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Photocatalytic performance of a visible light TiO_2 photocatalyst prepared by a surface chemical modification process

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ABSTRACT

A visible light TiO_2 photocatalyst was prepared by a surface chemical modification process with toluene 2,4-diisocyanate (TDI). Because of the LMCT excition of the surface complex, the as-prepared TiO_2-TDI has an obvious absorption in visible region. TiO_2-TDI photocatalyst presented a satisfactory photostability and a high photocatalytic performance for the degradation of organics. The turnover number of the photocatalyst for 2,4-dichlorophenol photodegradation reached 15.43 after five times recycled under visible light irradiation.

1. Introduction

How to improve the photocatalytic activity of TiO_2 in the visible region is the main focus of the recent TiO_2 photocatalysis research. Many efforts have been made to achieve the utilization of visible light for TiO_2 material, such as transitional metal ion doping [1–3], nonmetal element doping [4,5] and dye sensitization [6,7]. Nonmetal element doping such as N-doping narrows the band gap of TiO_2 by supplying a new hybrid energy band whose energy level is a little higher than that of the valence band of TiO_2 [4,8]. The doping process of the nonmental elements always involves thermal treatment at high temperatures [9,10] or a long time of hydrothermal treatment [8], both of which are unfavorable in energy. Visible light-induced dye-sensitized TiO_2 photocatalysts can be readily prepared under a mild condition through interfacial adsorption of dye molecules on TiO_2 in an ambient environment [6,11]. Dye-sensitized photocatalysis begins with the light absorption of dye and a subsequent electron transfer from the excited dye to the conduction band of TiO_2. However, the electron transfer from excited dye to TiO_2 usually depends strongly on the adsorption efficiency of dye molecules [12]; and it can be deeply depressed by the competitive adsorption of other coexisting species in the solution. Considering that pollutants usually exist at high concentration in the practical wastewaters, dye-sensitized photocatalysis may face difficulties of keeping a valuable electron transfer efficiency.

Recently, several works found that some colorless species can also be photodegraded with TiO_2 under visible irradiation [13–15]. TiO_2 surface complexes which can absorb visible light were observed in those works. The surface complexes were formed by a reversible interfacial chemical adsorption of organics. A visible light-induced charge transfer and a subsequent dissociation of the surface complexes from TiO_2 were supposed for the visible degradation of the organics [13]. Two types of sensitization have been reported in the TiO_2 photocatalysis. One involves the indirect electron injection, which is dominant in dye-sensitized TiO_2 photocatalysis [16] and of multi-exponential kinetics with fast components of tens of fs (from singlet excited state of dye to TiO_2) and slow components of several ps (from triplet excited state of dye to TiO_2) [17,18]. The second occurs through a direct electron injection from the organics to TiO_2 [19,20]. Such a direct injection mechanism gives rise to a new LMCT absorption band for the surface complexes, whereas no new absorption appears in the indirect mechanism. Since the LMCT process of the direct injection mechanism takes place in a time range of the photon absorption (<1.0 fs) [20,21], it is of high efficiency and occurs very rapidly.

In this work, a surface chemical reaction between the TiO_2 and organics was designed to build a solid connection between them. Thus, the surface complexes that employed to absorb the visible light would not be desorbed/dissociated by other coexisting species. Further attempts were also done to diagnose if TiO_2 that surface modified with colorless organics can be used to achieve the photocatalytic degradation of coexisting organics under visible light irradiation.

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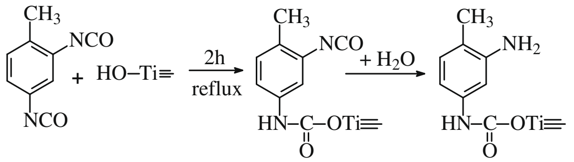
2. Experimental

2.1. Surface modification of TiO_2 with toluene 2,4-diisocyanate (TDI)

TDI (AR, 0.3 mL) was firstly mixed with pre-dried toluene (200 mL) under magnetic stirring. Then the TiO_2 powder (P-25, 0.5 g, pre-dried at 120 °C for 1 h) was slowly introduced into the solution under violent stirring. The suspension was heated under reflux for about 2 h, cooled down to the room temperature, and filtered. The obtained powder was washed with toluene several times to remove the unreacted TDI, treated with water, and dried in an oven at 120 °C for 2 h. The finally obtained salmon powder was thus TDI modified TiO_2 photocatalyst (labeled as TiO_2-TDI).

The isocyanate group of TDI generally reacts quickly with compounds containing active hydrogen groups. Combining TDI with TiO_2 powder carried out a chemical reaction of the isocyanate group of TDI with the surface hydroxyl group of TiO_2 (Eq. (1)). Thus, a TiO_2 surface-bonded organic complex (*N*-(3-amino-4-methyl)phenylcarbamate group) was formed through a condensation reaction.



(1)

2.2. Characterization of photocatalyst

UV–vis diffuse reflectance spectra (DRS) were obtained for the dry-pressed disk samples using a Scan UV–vis–NIR spectrophotometer (Varian Cary 500) equipped with an integrating sphere assembly, using $BaSO_4$ as reflectance sample. The content of surface chemical-bonded TDI of TiO_2-TDI sample was determined with the total organic carbon (TOC) analysis via an Apollo 9000 TOC analyzer (Techcomp). The photocatalyst samples used for TOC analysis were pre-dried at 120 °C for 1 h. The FTIR spectra of photocatalysts were recorded with a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique.

2.3. Photocatalytic experiment

Photocatalytic experiment was carried out by adding 0.1 g photocatalyst into a 160 mL glass tube reactor containing 100 mL target pollutant solution. Prior to irradiation, the suspension was magnetically stirred in the dark for 1 h to ensure the establishment of an adsorption–desorption equilibrium of organics pollutant on the surface of photocatalyst. All the photocatalytic reactions were carried out under visible irradiation ($\lambda > 420$ nm, 1000 W iodine-tungsten lamp with a glass filter). At given intervals of illumination, reaction solution (about 4.0 mL) was sampled and filtered through a Millipore membrane filter (0.22 μm pores) and analyzed with a UV–vis spectrophotometer (Varian Cary 100) to determine the residue concentration of target pollutant.

3. Results and discussion

FT-IR spectrum of TiO_2-TDI powder shows some new absorption peaks at 1652, 1600, 1538, 1448 and 1225 cm^{-1}, respectively. It confirmed a new amido group was formed in TiO_2-TDI powder by TDI surface chemical modification. The peaks of 1652 and 1225 cm^{-1} are the characteristic absorption of –C(O)NH– group, while the other three peaks are attributed to the phenyl group. Characteristic absorption of isocyanate group (–NCO) at 2220 cm^{-1} was not observed in the FT-IR spectrum of TiO_2-TDI, which means the isocyanate groups of TDI molecule entirely reacted.

The UV–vis DRS spectra of TiO_2, TiO_2-TDI and the UV–vis absorption spectrum of TDI are shown in Fig. 1. TDI is a colorless liquid and has a maximum absorption at 295 nm. TiO_2 itself has an upper absorption edge at about 400 nm. Both TiO_2 and TDI have no absorption in the visible region. The absorption of TiO_2-TDI is greatly extended to the visible region, with two peaks at 469 and 597 nm. The two new absorption peaks should be attributed to the LMCT absorptions of the surface complex of TiO_2-TDI. Since the intrinsic excitations of both TiO_2 and *N*-phenylcarbamate group can only be achieved with UV photons, the visible absorptions of TiO_2-TDI are proposed as direct surface electron transfers from lone pair electrons of N atom (597 nm) and O atom (469 nm) to the conduction band of TiO_2 (Scheme 1).

Conduction band electron generated from the LMCT excitation of TiO_2-TDI tends to react with the surface adsorbed oxygen to produce superoxide radical anion, hydrogen peroxide, and then hydroxyl radical. Thus, it is reasonable that a visible light-induced photocatalytic reaction can be achieved by TiO_2-TDI. Previous literature also shows that the TiO_2 surface-complexed phenol can be photoexcited under the visible irradiation [13].

Fig. 2 presents the photodegradation of 2,4-dichlorophenol (DCP) aqueous solution by TiO_2 and TiO_2-TDI under visible irradiation. DCP itself does not absorb visible light. The concentration of DCP remained almost constant throughout the irradiation period. The surface chemical interaction of DCP with TiO_2 can induce a new weak absorption in visible region [13,14]; therefore, DCP was

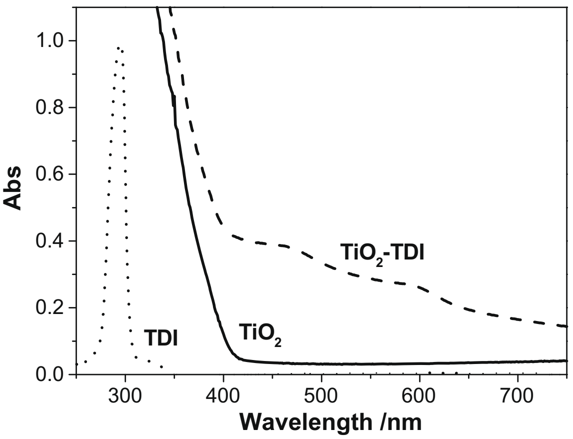
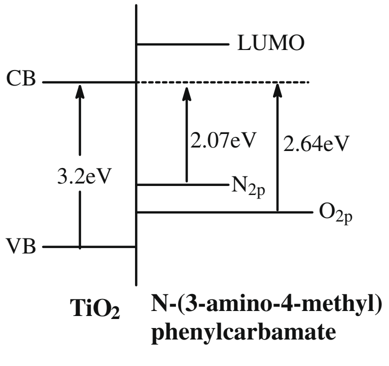


Fig. 1. UV–vis DRS spectra of TiO_2, TiO_2-TDI and UV–vis absorption spectrum of TDI.



Scheme 1. Proposed LMCT excitation of TiO_2-TDI under visible irradiation.

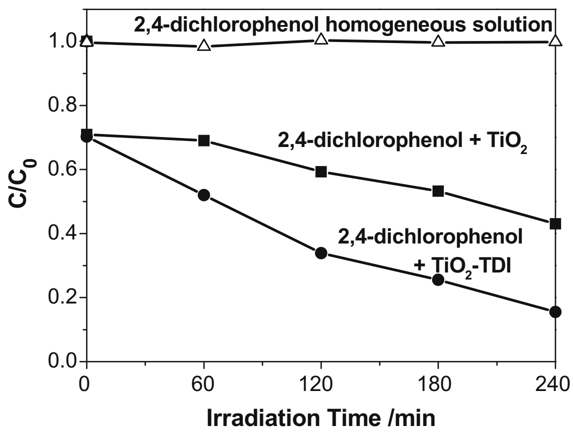


Fig. 2. Photodegradation of DCP under various conditions. [DCP] = 100 mg/L, λ > 420 nm, pH 7.0.

photodegraded to some extent in the presence of TiO_2 under the visible irradiation. Although the adsorption amount of DCP on the surface of TiO_2-TDI was almost equal to that on the surface of TiO_2, the photodegradation of DCP in the presence of TiO_2-TDI was much faster than that in the presence of bare TiO_2. About 77.9% of the DCP was photodecomposed by TiO_2-TDI while that by bare TiO_2 was only 39.3% for 240 min visible irradiation. It seems the visible light photocatalytic activity of the photocatalyst is effectively enhanced by the LMCT excitation of TiO_2-TDI.

The photocatalytic performance of TiO_2-TDI was also measured in terms of the degradation of methyl orange, fluorescein and phenol (Fig. 3). TiO_2-TDI again exhibits much higher visible light photocatalytic activities than TiO_2. Methyl orange is quite resistible to photocatalytic degradation at the neutral pH value [22,23]. As a result, methyl orange was photodegraded very little (only ca. 3%) by TiO_2 at pH 7.0. Meanwhile, 34% of the methyl orange was decomposed by TiO_2-TDI at the same pH value for 240 min visible irradiation.

The photodegradation of methyl orange and fluorescein by bare TiO_2 under visible irradiation is generally attributed to the dye-sensitized photocatalysis, of which the electron transfer from the excited dye to the conduction band of TiO_2 is regarded as the key step [24,25]. It should be taken into consideration that the direct LCMT process of TiO_2-TDI photocatalyst proceeds much faster than the indirect electron transfer process between the excited dye and TiO_2. Therefore, TiO_2-TDI has high visible light photocatalytic activities for the degradation of phenol, DCP, and the dyes, which means that TiO_2-TDI is a preferable visible light photocatalyst.

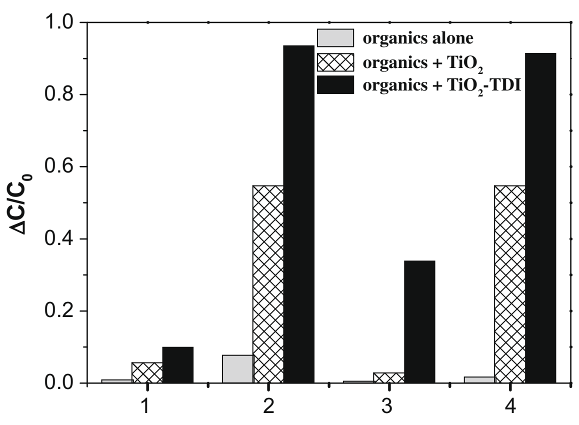


Fig. 3. Photodegradation of (1) phenol ([phenol] = 23 mg/L, pH 7.0), (2) fluorescein ([fluorescein] = 10 mg/L, pH 7.0), (3) ([methyl orange] = 10 mg/L, pH 7.0) and (4) methyl orange ([methyl orange] = 10 mg/L, pH 4.0) under various conditions for 240 min visible irradiation (λ > 420 nm).

The photostable property of the TiO_2-TDI was also under consideration. Fig. 4 exhibits the FTIR spectra of TiO_2-TDI photocatalyst before and after photocatalytic degrading organics. It can be seen that the characteristic absorptions of –C(O)NH– group at 1652 and 1225 cm^{-1} and of phenyl group at 1600, 1538 and 1448 cm^{-1} has no obviously change throughout the whole photodegradation process of organics. A TOC measurement was also carried out to check the photostability of TiO_2-TDI. TiO_2-TDI in 2% ethanol aqueous solution (250 mg/100 mL) was irradiated under the visible light. TOC measurement showed that ca. 2.5% of the initial TOC value of TiO_2-TDI was degraded for 120 h irradiation. It is suggested that TiO_2-TDI has desirable photostability as a photocatalyst.

Some colorless compounds such as H_2O_2 [25], phenol, chlorophenol, and Triton X-100 [14] can chemical adsorbed on the surface of TiO_2 to form colored surface-complexes. Under the visible light irradiation, the colored surface-complexes would be excited, which induces the photo-decomposition of the surface complexes [13,14,26]. In the case of TiO_2-TDI, a direct electron transfer from the organic ligand moiety to the conduction band of TiO_2 is achieved upon the absorption of visible light. The conduction band electron then reacts with surface adsorbed oxygen to produce superoxide radical, which subsequently induces the degradation of coexisting organics in the solution (Scheme 2).

Different from the previous studies, the organic ligand moiety, however, was not cleaved from the surface of TiO_2. It was subsequently recovered by capturing an electron from the environment (e.g. the reductive species generated during the photodegradation of organics), and then carried out another reaction cycle with the

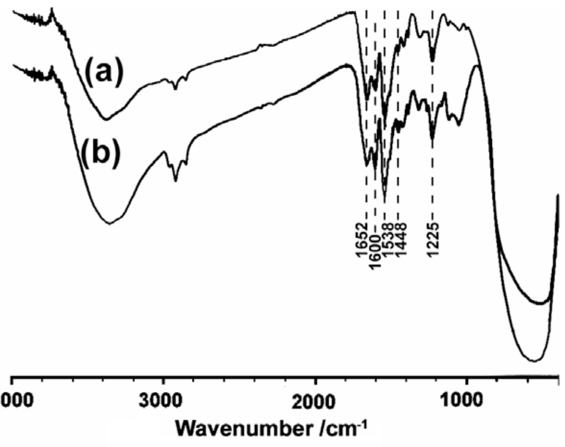
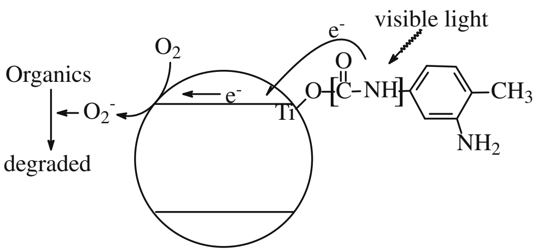


Fig. 4. FTIR spectra of TiO_2-TDI photocatalyst (a) before use, and (b) after photocatalytic degrading DCP for 240 min.



Scheme 2. Proposed visible light-induced photocatalytic mechanism of TiO_2-TDI photocatalyst.

absorption of another visible light photon. TOC measurement of TiO_2-TDI photocatalyst gave a carbon element content of 1.55 wt%, which means amount of the surface chromophores of TiO_2-TDI photocatalyst is 1.44×10^{-4} mol/g. The amount of the bonded hydroxyl groups on the surface of P-25 TiO_2 is about 9.5×10^{19}/g (equals 1.58×10^{-4} mol/g) as previously reported [27]. Thus, ca. 91.0% of the surface hydroxyl group was reacted with TDI to produce TiO_2-TDI chromophore. As a result, if we regard the target organic molecule as a catalysant, the turnover number of TiO_2-TDI photocatalyst in the photocatalytic degradation reaction of DCP was 3.32 in 240 min and reached 15.43 after 5 times recycled (data not shown). Thus, the whole visible light-induced photocatalytic process of TiO_2-TDI can be expressed briefly as follows:

$$\mathrm{TiO_2\text{-}TDI} + h\nu(\mathrm{vis}) \rightarrow [\mathrm{TiO_2(e)\text{-}TDI^+}]^* \qquad (2)$$

$$[\mathrm{TiO_2(e)\text{-}TDI^+}]^* + \mathrm{O_2} \rightarrow [\mathrm{TiO_2\text{-}TDI^+}] + \mathrm{O_2^{\cdot -}} \qquad (3)$$

$$\mathrm{O_2^{\cdot -}} + \mathrm{Organics} \rightarrow\rightarrow \mathrm{degradation\ products} \qquad (4)$$

$$[\mathrm{TiO_2\text{-}TDI^+}] + \mathrm{M(environment)} \rightarrow \mathrm{TiO_2\text{-}TDI} + \mathrm{M^+} \qquad (5)$$

4. Conclusions

A visible light TiO_2 photocatalyst was prepared by a surface chemical modification process with toluene 2,4-diisocyanate. The as-prepared TiO_2-TDI photocatalyst has an obviously absorption in visible region, which is proposed as the direct surface electron transfers from the lone pair electrons of N atom (597 nm) and O atom (469 nm) to the conduction band of TiO_2. TiO_2-TDI photocatalyst exhibited a satisfactory photostability and high photocatalytic performance for the degradation of phenol, 2,4-dichlorophenol, fluorescein and methyl orange. The turnover number of the photocatalyst for 2,4-dichlorophenol photodegradation can reach 15.43 after five times recycled under visible light irradiation.

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