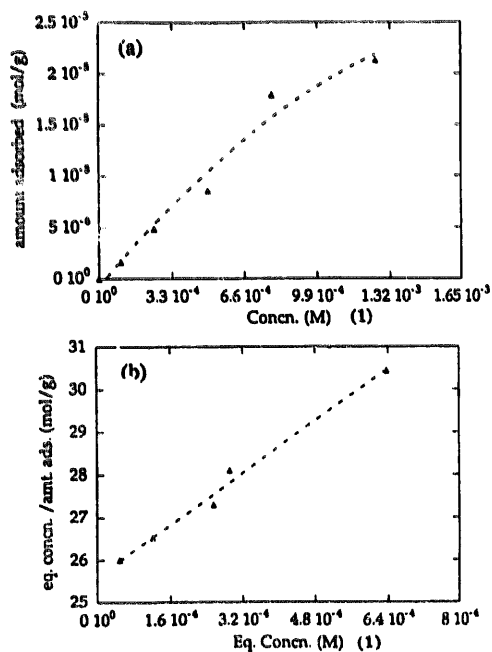

Fig. 2. (a) Adsorption isotherm for 1,4-dimethoxybenzene over V^{2+}-TiO_2 catalyst. (b) Langmuir analysis for the adsorption isotherm of 1,4-dimethoxybenzene on V^{2+}-TiO_2.

rodioxin is one of the most hazardous compounds and its polluting hazard of water reservoirs and ground water is of special concern [22,23]. Photochemical degradation of dialkoxybenzene derivatives could provide a model system for the light-induced degradation of aromatic ether substances and specifically dioxin derivatives.

The photocatalytic degradation of 1,4-dimethoxybenzene (1) was examined in the presence of bare unmodified TiO_2 and the bipyridinium-modified TiO_2, V^{2+}-TiO_2. Fig. 1 shows the rate of degradation of 1 as a function of irradiation time. It is evident that the rate of degradation of 1,4-dimethoxybenzene is about 2.5-fold higher in the presence of V^{2+}-TiO_2. After irradiation for 1 h, about 72% of 1 is degraded by V^{2+}-TiO_2, whereas only 29% of 1 is degraded by the unmodified TiO_2 photocatalyst.

To account for the enhanced photocatalytic activity of V^{2+}-TiO_2, the adsorption of 1 onto the modified and unmodified photocatalyst was examined. Fig. 2(a) shows the

adsorption isotherm of 1,4-dimethoxybenzene onto the modified photocatalyst, V^{2+}-TiO_2. The amount of adsorbed 1 increases as the bulk concentration of the organic substrate increases and it levels off at a bulk concentration of 1 that corresponds to about 1×10^{-5} M. The adsorption isotherm can be analyzed in terms of the Langmuir [24] theory (Fig. 2(b)). A linear relationship between $[S]_{eq}/S_{ads}$ as a function of $[S]_{eq}$ is observed, where $[S]_{eq}$ is the equilibrium bulk concentration of 1,4-dimethoxybenzene and S_{ads} is the amount (in moles) of 1 adsorbed onto the photocatalyst. From the slope, the derived adsorption constant corresponds to $K = 1.3 \times 10^{-4}$ M^{-1}. Fig. 3(a) shows the adsorption isotherm of 1 onto unmodified TiO_2 and Fig. 3(b) shows the analysis of the adsorption isotherm in terms of the Langmuir theory. The adsorption constant of 1 onto unmodified TiO_2 was found to be $K = 5.7 \times 10^{-5}$ M^{-1}. The enhanced adsorption of 1 onto the modified photocatalyst V^{2+}-TiO_2 can be attributed to the formation of a supramolecular donor–acceptor complex between 1,4-dimethoxybenzene and the N,N'-bipyridinium units as schematically outlined in Scheme 2. The concentration of the organic substrate at the semiconductor surface could then explain its enhanced photodegradation.

In order to extend the generality of the principle to enhance photodegradation of electron-rich organic substrates by the acceptor-modified TiO_2, we examined the photocatalytic degradation of two additional electron donors, 1,2-dimethoxybenzene (2) and indole (3). The photodegradation of these two organic substrates was similarly examined in the presence of V^{2+}-TiO_2 and unmodified TiO_2 and the results were correlated with the adsorption features of the organic substrates to the respective photocatalysts. Table 1
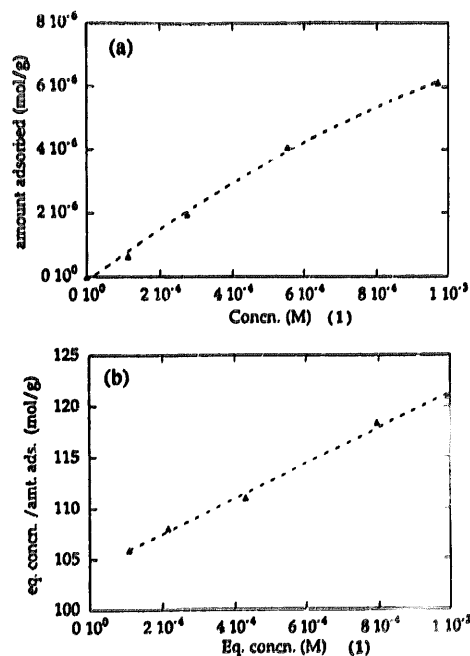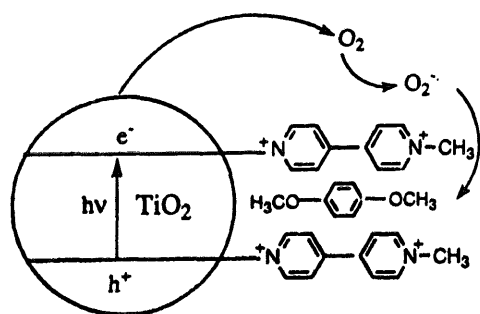

Fig. 3. (a) Adsorption isotherm for 1,4-dimethoxybenzene over Degussa P-25 catalyst. (b) Langmuir analysis for the adsorption isotherm of 1,4-dimethoxybenzene on Degussa P-25 catalyst.

Scheme 2. Schematic presentation of the supramolecular donor–acceptor complex between 1,4-dimethoxybenzene and N,N'-bipyridinium units, leading to enhanced photodegradation.

Fig. 4. Adsorption isotherm for p-chlorobenzaldehyde over the catalysts Degussa P-25 (curve (a)) and V^{2+}-TiO$_2$ (curve (b)).

summarizes the adsorption constants of the various substrates to the two photocatalysts and the yields of substrate degradation after irradiation for 1 h. The photocatalytic degradation of the two compounds 2 and 3 is similarly enhanced in the presence of V^{2+}-TiO$_2$. For example, indole 3 is degraded about two-fold more rapidly than the unmodified TiO$_2$ photocatalyst. The enhanced photodegradation of the organic substrates correlates nicely with the increased association constants of the two electron donors to the acceptor-modified photocatalyst, V^{2+}-TiO$_2$. It is interesting to note the difference in the photodegradation rates of 1,4-dimethoxybenzene and 1,2-dimethoxybenzene (2) in the presence of V^{2+}-TiO$_2$. While about 72% of 1 is photodegraded after irradiation for 1 h with V^{2+}-TiO$_2$, only 25% of 2 is decomposed upon illumination under similar conditions. This is consistent with the fact that 2 exhibits a substantially lower adsorption constant ($K = 2.0 \times 10^{-6}$ M^{-1}) than the adsorption constant of 1 to V^{2+}-TiO$_2$ ($K = 1.3 \times 10^{-4}$ M^{-1}).

In order to confirm that enhanced adsorption of the electron donor substrates onto the modified V^{2+}-TiO$_2$ photocatalyst leads to faster photodegradation, the photocatalytic mineralization of p-chlorobenzaldehyde (5) was examined under similar conditions. The latter compound lacks electron donor properties and thus formation of a surface supramolecular complex with the bipyridinium sites is prevented. Fig. 4 shows the adsorption isotherm of 5 onto the modified V^{2+}-TiO$_2$ (curve (a)) and unmodified TiO$_2$ (curve (b)). Supe-
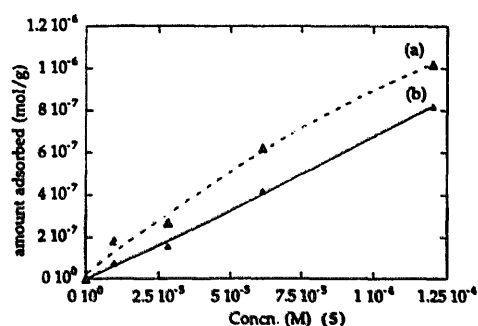
rior adsorption of p-chlorobenzaldehyde onto the bare TiO$_2$ is observed. By analysis of the two adsorption isotherms, the adsorption constants of p-chlorobenzaldehyde onto the bare TiO$_2$ and V^{2+}-TiO$_2$ were derived: $K = 1.4 \times 10^{-6}$ M^{-1} and $K = 2.3 \times 10^{-6}$ M^{-1} respectively. Thus, the adsorption properties of 5 onto the modified semiconductor V^{2+}-TiO$_2$ and bare photocatalyst are reversed compared with the adsorption of 1–3 onto the respective photocatalysts. That is 5 exhibits improved association to bare unmodified TiO$_2$ (Table 1). These results clearly indicate that surface modification of TiO$_2$ by the bipyridinium salt does not improve the adsorption of the aromatic substrate by π–π or hydrophobic interactions. Thus the improved adsorption of 1–3 originates from the formation of donor–acceptor complexes of the surface of the photocatalyst. The superior adsorption of p-chlorobenzaldehyde onto the bare TiO$_2$ photocatalyst is reflected in the effectiveness of photodegradation. Upon irradiation of 5 for a period of 1 h, 42% of 5 is degraded by bare TiO$_2$, whereas only 14% is decomposed by the V^{2+}-TiO$_2$. Furthermore, the control experiments employing p-chlorobenzaldehyde suggest that the enhanced degradation of the respective substrates by the V^{2+}-TiO$_2$ photocatalyst is controlled by adsorption features of the organic materials on the modified semiconductor rather than from the effective trapping of conduction band electrons by the bipyridinium electron acceptor layer that could efficiently generate O$_2^-$. If the latter mechanism operates, one would expect to observe also enhanced photodegradation of 5 with V^{2+}-TiO$_2$.

Table 1
Adsorption constants and photodegradation yields of 1–5 in the presence of modified and non-modified TiO$_2$ photocatalysts

| Substrate	Catalyst	Adsorption constant K_{ads} (M^{-1})	Amount degraded (%)
1,4-Dimethoxybenzene (1)	Modified	1.3×10^{-4}	72
1,4-Dimethoxybenzene (1)	Degussa P-25	5.7×10^{-5}	29
1,2-Dimethoxybenzene (2)	Modified	2.0×10^{-6}	25
1,2-Dimethoxybenzene (2)	Degussa P-25	6.6×10^{-7}	12
Indole (3)	Modified	5.0×10^{-6}	53
Indole (3)	Degussa P-25	2.1×10^{-6}	25
Eosin (4)	Modified	4.2×10^{-8}	67
Eosin (4)	Degussa P-25	2.4×10^{-9}	23
p-Chlorobenzaldehyde (5)	Modified	1.4×10^{-6}	14
p-Chlorobenzaldehyde (5)	Degussa P-25	2.3×10^{-6}	42
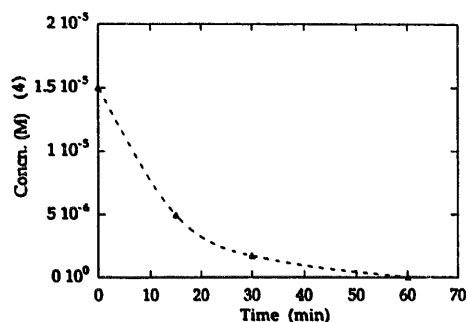
Fig. 5. Photodegradation of eosin (1.5×10^{-5} M) over V^{2+}–TiO_2 (2.1 mg) at various time intervals of irradiation.

Xanthene dyes, i.e. eosin, form tight donor–acceptor complexes with N,N'-bipyridinium salts [18,25]. Thus the concentration of eosin at the photocatalyst surface could enhance its photochemical degradation. Examination of the photodegradation of eosin by the bipyridinium-modified TiO_2, V^{2+}–TiO_2, is of further interest since xanthene dyes are capable, upon excitation, of injecting electrons into the semiconductor conduction band. As a result, the radical intermediates could be formed by two complementary pathways that include the direct excitation of the semiconductor and the injection of electrons to the semiconductor by excitation of the dye. The formation of donor–acceptor complexes between the eosin chromophore and the bipyridinium electron acceptor is expected to concentrate the dye at the semiconductor surface. However, the formation of this supramolecular complex could adversely affect the photophysical properties of the dye and its charge injection properties, to the semiconductor. Efficient intracomplex quenching of excited singlet eosin is observed in the eosin–bipyridinium assemblies [26], and thus electron injection to the semiconductor by excitation of the chromophore would be inefficient.

The adsorption properties of eosin (4) to TiO_2 and V^{2+}–TiO_2 photocatalysts were examined. By analysis of the respective adsorption isotherms, we estimated that the adsorption constants of eosin to TiO_2 and V^{2+}–TiO_2 correspond to $K = 2.4 \times 10^{-9}$ M^{-1} and $K = 4.2 \times 10^{-8}$ M^{-1} respectively. Thus the adsorption of eosin to the modified photocatalyst V^{2+}–TiO_2 is substantially higher. This is attributed to the formation of supramolecular donor–acceptor complexes between eosin and the bipyridinium units at the semiconductor surface. Fig. 5 shows the rate of degradation of eosin upon irradiation of the dye in the presence of V^{2+}–TiO_2.

These results indicate that the decomposition of the dye is controlled by its adsorption properties to the photocatalyst surface and that the charge injection mechanism by direct excitation of the dye is not operative in the photodecomposition of eosin.

To conclude, we describe a novel method to enhance the photodegradation activities of semiconductor photocatalyst towards the class of electron donor organic substrates by surface modification of the photocatalyst with N,N'-bipyri-

dinium electron acceptor sites. Formation of supramolecular complexes between the electron donor substrates and the bipyridinium units concentrates the substrates at the photocatalyst surface. This results in the enhanced photochemical degradation of these compounds.

Acknowledgments

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