

## Review

# Azo dyes decomposition on new nitrogen-modified anatase TiO<sub>2</sub> with high adsorptivity

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## ABSTRACT

New vis active photocatalyst was obtained by the modification of commercial anatase TiO<sub>2</sub> (Police, Poland) in pressure reactor in an ammonia water atmosphere at 100 °C for 4 h. The photocatalytic activity of new material was tested during three azo dyes decomposition: monoazo (Reactive Red), diazo (Reactive Black) and poliazodye (Direct Green). Obtained photocatalyst had new bands at 1430–1440 cm<sup>-1</sup> attributed to the bending vibrations of NH<sub>4</sub><sup>+</sup> and at 1535 cm<sup>-1</sup> associated with NH<sub>2</sub> groups or NO<sub>2</sub> and NO. UV–vis/DR spectra of photocatalyst had also insignificant decrease in visible region. Fluorescence technique was used for studying the amount of hydroxyl radicals produced on TiO<sub>2</sub> surface during visible light irradiation. The hydroxyl radicals produced react with coumarin present in the solution to form 7-hydroxycoumarin which has fluorescent capacity. Photocatalytic activity of modified TiO<sub>2</sub> was compared with commercial titanium dioxide P25 (Degussa, Germany). The photocatalytic activity of TiO<sub>2</sub>/N was higher than that of unmodified material and P25 under visible light irradiation. The ability for dye adsorption (Reactive Red) on photocatalyst surface was also tested. Unmodified TiO<sub>2</sub> and P25 has isotherm of adsorption by Freundlich model, and nitrogen-modified TiO<sub>2</sub> by Langmuir model. The presence of nitrogen at the surface of TiO<sub>2</sub> significantly increased adsorption capacity of TiO<sub>2</sub> as well as OH<sup>•</sup> radicals formation under visible radiation.

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## 1. Introduction

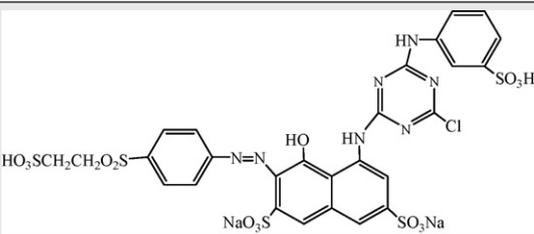
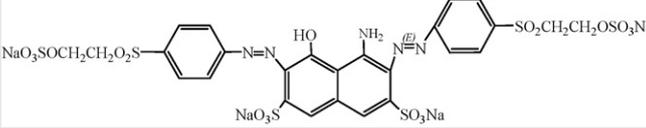
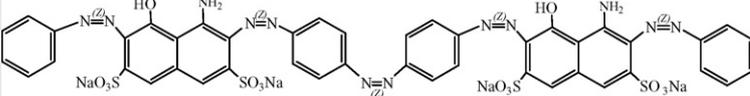
The treatment of wastewater containing dyes is difficult. Traditional methods (for example adsorption on activated carbons) only transfer contaminations from one phase to another. The most

promising way for removing dyes is photocatalysis, because this process decomposes the end dyes to water and carbon dioxide. For photocatalysis process, photocatalysts and suitable irradiations are necessary. The researchers decomposed dyes under UV, visible and simulated sunlight [1–3]. They used different types of photocatalysts, but the most active one is titanium dioxide, to increase its activity is often modified. In many works it has been shown that doping nitrogen into the structure of titanium dioxide (N-doped) can efficiently increase the optical response to the visible light. TiO<sub>2</sub> is the most promising photocatalyst for its low cost, high stability, non-toxic and high efficiency in removing organic compounds. At

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**Table 1**  
Characteristics of dyes.

Compounds	Structural formula	Molecular weight [g/mol]	$\lambda_{\max}$ [nm]
Reactive Red		887.2	516
Reactive Black		991.8	597
Direct Green		1169.0	625

present there are many synthesis methods for the preparation of nitrogen-doped TiO<sub>2</sub>.

Asahi et al. [4] reported a visible light active TiO<sub>2-x</sub>N<sub>x</sub> films obtained by sputtering of the TiO<sub>2</sub> target in N<sub>2</sub> (40%)/Ar gas mixture. Ihara et al. [5] receive a visible light active photocatalyst by using the hydrolysis product of Ti(SO<sub>4</sub>)<sub>2</sub> with ammonia solution as N-doped precursor. Wang et al. [6] also took the hydrolysis product of tetra-butyl titanate (Ti(OBu)<sub>4</sub>) with ammonia solution as N-doped precursor and found the visible light photoactivity in phenol decomposition.

Gole et al. [7] have reported of TiO<sub>2</sub> nanoparticles using alkylammonium salt at room temperature. Some study is based on nitrogen-doped TiO<sub>2</sub> using the atmospheric microwave plasma.

Wong and Pang [8] prepared N-doped TiO<sub>2</sub> films by reactive sputtering of a titanium metal target in gas mixtures of argon, oxygen and nitrogen. Two types of nitrogen species were formed in the films following the fraction of N<sub>2</sub> in the reactive atmosphere. From the analyses, was demonstrated the state of nitrogen in the N-doped TiO<sub>2</sub> films to promote the visible light-induced photocatalytic activity.

Traditional synthesis method of N-doped TiO<sub>2</sub> was followed by the calcinations of TiO<sub>2</sub> in ammonia atmosphere at high temperature [9]. Wawrzyniak et al. [10] have received N-doped TiO<sub>2</sub> catalysts by calcinations at temperatures of 300, 400 and 500 °C in the gaseous NH<sub>3</sub> atmosphere for 4 and 20 h.

In this work, N-doped TiO<sub>2</sub> was prepared for azo-dye decomposition under UV and vis irradiation. The photocatalyst was characterized by the FTIR/DRS, UV-vis/DR spectroscopy and the X-ray powder diffraction (XRD). The activity was compared with commercial P25 of Degussa.

## 2. Experimental

### 2.1. Materials

The commercial anatase titanium dioxide was used as a base material (Z.Ch. Police company, Poland), mainly anatase form with crystallite size of 11 nm and particle size ca. 390 nm Titanium dioxide TiO<sub>2</sub>-P25 was supplied by the Degussa company (Germany). Degussa P25 has a surface area of 50 ± 5 m<sup>2</sup>/g and is composed of 80% anatase and 20% rutile with elementary particles 25 and 85 nm, respectively.

Three azo dyes were used for photocatalytic tests: mono azo dye (Reactive Red (RR)), diazo dye (Reactive Black (RB)) and poly-azo dye (Direct Green (DG)), produced by The Chemical Factory Boruta-Color company (Poland). In Table 1, a chemical structure, a molecular weight and  $\lambda_{\max}$  of a model compounds are presented.

### 2.2. Preparation of modified photocatalyst samples

4 g of anatase TiO<sub>2</sub> and 15 ml of ammonia water (NH<sub>3</sub> aq) were placed in a pressure reactor (BLH-800, BERGHOF, Germany); this was presented in an earlier work [11]. The reactor was closed and heated up to 100 °C, after that the mixture was kept in this temperature for 4 h, generated 6 bar pressure. After heating, the reactor was cooling slowly to the room temperature and valves were opened. The catalyst was dried for 20 h in 105 °C.

### 2.3. Photocatalysts characterization

The surface of the photocatalysts was analyzed on the basis of the FTIR/DRS spectra. The measurements were performed using the Jasco FT-IR 430 (Japan) spectrophotometer equipped with a diffuse reflectance accessory (Harrick, USA).

The photocatalysts were characterized by the UV-vis/DR technique using the Jasco V-530 (Japan) spectrophotometer equipped with the integrating sphere accessory for the diffuse reflectance spectra (BaSO<sub>4</sub> was used as a reference).

N<sub>2</sub> adsorption measurements at 77 K for the calculation of N<sub>2</sub>-BET SSA were performed using ASAP2010 (Micromeritics) instrument.

The crystalline structure of the photocatalysts was characterized by X-ray powder diffraction analysis (X'Pert PRO Philips diffractometer) using Cu K $\alpha$  radiation. The mean size of crystallite was calculated from full-width at half-maxima (FWHM) of corresponding X-ray diffraction peaks using Scherrer's formula  $D = \lambda / (\beta \cos \theta)$ , where  $\lambda$  is the wavelength of the X-ray radiation ( $\lambda = 1.54056$  nm Cu K $\alpha$ ),  $\beta$  is the full-width at half-maximum (rad) and  $\theta$  is the reflect angle. The width of the peak at half maximum was calculated after the correction of the instrument error. The presented method was applied to estimate the change in crystallite size of TiO<sub>2</sub> particles.

## 2.4. Experimental procedures

Photocatalytic decomposition under visible light irradiation of three azo dyes was carried out in the glass beakers. 0.1 g of photocatalyst anatase TiO<sub>2</sub> was added to 500 ml of aqueous dyes solution (RR, RB, DG) with a concentration of 5 mg/l. The dye solution was mixed with a magnetic stirrer during reaction.

The irradiation of the solution was operated under visible light (bulk, Philips 100 W) with the radiation intensity of about 385 W/m<sup>2</sup> for vis and 0.09 W/m<sup>2</sup> for UV (emission spectra in Fig. 1). The blank experiments were also done and there were not any changes in dye concentration during irradiation without photocatalysts.

Firstly, the solution mixture was stirred for 15 min without irradiation in order to get the equilibrium of dye adsorption. After 15 min in the dark, the solutions of azo dyes were irradiated under the visible light for 5 h. To determine the concentration of dye, after 5 h decomposition, the photocatalysts were separated from the solutions using a centrifugal clarifier (Universal 320, Hettich Zentrifugen, Germany) for 10 min. Next, the solution was loaded in a UV–vis spectrometer (Jasco, Japan). The concentration of the model compounds was calculated by a computer program based on the calibration curve. The program determines the absorbance of dye solution at maximum wavelength of dyes: Reactive Red – 516 nm, Reactive Black – 597 nm, Direct Green – 625 nm.

The active hydroxyl radicals (OH•) produced on photocatalysts surface in aqueous solutions were investigated by the fluorescence technique. Terephthalic acid reacted with photocatalyst surface (OH•) radicals and generated highly fluorescent hydroxy product 2-hydroxyterephthalic acid. Fluorescence spectra of generated 2-hydroxyterephthalic acid were measured on F-2500 Hitachi (Japan) fluorescence spectrophotometer. Using this fluorescence method, the effect of light intensity on the generation efficiency of active oxidative species was examined. The intensity of the peak attributed to 2-hydroxyterephthalic acid was known to be proportional to the amount of (OH•) radicals formed [12]. For this experiment, 0.02 g of photocatalyst was magnetically stirred in 100 ml of prepared terephthalic acid under vis irradiation. After filtration by using a membrane filter with 0.45 μm pore diameter, the solution was analyzed in the fluorescence spectrophotometer (Hitachi F-2500). The product of terephthalic acid, 2-hydroxyterephthalic acid, was presented as a peak at the maximum wavelength of 420 nm, by the excitation of 314 nm.

Adsorption capacity of photocatalyst was also measured. The analysis of isotherm data is important to develop an equation which represents the experimental results. The best known and most often used isotherm applied in solid/liquid system is theoretical equilibrium isotherm; Langmuir and also the most known isotherm Freundlich describing the adsorption equation. The adsorption of mono azo dyes RR 198 on unmodified and nitrogen-modified anatase and P25, were carried out in thermostated bath (LWC-1500)

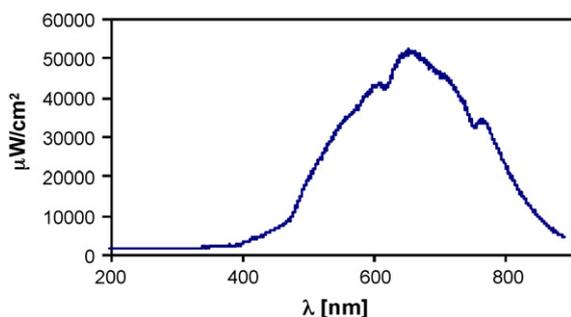


Fig. 1. Emission spectra of visible lamp (100 W, Philips).

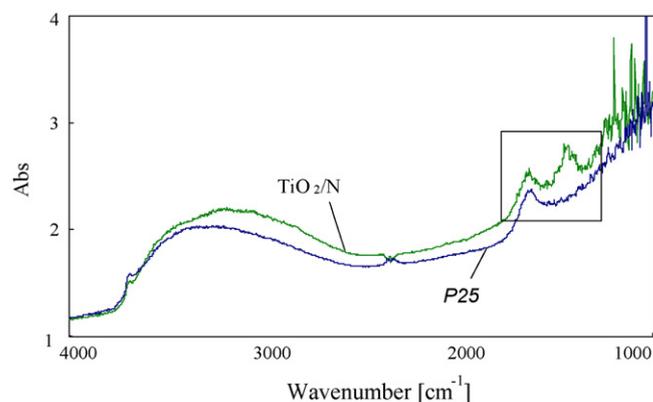


Fig. 2. The FTIR/DRS spectra of the TiO<sub>2</sub>/N and P25.

for 4 h without stirring. All studies were made at a temperature of 25 °C. After 4 h, the samples were taken off and separated by using centrifugal clarifier. Their absorbance was measured by using the UV–vis spectrophotometer. The quantity of mono azo dye solution by mass of TiO<sub>2</sub> (modified and unmodified) and P25 at time  $t$  (4 h) is

$$Q = \frac{C_0 - C}{m}$$

where  $Q$  is the quantity of azo dye Reactive Red adsorbed at time  $t$  by mass of TiO<sub>2</sub> (mg/l),  $C_0$  is the initial concentration of Reactive Red (mg/l),  $C$  is the concentration of Reactive Red at time  $t$  (mg/l) and  $m$  is the concentration of the photocatalyst (g/l) [13].

## 3. Results and discussion

The modification method of anatase TiO<sub>2</sub> by ammonia water (NH<sub>3</sub> aq) is a new way for increasing its photocatalytic activity. Modification of TiO<sub>2</sub> by ammonia, earlier studied by Morawski and co-workers [14,15] showed significant increase in its photocatalytic activity under visible light irradiation. The activity of N-doped TiO<sub>2</sub> was compared with that of commercial TiO<sub>2</sub> Degussa P25.

Modification of TiO<sub>2</sub> carried out in low temperature (100 °C) and pressure (6 bar) in water ammonia atmosphere introduced new groups to the surface of anatase TiO<sub>2</sub>. In Fig. 2 FTIR/DRS spectra of nitrogen-modified TiO<sub>2</sub> and P25 are presented. These modifications have led to the increasing photocatalytic activity of the photocatalyst. One can see bands that are positioned at 3695–3700 cm<sup>-1</sup> in both spectra, assigned to the stretching of a hydroxyl group that was chemisorbed on a surface defect site, 3300–3500 cm<sup>-1</sup>, assigned to hydroxyl for both the dissociated water and molecularly adsorbed water; and 1623 cm<sup>-1</sup>, pertaining to H–O–H bending for a molecular water [16]. The small changes in intensity of surface hydroxyl groups at 3300–3500 cm<sup>-1</sup> were observed on FTIR/DRS spectra of modified TiO<sub>2</sub>. The spectra of the catalyst modified with ammonia also showed new bands at 1430–1440 cm<sup>-1</sup> that could be attributed to the bending vibrations of NH<sub>4</sub><sup>+</sup> [5] and at 1535 cm<sup>-1</sup> associated with NH<sub>2</sub> groups [17].

In the XRD (Fig. 3) spectra it was possible to observe that nitrogen modification in elevated pressure at 100 °C does not change the ratio of anatase (90%) and rutile (10%) in TiO<sub>2</sub> structure and also does not change their crystal sizes, which was 18 nm, before and after modification.

The results of photocatalytic activity under visible light irradiation in Fig. 4 are presented. The best photocatalytic activity during azo dyes had nitrogen-modified titanium dioxide, after 5 h TiO<sub>2</sub>/N decomposed: 100% of RR, 77% of RB and 100% of DG. The best efficiency was obtained by the decomposition of poli azo dyes Direct

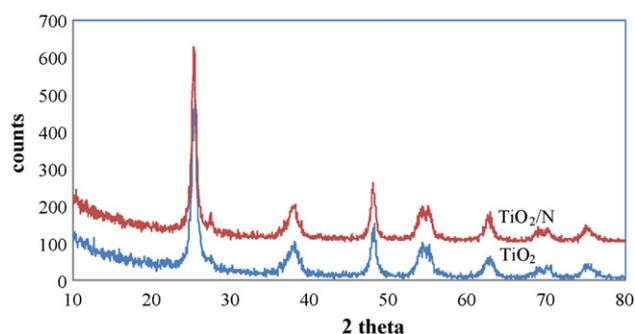


Fig. 3. XRD spectra of modified and unmodified TiO<sub>2</sub>.

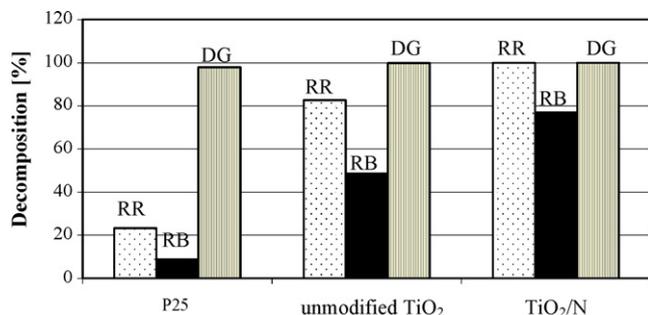


Fig. 4. Decomposition of mono, di and poly azo dye solution during photocatalysis under visible light irradiation. Dye concentration = 5 mg/l, amount of photocatalyst = 0.2 g/l.

Green. The percentage of decomposition azo dyes by using Degussa P25 was smaller than that by using TiO<sub>2</sub>/N.

In Fig. 5 the formation of OH<sup>•</sup> radicals on the surface of TiO<sub>2</sub> under visible irradiation was presented. The nitrogen-modified TiO<sub>2</sub> accelerates OH<sup>•</sup> radicals formation in visible region. The rate of the OH<sup>•</sup> radicals formation was expressed by the slope of line. The fluorescence intensity by visible light illumination increased linearly with time. Faster formation of OH<sup>•</sup> radicals can be observed on TiO<sub>2</sub>/N than on the basic one. The values of the amounts of radicals for TiO<sub>2</sub>/N increase while line of unmodified TiO<sub>2</sub> does not increase during the experiment. This fact was proved that TiO<sub>2</sub>/N had higher efficiency under visible light and formed much more hydroxyl radicals on their surface than unmodified TiO<sub>2</sub> had. Most active to OH<sup>•</sup> radicals formation under vis was observed for P25.

To check the adsorption capacity of new photocatalyst, BET surface area was measured for modified and unmodified material and amounted 183 and 222 m<sup>2</sup>/g, respectively and was higher than for P25 (~55 m<sup>2</sup>/g).

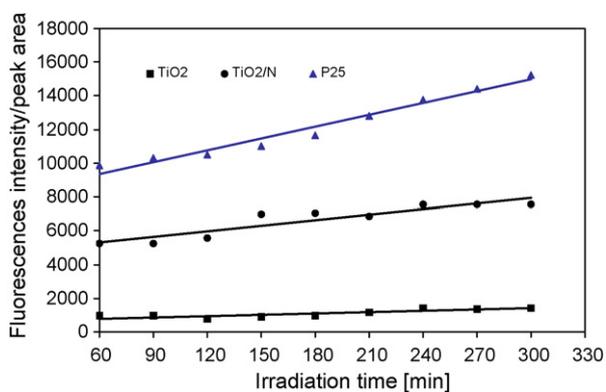


Fig. 5. Formation of OH<sup>•</sup> radicals under visible light irradiation on the TiO<sub>2</sub> surface.

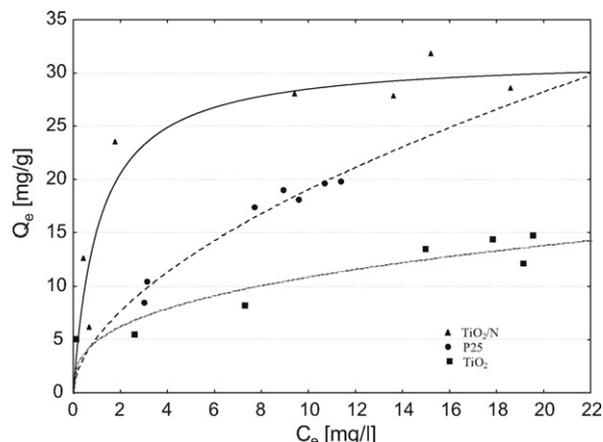


Fig. 6. Isotherm of adsorption of Reactive Red by unmodified TiO<sub>2</sub>, TiO<sub>2</sub>/N, P25.

At a constant temperature, the variation of the adsorbed quantity of Reactive Red on photocatalysts surface was measured (Fig. 6). The different values of Reactive Red adsorbed by the mass of the catalysts at equilibrium  $Q_e$  will serve to establish adsorption isotherm. In Tables 2 and 3 and Fig. 6 were shown equilibrium data and adsorption isotherms. After analysis correlation coefficient  $R^2$ , it was stated that the isotherm of adsorption of Reactive Red by unmodified TiO<sub>2</sub> and P25 represented better by Freundlich model while the isotherm of adsorption of Reactive Red by TiO<sub>2</sub>/N represented better by Langmuir model. After the modification maximal quantity of dye adsorbed by mass of photocatalyst  $Q_{max}$  was much higher besides the changes of character of isotherm. It means that the maximal quantity of dye adsorbed by mass of photocatalyst described by Langmuir model was 31.54. The adsorption constant  $K$  for Langmuir model  $K_L$  and Freundlich model  $K_F$  was also analyzed. Degussa P25 had a higher value of adsorption constant  $K_F$  than unmodified TiO<sub>2</sub>.

During nitrogen modification BET surface area of modified photocatalysts slightly decrease, but adsorption capacity increases (there is even different adsorption model). From that data it is possible to conclude that nitrogen introduced to TiO<sub>2</sub> surface increased adsorption capacity of this material, as well as radical formation.

For dye decomposition Nasr et al. [18] and Zhang et al. [19] proposed a mechanism, "photosensitizing oxidation". Their proposed photosensitizing oxidation mechanism suggests that the electron from the excited and adsorbed dye molecule is injected into the conduction band of TiO<sub>2</sub> and the cation radical formed at the sur-

Table 2  
Constants of adsorption isotherm Freundlich.

Photocatalysts	$Q_e = aC_e^b$		
	$a (K_F)$	$b$	$R^2$
Degussa P25	4.9385	0.3449	0.8464
TiO <sub>2</sub>	5.1689	0.5665	0.9649

Table 3  
Constants of adsorption isotherm Langmuir.

Photocatalysts	TiO <sub>2</sub> /N
$Q_e = \frac{a b C_e}{1 + b C_e}$	
$a (Q_{max})$	31.5392
$b (K_L)$	0.9321
$R^2$	0.8601

face quickly undergoes degradation to yield products. In the case of this mechanism very important is the good adsorption of dyes at surface of TiO<sub>2</sub>. As was found in this study for good adsorption capacity not just high BET surface area of material is required. It seems that the most important fact is the character of the surface of the photocatalyst. Presence of nitrogen at the surface of TiO<sub>2</sub> carried out of these requirements because significantly increase adsorption capacity of TiO<sub>2</sub> in spite of decreasing BET surface area from 222 to 183 m<sup>2</sup>/g.

#### 4. Conclusion

In the present investigation on the preparation of photocatalysts of visible light response, azo dye photodecomposition was described. Modification in ammonia water precursor atmosphere and in elevated pressure has led to receiving material with the amount of nitrogen groups on the surface and with better photocatalytic activity to azo dyes. Better results were achieved by using TiO<sub>2</sub>/N in removing azo dyes from solutions than by using P25 Degussa. The formation of OH• radicals on the surface of TiO<sub>2</sub> under UV and vis irradiation was monitored. The TiO<sub>2</sub>/N of higher photocatalytic efficiency under visible light formed much more hydroxyl radicals on their surface than anatase TiO<sub>2</sub>. The Freundlich adsorption isotherm is fitted to unmodified TiO<sub>2</sub> catalyst and P25 but the Langmuir adsorption isotherm is more suitable to nitrogen-modified TiO<sub>2</sub> photocatalysts. Adsorption capacity is higher for nitrogen-modified photocatalyst probably because of the presence of nitrogen groups on its surface in spite of practically the same crystal size and lower BET surface area. In the case of dyes high adsorption of photocatalyst surface is very important because “photosensitizing oxidation” mechanism takes place. This mechanism suggests that the electron from the excited and adsorbed dye molecule is injected into the conduction band of TiO<sub>2</sub> and the cation radical formed at the surface quickly undergoes degradation to yield products. Higher adsorption capacity of photocatalysts brings faster decomposition of dyes.

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