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# Synthesis of visible light-activated $TiO_2$ photocatalyst via surface organic modification

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## Abstract

A visible light-activated $TiO_2$ photocatalyst was successfully synthesized by the surface organic modification to sol–gel–hydrothermal synthesized $TiO_2$. The surface hydroxyls of $TiO_2$ nanoparticles reacted with the active –NCO groups of tolylene diisocyanate (TDI) to form a surface complex that was confirmed by the FT–IR and XPS spectra. Due to the existence of surface complex, the absorption edge of as-prepared TDI-modified $TiO_2$ nanomaterial extended well into visible region. Compared with unmodified $TiO_2$ and Degussa P25, the TDI-modified $TiO_2$ photocatalysts showed higher activity for the photocatalytic degradation of methylene blue under visible light irradiation.
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*Keywords:* Surface organic modification; Photocatalytic degradation; Visible light irradiation

## 1. Introduction

For a long time, nanocrystalline $TiO_2$ has attracted much research attention because of its numerous advantages as a highly effective UV-activated photocatalyst. $TiO_2$ could become a very promising material for photocatalytic treatment of water pollutants. However, the relatively wide bandgap (about $3.2\,eV$ for anatase $TiO_2$) hampered its further application. Therefore, more and more recent efforts have been focused on the modified $TiO_2$ materials that can absorb visible light (400–700 nm in wavelength). In earlier investigations, the lattice Ti ions were substituted with various kinds of transition-metal ions such as V, Mn, Cr, Au and Pt ions [1–6] and, in a few cases, the resultant materials were active under visible light irradiation. Later it was also found that doping or modifying $TiO_2$ with nonmetals such as C, N, S, F and B [7–14] could endow it photocatalytic activity under

visible light. Especially, nitrogen-doped $TiO_2$ material has received much attention since the report of Asahi et al. [8] Unfortunately, those metal/nonmetal-doped $TiO_2$ materials were generally somewhat difficult to be prepared with the needs of lattice exchange at high temperature and multistep experimental process. Moreover, much interest has also been shown in surface modification of $TiO_2$ with organic dyes for construction of dye-sensitized photocatalytic systems under visible-light irradiation [15,16]. However, in the case of the dye-sensitized $TiO_2$ photocatalyst, the dye molecules are only absorbed in the $TiO_2$ surface by physical/chemical adsorption. No steady chemical bond is formed between $TiO_2$ and dye molecules. So the dye molecules as a sensitizer tend to partially desorb, which can decrease photocatalytic activity during the photocatalytic reaction process.

Here, we try a simple surface modification to $TiO_2$ nanocrystals through a traditional organic reaction between the surface hydroxyls on $TiO_2$ nanoparticle and the –NCO groups of tolylene diisocyanate (TDI). It is noteworthy that a steady chemical bond is formed in the TDI-modified $TiO_2$ by the chemical reaction. It was found

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that the TDI-modified $TiO_2$ material that could largely absorb visible light and showed improved photocatalytic performance.

## 2. Experimental sections

In the present study, all chemical reagents were used without further purification. Original $TiO_2$ was obtained by the sol–gel–hydrothermal method [17] and was used as a raw material in next synthesis. In a typical procedure, 0.01 mol of unmodified $TiO_2$ was dispersed in dichloromethane ($CH_2Cl_2$) (99.5% +, Beijing Reagent Company) under magnetic stirring and produced a pale yellow suspension. Then, 0.005 mol of TDI (99.5% +, Aldrich) was added dropwise into the above $CH_2Cl_2$ suspension and the system gradually turned to deep yellow, indicating that the TDI has reacted with unmodified $TiO_2$. In the reaction system, a reaction schematically represented by Scheme 1 may occur between $TiO_2$ particles and TDI. After stirring at room temperature for 2 h, the finally formed suspension was filtrated and washed three times with $CH_2Cl_2$. The obtained products were dried at 60 °C and designated as TTi0.2 and TTi0.5 according to the molar ratio of TDI/$TiO_2$: 0.2/1 and 0.5/1.

The photocatalytic activities of unmodified $TiO_2$, TTi0.2 and TTi0.5 were studied by measuring the decomposition of methylene blue (MB) aqueous solution under visible irradiation. For a comparison purpose, photocatalytic activity of the commercial Degussa P25 (75% anatase, 25% rutile, BET surface area: 50 $m^2 g^{-1}$, size: 30 nm) was also measured under identical conditions. A 250-W metal halide lamp (Philips) was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket to cool the lamp. A cutoff filter was also placed outside the Pyrex jacket to remove the radiation below 400 nm, ensuring the reaction system to be irradiated only by visible light wavelengths. An aqueous $TiO_2$ dispersion was prepared by adding 250 mg of photocatalyst to a 250 mL of MB solution at an appropriate concentration of 50 ppm. In all experiments, prior to irradiation, the suspension of photocatalyst in MB solution was stirred in the dark for 30 min to achieve adsorption/desorption equilibrium. The

concentration of MB at this point was used as the initial value for the further kinetic treatment of the photodecomposition process. At given irradiation time intervals, the dispersion was sampled (4 mL), centrifuged, and subsequently filtered through a Millipore filter (pore size, 0.22 μm) to separate the $TiO_2$ particles. The filtrates were analyzed by UV–visible (vis) spectrophotometer and the concentration of MB was measured at a wavelength of 665 nm using UV–vis spectrophotometer. Firstly, a series of standard MB solutions (2.5, 5, 10, 15 and 20 ppm) were prepared and measured using UV–vis spectrophotometer. Then, a standard curve could be obtained. The concentration of MB during the process of degradation could be obtained from the standard curve. Absorption spectra were recorded after 4-fold dilution.

The X-ray powder diffraction (XRD, CuKα, 40 kV, 40 mA, D8, Advance Bruker Axs) was used for studying the phase composition. FT–IR spectra of the samples were recorded with Nicolet 470 Spectrometer at 4 $cm^{-1}$ resolution. All IR measurements were carried out at room temperature using KBr technique. The X-ray photoelectron spectroscopy (XPS, MgKα as radiation source, PHI-5300X, Perkin-Elmer Physics Electronics) was used to investigate the composition of samples. The BET surface areas of samples were measured by nitrogen adsorption at 77 K (Tristar3000, Micromeritics). Diffuse reflectance spectra (DRS) were recorded by a Shimadzu UV-3150 apparatus between 200 and 700 nm range, equipped with an integrating sphere, using $BaSO_4$ as reference.

## 3. Results and discussion

Scheme 1 gives the schematic representation of the formation of TDI-modified $TiO_2$. On the surface of $TiO_2$ nanoparticle, there are a lot of free hydroxyls that can react with those active –NCO groups of TDI to form a surface complex such as the structure –NHCOOTi–. Hence, $TiO_2$ can link with TDI by the bond –NHCOOTi not by adsorption. Due to the formation of chemical bond, the TDI molecules cannot desorb from the $TiO_2$ surface. Moreover, the formed surface complex structure can lead
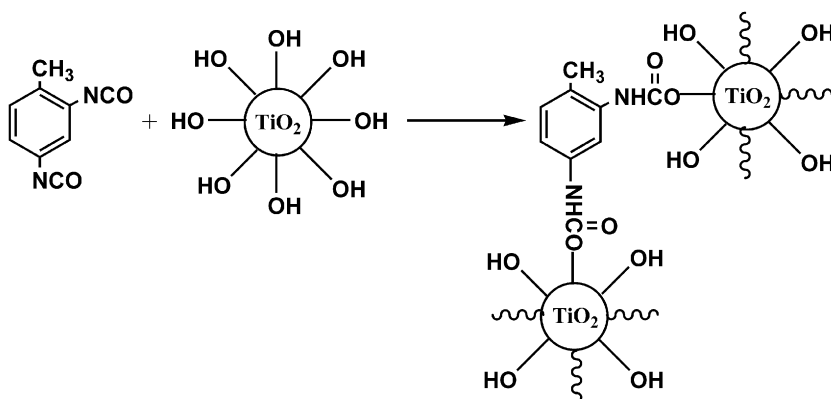


Scheme 1. Schematic representation of the formation of the TDI-modified $TiO_2$.

to a red shift in UV–vis absorption [18], which is confirmed by the following UV–vis spectra.

The XRD patterns of the unmodified $TiO_2$ and TTi samples are shown in Fig. 1. As shown in Fig. 1, unmodified $TiO_2$, TTi0.2 and TTi0.5 are all anatase structured, suggesting that the TDI molecules modified on the surface of $TiO_2$ particles have no effect on the crystalline phase of $TiO_2$. However, the TDI modification to $TiO_2$ influences the surface area of $TiO_2$. The BET surface area of unmodified $TiO_2$ is $239.3 \, m^2 \, g^{-1}$. TTi0.2 and TTi0.5 possesses only 91.9 and $54.0 \, m^2 \, g^{-1}$ surface area, respectively. The decrease of surface area of TDI-modified $TiO_2$ samples should be attributed to the aggregation between $TiO_2$ particles due to the TDI modification to $TiO_2$.

The FT–IR spectra of original materials (TDI and $TiO_2$), TTi0.2 and TTi0.5 are exhibited in Fig. 2. As shown in the FT–IR spectrum of $TiO_2$, a strong and wide peak at
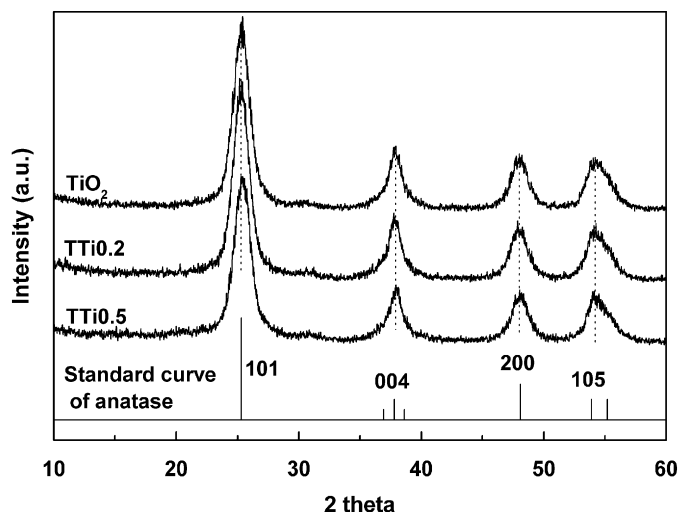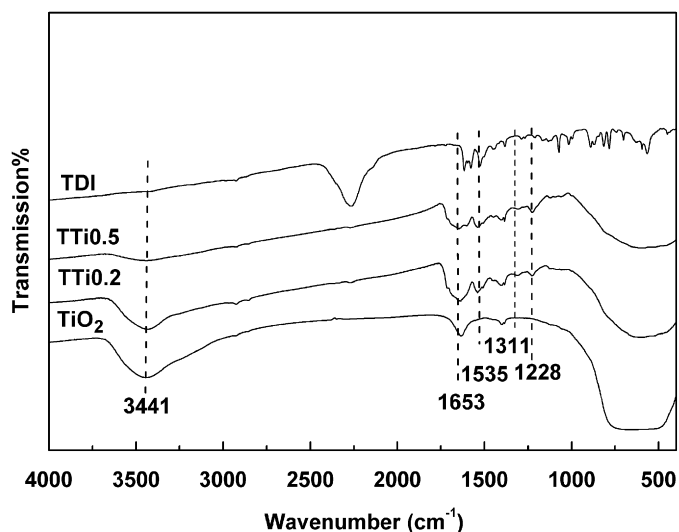
$3441 \, cm^{-1}$ should be attributed to the hydroxyl groups of Ti–OH with which physisorbed water molecules are bound by weak hydrogen bonds [19] and the strong absorption centered at $600 \, cm^{-1}$ is the typical Ti–O–Ti vibration. A strong absorption at $2278 \, cm^{-1}$, being a typical vibration absorption of –NCO, can be observed in the FT–IR spectrum of TDI. When TDI reacted with $TiO_2$ (as TDI/$TiO_2$ molar ratio $\leqslant 0.5$) to form TDI-modified $TiO_2$, the peak at $2285 \, cm^{-1}$ of –NCO disappeared as shown in the FT–IR spectra of TTi0.2 and TTi0.5, suggesting the –NCO of TDI have really reacted with the hydroxyls of $TiO_2$ and there were not TDI molecules adsorbed on the TDI-modified samples at all. Meanwhile, some new absorption at 1653, 1535, 1311 and $1228 \, cm^{-1}$ were obviously observed for TDI-modified $TiO_2$ samples, compared with the original materials. The peaks at 1653 and $1228 \, cm^{-1}$ should attribute to the asymmetric and symmetric stretching vibration of –COOTi, respectively. Generally speaking, the asymmetric and symmetric stretching vibrations of –COOTi should correspond to the peaks at about 1720 and $1270 \, cm^{-1}$ [20]. Here, the 1720 and $1270 \, cm^{-1}$ bands shift to lower wavenumber of 1653 and $1228 \, cm^{-1}$ due to the formation of the conjugated structure Ph–NHCOOTi. The absorptions at 1535 and $1311 \, cm^{-1}$ correspond to the deformation vibration of N–H and the stretching vibration of N–C. The above groups confirmed by FT–IR could all be found in the structure of Scheme 1 and this further proves that the hydroxyls on the surface of $TiO_2$ particles have reacted with TDI to form the –NHCOOTi band.

The XPS spectra of $TiO_2$, TTi0.2 and TTi0.5 are also used to determine the structure of TDI-modified $TiO_2$ nanomaterials and shown in Fig. 3. From Fig. 3, the photoelectron peaks of Ti 2p, O 1s and C 1s can be observed in all samples. The C 1s peak can also be seen for unmodified $TiO_2$ due to the presence of a contamination layer of carbon [21]. The Aguer peaks O(A), C(A) and



Fig. 1. XRD patterns of $TiO_2$, TTi0.2 and TTi0.5.



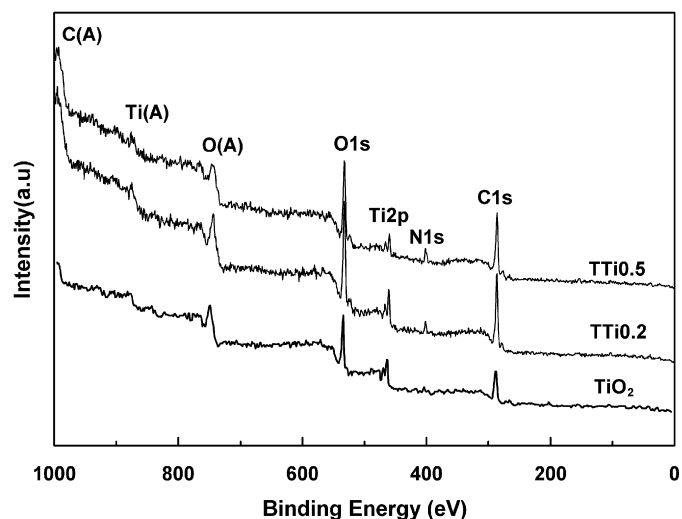Fig. 2. The FT–IR transmission spectra of samples.



Fig. 3. The XPS spectra of the surfaces of $TiO_2$, TTi0.2 and TTi0.5.

Ti(A) are also present in the spectra at higher energies, but they will not be considered in the following discussion. It is noteworthy that the XPS spectra of TTi0.2 and TTi0.5 contain N 1s peaks, but does not for unmodified $TiO_2$. The N elements of TTi0.2 and TTi0.5 can only come from the TDI ($C_9H_6N_2O_2$) molecules. The results are well agreed with the results of the FT–IR analysis and indicate the modification to surface of $TiO_2$ by TDI molecules has been realized.

Fig. 4 gives the UV–vis DRS of samples. The unmodified $TiO_2$ exhibits very weak absorption in visible region. The inset gives the UV–vis spectra of TDI, and shows no absorption above 400 nm. However, the TDI-modified $TiO_2$ has stronger absorption in the band of 420–600 nm, compared with unmodified $TiO_2$. The absorption intensity of the TDI-modified $TiO_2$ in the visible region increases with the increasing content of TDI. Obviously, the TDI modification to $TiO_2$ causes the absorption spectra to shift to the visible region. These changes should be attributed to the surface complex structure –NHCOOTi– formed between $TiO_2$ and TDI (Scheme 1), which has been confirmed by the FT–IR and XPS spectra.

Fig. 5 exhibits the kinetics of the photocatalytic decomposition of MB under visible light. Noticeably, the MB concentration at zero exposure time is about 35 ppm (lower than the original concentration 50 ppm) for pure $TiO_2$ and the TDI-modified $TiO_2$ samples due to the adsorption of catalysts to MB. Specially, the TDI-modified $TiO_2$ samples (TTi0.2 and TTi0.5) possesses the lower surface area than pure $TiO_2$, but their adsorption capacity are almost the same as that of pure $TiO_2$. It could be explained that the organic modification to $TiO_2$ increased the compatibility between $TiO_2$ and MB to enhance the MB adsorption content for TTi0.2 and TTi0.5 despite their lower surface area [22]. From Fig. 5, it can be seen that the photocatalytic activity of TDI-modified $TiO_2$ is obviously better than that of Degussa P25 and unmodified $TiO_2$. And that its photocatalytic activity increases with the increase of
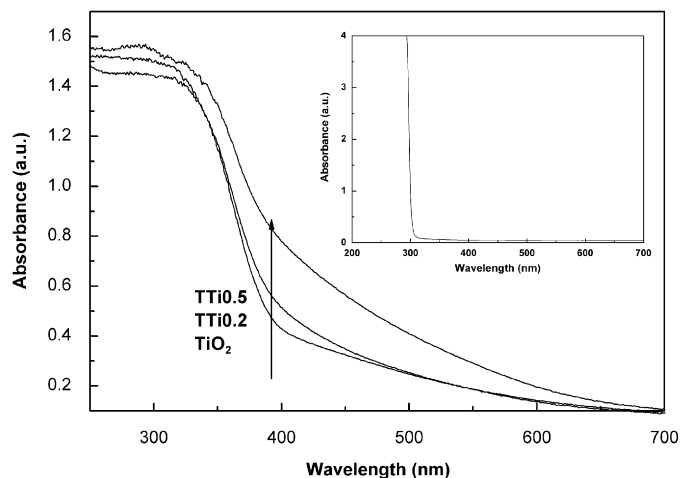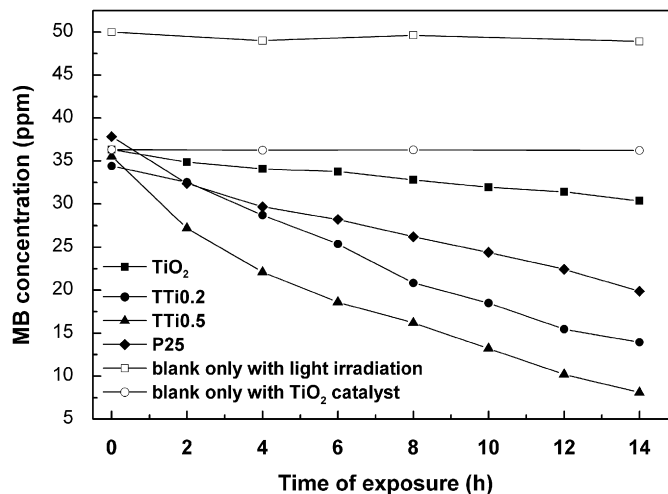


Fig. 5. Kinetics of the photocatalytic decomposition of MB under visible light in catalysts suspension at natural PH, [catalyst] = $1\,g\,L^{-1}$, [MB]$_0$ = 50 ppm, absorption spectra were recorded after 4-fold dilution.

TDI/$TiO_2$ molar ratio. Especially, TTi0.5 displays the high visible photocatalytic activity due to the strong absorption in visible region (see Fig. 4). A blank experiment was conducted with visible-irradiation without pure $TiO_2$ catalyst, and another was in the dark with pure $TiO_2$ catalyst under the same experimental conditions. Both of them show no MB degradation. Moreover, the catalytic activity of the TDI-modified sample without irradiation has been investigated by blank experiments without irradiation. The results showed the TDI-modified samples did not show any catalytic activity without irradiation, because the MB concentration did not change during the experiment.

Also, we investigated the TDI modification to $TiO_2$ with other molar ratios of TDI/$TiO_2$ ($>0.5:1$). The experimental results indicated that the $TiO_2$ materials modified by too many TDI had excess –NCO groups on the catalyst surface. So, in this case, only one –NCO group of those excess TDI molecules reacted with surface hydroxyl of $TiO_2$ and another remained unreacted (a characteristic peak of –NCO at $2285\,cm^{-1}$ can be observed in FT–IR spectrum). Because the unreacted –NCO have high reactive activity and can react with water and dye, the obtained catalyst with molar ratio of TDI/$TiO_2$ $>0.5:1$ cannot reflect its true photocatalytic activity. Meanwhile, the stability of TTi samples were also investigated by irradiating TTi samples aqueous suspension without substrate (MB) under visible light for 24 h. The experimental result showed the TTi catalysts were very steady under visible irradiation and no detectable TDI or other organic species existed in the reacted water solution. In addition, the TTi0.5 catalyst could be circularly used and still exhibited high photocatalytic activity (see Supporting Information).

Additionally, the mechanism of the photocatalytic decomposition of MB over TDI-modified $TiO_2$ under visible



Fig. 4. UV–vis diffuse reflectance spectra of samples. The inset gives the UV–vis spectra of TDI.
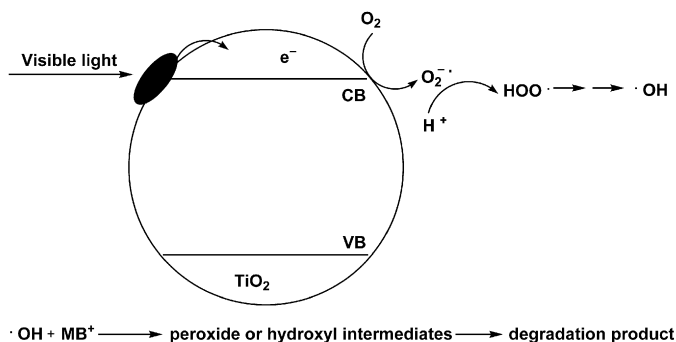
Fig. 6. The mechanism of the photocatalytic decomposition of MB over TDI-modified $TiO_2$ under visible light.

light was also discussed (see Fig. 6). The modification of TDI to $TiO_2$ led to the formation of a surface complex on the $TiO_2$ surface. The surface complex was excited by visible light followed by electron injection into the conduction band of $TiO_2$. The electron was scavenged by the $O_2$ preadsorbed on the $TiO_2$ surface to form superoxide anion radical ($O_2^- \cdot$), which futher converted to hydrogen peroxide radicals (HOO·) and hydroxyl radicals (HO·) via a series of protonation, disproportionation and reduction steps. The hydroxyl radicals were proposed to be the primary oxidant in the photocatalytic system. The hydroxyl radicals reacted with the MB molecules to generate some intermediates and finally produced the degradation product [23].

In summary, TDI-modified $TiO_2$ was prepared by an organic reaction between TDI molecules and the hydroxyls on the $TiO_2$ surface. The as-prepared TDI-modified $TiO_2$ has strong absorption in visible light region. Compared with the commercially available Degussa P25 and unmodified anatase $TiO_2$, the TDI-modified $TiO_2$ samples show higher photocatalytic activity for the decomposition of MB under the visible region.

## Acknowledgments

## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc. 2007.03.010.

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