

Novel TiO₂ nanocatalysts for wastewater purification: tapping energy from the sun

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Abstract Water treatment using TiO₂ semiconductor as a durable heterogeneous photocatalyst has been the focus of environmentalists in recent years. Currently, we developed an inexpensive and highly efficient approach for synthesizing nitrogen-doped TiO₂ with lower band-gap energy that can respond to visible light. Doping on the molecular scale led to an enhanced nitrogen concentration of up to 21.8%. Reflectance measurements showed the synthesized N-doped TiO₂ nanoparticles are catalytically active with the absorbance that extends into the visible region up to 600 nm. The water purification potential of this new class of compound was evaluated by studying the photodegradation of Acid Orange 7 (AO7) and *E. coli*. Experiments were conducted to compare the photocatalytic activities of N-doped TiO₂ nanocatalysts and commercially available Degussa P25 power under identical solar light exposure. N-doped TiO₂ demonstrated superior photocatalytic activities in both chemical compound degradation and bactericidal reactions. The result of this study shows the potential of applying new generations of catalyst for wastewater purification and disinfection.

Keywords Azo dye; *E. coli*; nitrogen-doped TiO₂; photocatalysis; solar light; wastewater

Introduction

Since the discovery of photoinduced water cleavage on titanium dioxide electrodes by Fujishima and Honda (1972) in the early 1970s, the interest in applying TiO₂ as heterogeneous photocatalyst to purify water and wastewater has been increasing rapidly. Compared with conventional water treatment approaches, such as chlorination, ozonation, UV radiation and advanced filtration processes, TiO₂ as a durable semiconductor has a number of advantages, including high oxidation efficiency for complete decomposition and mineralization of organic waste, cost effectiveness, and minimal disinfection by-products (Hoffmann *et al.*, 1995; Mills and Le-Hunte, 1997; Silva *et al.*, 2004; Son *et al.*, 2004). Under ultraviolet (UV) light illumination, TiO₂ undergoes charge-transfer processes and produces electron–hole pairs on the surface. These charged points ultimately result in either direct contaminant oxidization or reaction with electron donors, such as water or hydroxide ions to form hydroxyl radicals ($\cdot\text{OH}$), which are also potent oxidants. It has been shown that TiO₂ is useful for the complete degradation of recalcitrant organic compounds (Lachheb *et al.*, 2002; Hu *et al.*, 2003; Liu *et al.*, 2005) and the destruction of microorganisms such as bacteria and viruses (Bekbolet and Araz, 1996). Currently, wide application of TiO₂-based photocatalysis in the water and wastewater industry is still limited. One of the main problems is that TiO₂ responds to only a small portion (<8%) of the solar spectrum in the UV region (band-gap energy of TiO₂ is 3.0–3.2 eV). Therefore, shifting the TiO₂ optical response from UV to the visible spectral range will have a profound impact on the application of TiO₂-based photocatalysts for the degradation of water-bound contaminants; and solar-induced photocatalytic material is one of the hottest

research topics in recent years (Heller, 1995; Linsebigler *et al.*, 1995; Sauer and Ollis, 1996).

Early attempts to lower the band-gap energy were focused mainly on transition metal doped TiO₂. Metal-doped materials, however, are thermally instable and can act as electron traps. Alternatively, nonmetal element doping seems to be more successful. Asahi *et al.* (2001) reported visible light photocatalytic degradation of methylene blue and acetaldehyde by TiO₂ films doped with N by sputtering methods. They showed that the substitution of oxygen is anticipated to lower the band-gap energy of TiO₂ as the p states of dopants mix with the oxygen 2p states, contributing to a net band-gap narrowing. Reports from Khan *et al.* (2002) demonstrated a chemical modified n-type TiO₂ synthesized by controlled combustion of Ti metal in a natural gas flame. The material could absorb UV and visible light (<520 nm) while retaining its stability.

In this study, we developed a low cost synthesis route that led to increased nitrogen dopant concentration in titania. The titanium precursor is hydrolysed and the dopant is added to the colloidal solution under continuous stirring. Simply by changing precursor solution concentrations, we are able to prepare TiO₂ with different sizes; and by varying the amine concentration and reaction time, the nanoparticles can be doped with different amounts of nitrogen. The synthesized nitrogen-doped TiO₂ particles are photocatalytically active, with absorbance that extends into the visible region up to 600 nm. The effectiveness of this new class of catalyst was investigated in terms of degradation of organic contaminant Acid Orange 7 and bactericidal activity using *E. coli* as a model organism.

Materials and methods

TiO₂ nanoparticle preparation and characterization

The preparation of nitrogen-doped titanium dioxide nanocatalysts followed a sol-gel method described previously (Burda *et al.*, 2003; Liu *et al.*, 2005). Ti[OCH(CH₃)]₄ (Aldrich, 97%) was reacted in excess of ethanol and then controllably hydrolysed under rigorous stirring. The resulting sol-gel were washed with water and ethanol, respectively, and then dried under vacuum. The final products were yellowish powder, which demonstrates the strong effect of nitrogen incorporation on the physical properties (Asahi *et al.*, 2001; Burda *et al.*, 2005). The synthesized N-doped TiO₂ were also characterized by X-ray photoelectron spectroscopy (XPS) and reflectance measurements. The XPS spectra were measured on a Perkin-Elmer PHI 5600 XPS System. The UV-visible reflectance spectra were obtained using a Cary 5000 UV-visible-IR spectrometer.

Irradiation source and procedure

Solar light and UV light were used as the irradiation source in the experiment. The UV light source is a 150 w high-pressure mercury lamp (UXL-151H) with maximum output between 250 and 450 nm. A broad range light meter (Sper Scientific) was used to measure the light intensity.

Degussa P25 consisting of 75% anatase and 25% rutile with primary particle size of 30 nm was applied in the experiments to compare the photocatalysis efficiency with N-doped TiO₂. All TiO₂ aqueous suspensions were stirred by magnetic stirrer for 24 h before the experiments to uniformly disperse particles. The stirred suspension was added to bacteria suspensions and dye solutions at initial time point $t = 0$.

E. coli inactivation tests

E. coli DH5 α was used in the experiment to examine the disinfection efficiency of TiO₂. Bacterial cells were incubated at 37 °C in a shaking incubator in Luria-Bertani (LB) broth. Optical density (OD) was observed to obtain an approximately 10⁹ colony-forming

units (CFU)/ml cell concentration. The culture was harvested by centrifugation and washed before use. Ten mL of the mixture was then added to each Petri dish, placed under solar light. Samples (1.5 mL) were withdrawn periodically, and the number of viable cells was determined by plating appropriate dilutions. All solutions were autoclaved before being used in the experiment.

AO7 decolourization tests

The photocatalytic activity of the doped TiO₂ nanoparticles was examined for the degradation of organic compound Acid Orange 7 (AO7), which is one of the most common azo dyes. AO7 with purity greater than 85% was obtained from Aldrich. The solutions were prepared with deionized water. The initial concentration was 20 mg/L AO7 and 10 mg/L TiO₂ solution. The natural pH of the solution was 4.5–5.0. Experiments were carried out in Petri dishes containing 15 mL of dye and TiO₂ suspensions. During UV and solar light illumination, Petri dishes were covered with plastic film to prevent evaporation of the dye solution. Neither forced aeration nor stirring of the dye solution was conducted. Five Petri dishes were used in each experiment set, one of the Petri dishes was wrapped with aluminum foil at the end of each experimental period, and the solution was transferred into a 15 mL graduated tube covered with aluminum foil for further analysis. AO7 decolourization was determined by measuring the dye concentration at its maximum absorbance in a UV-visible spectrophotometer (Milton Roy, Spectronic Genesys).

Results and discussion

TiO₂ nanoparticle characterization

Figure 1 shows the optical reflectance spectrum for Degussa P25 and the newly developed N-doped TiO₂. Degussa P25 displays a clear UV absorption, with reflectance spectrum onset sharply at 380 nm, while the spectrum for N-doped TiO₂ nanoparticles has a huge long-tailed absorption in the visible-light region, though with less intensity. The reflectance spectra shows that the band edge of the N-doped TiO₂ shifts, indicating that the nitrogen-doped TiO₂ has a narrower band gap, which enables the modified TiO₂ to absorb visible light.

The powders were also analysed by X-ray photoelectron spectroscopy (XPS) and reflectance measurements. The XPS spectrum in Figure 2 clearly show that the

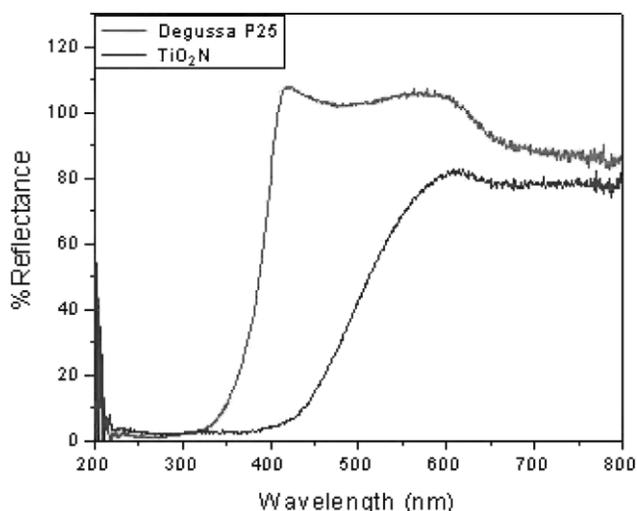


Figure 1 UV-Vis reflectance spectra of N-doped TiO₂ and Degussa P25

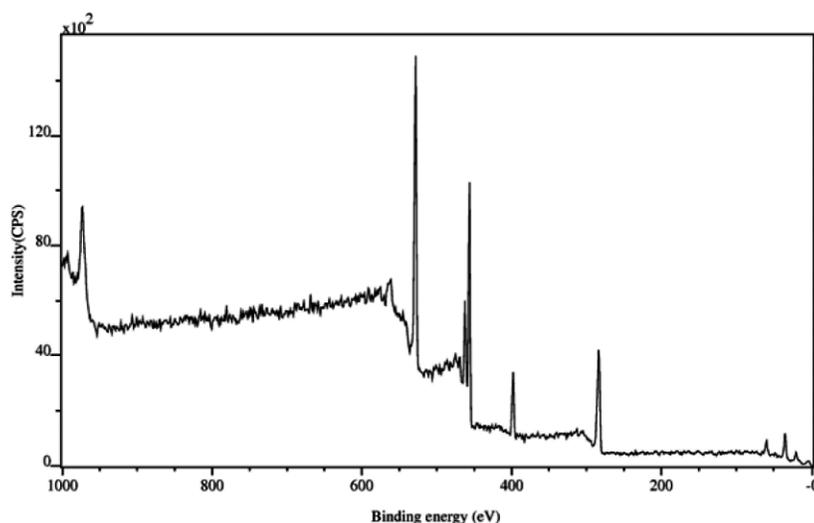


Figure 2 XPS pattern of N-doped TiO₂ nanoparticles (N 1s 21.38% atomic concentration)

synthesized TiO₂ is heavily doped and nitrogen concentration reaches as high as 21.38% (atomic ratio), which is large compared to values reported for nanoparticles (~8%). The nitrogen 1s peak shows up at 399 eV, which is in agreement with previous reports (Burda *et al.*, 2003; Chen and Burda, 2004; Gole *et al.*, 2004). The high dopant concentration (>20%) is believed to facilitate the transformation of photoexcited charges to surface reactive sites during their lifetime by mixing up N 2p states with O 2p valence band (Lin *et al.*, 2005).

Photocatalytic degradation of *E. coli* in water

The development of new technologies has affected the design of disinfection systems in wastewater treatment plant. Historically, a chlorination and dechlorination system is the most commonly used disinfection method to kill pathogenic organisms. With increasing concerns about the potential toxicity of by-product trihalomethanes (THMs), such as the carcinogen chloroform (CHCl₃), alternative disinfection systems have been studied. UV/TiO₂ has been proposed as one of the best disinfection technologies, because no dangerous (carcinogenic or mutagenic) or malodorous halogenated compounds are formed. The effectiveness of TiO₂ in killing many organisms, including bacteria, fungi, algae and viruses, has received widespread attention in the last decade (Bekbolet, 1997; Butterfield *et al.*, 1997; Yeber *et al.*, 2000; Ibanez *et al.*, 2003; Kim *et al.*, 2003; Liu and Yang, 2003). However, research conducted on the photocatalytic disinfection of water using TiO₂ under sunlight is limited, due to the relatively low inactivation rate and resulting long contact times compared with conventional disinfection methods (Watts *et al.*, 1995). In the present study, N-doped TiO₂ nanoparticles were applied to investigate the possibility of using the solar light-induced bactericide for water treatment.

During control studies without solar light irradiation, viable *E. coli* cell counts were observed to be nearly identical to initial condition. As shown in Figure 3, cell counts decreased from 10⁹ CFU/mL to 10⁵ CFU/mL after two h with solar illumination only. Both Degussa P25 and N-doped TiO₂ showed capability of inactivating bacteria in aqueous solution during the reaction time course of 120 min. The initial cell counts for these two experimental runs were 10⁹ CFU/mL. At the end of reactions, the residual cell counts for *E. coli* were almost non-detectable when N-doped TiO₂ was used as the photocatalyst. The same amount of Degussa P25 caused a residual cell concentration of 10³ CFU/mL.

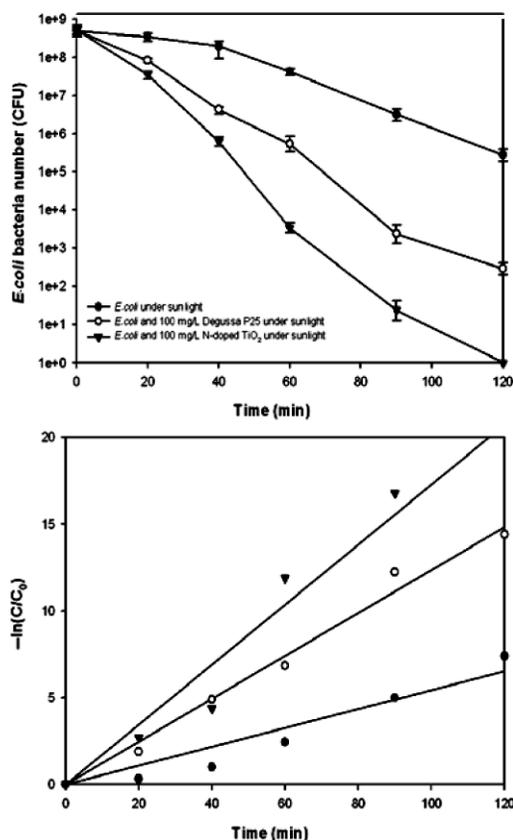


Figure 3 *E. coli* bacteria disinfection by Degussa P25 and N-doped TiO₂ nanoparticles under solar light with average light intensity 10 mW/cm²

This result indicates that N-doped TiO₂ provided more favourable photocatalytic inactivation than Degussa P25. The *E. coli* inactivation rate could be expressed by the first order reaction kinetics, as shown in Figure 3. Similar disinfection kinetics could be found in other studies (Watts *et al.*, 1995; Bekbolet and Araz, 1996).

It is well known that direct UV irradiation produces deleterious effects on bacteria cells, with the formation of double bonds in microorganisms to disrupt the replication process, as well as rupturing some DNA strands. However, high UV lamp costs limited the wide use of UV disinfection technology in the water and wastewater treatment industry. Efficient utilization of solar energy is undoubtedly one of the fundamental goals for the improvement of disinfection facilities. Results from this study explored the possibility of using N-doped TiO₂ for wastewater disinfection under direct solar light, which is especially important for small-scale treatment facilities in the field.

Photocatalytic degradation of AO7 in water

Since azo dyes are intentionally designed to resist degradation, it is very difficult to degrade them by conventional wastewater treatment methods. In addition, the toxicity, mutagenicity and carcinogenicity of azo dye degradation by-products are of great environmental concerns (Oh *et al.*, 1997). Doped TiO₂-based nanoparticles are materials that recently demonstrated enhanced photocatalytic efficiency when used with electron deficient model compounds such as methylene blue in water. The application of these

materials for relevant industrial dyes is an important step in order to establish semiconductor-based photocatalysis for environmental use (Liu *et al.*, 2005).

The decolourization kinetics of AO7 are given in Figure 4. All the degradation followed first-order kinetics. By plotting the logarithm of the normalized dye concentration against irradiation time, fairly good linear relationship was observed. Under solar light illumination, with average solar light intensity of 12 mW/cm^2 , AO7 decolourization could be achieved within 4h, while less than 5% of the colour was removed with Degussa P25 under identical conditions.

Experiments were also carried out to examine the degradation efficiency of N-doped TiO_2 and Degussa P25 under UV light irradiation with initial azo dye concentration of 20 mg/L and a catalyst loading of 10 mg/L . It is seen that 95% of the colour was removed after one hours irradiation, and complete decolourization of the AO7 was achieved within 2 hours using N-doped TiO_2 . The same experiment performed with Degussa P25 used four hours for 100% degradation of the AO7. The overall rate constants for AO7 decolourization in reciprocal hours are given as $K'_{\text{N-doped TiO}_2} = 3.22 \text{ hr}^{-1}$ and $K'_{\text{Degussa P25}} = 0.73 \text{ hr}^{-1}$ where K' denotes the first order rate constants under UV illumination. The result indicates that faster dye decolourization and higher catalytic activity can be achieved using N-doped TiO_2 . Although there was not as much photoactivity improvement as under the solar light illumination, N-doped TiO_2 showed higher photocatalytic activities under UV exposure compared to Degussa P25 particles. The better degradation efficiency of N-doped TiO_2 may be explained by the higher surface area created by the smaller diameter (10 nm) compared with the 30 nm average diameter in the Degussa P25 sample. In addition, N-doped TiO_2 is well crystallized with higher surface hydroxyl

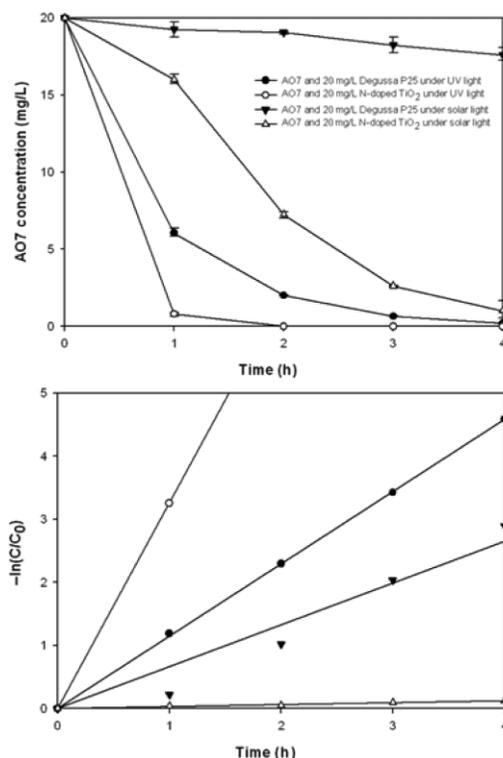


Figure 4 Decolourization of AO7 by Degussa P25 and N-doped TiO_2 nanoparticles under solar light with average light intensity 12 mW/cm^2 , UV light with average light intensity 80 mW/cm^2

group density, which also contributes to high catalytic activity, compared with Degussa P25.

Conclusions

This study demonstrates a novel approach for the efficient utilization of sunlight in wastewater purification through heterogeneous photocatalysis using nitrogen-doped TiO₂. The photodegradation properties of N-doped photocatalysts were demonstrated by its ability to inactivate *E. coli* and decolourize AO7 under both solar light and UV light. The nitrogen-doped titania nanoparticles showed significant improvement in reactivity compared with Degussa P25 particles, particularly in the visible light range. The superior photoactivity of doped nanocatalysts could be attributed to their smaller grain sizes, crystallinity, and improved visible light adsorption.

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