



## N-doped TiO<sub>2</sub> nanoparticles as a photocatalyst for photocatalytic oxidative desulfurization

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### **Abstract**

N-doped TiO<sub>2</sub> nanoparticles were synthesized via an ultrasonic assisted impregnation method using ammonium nitrate as nitrogen source. The prepared sample was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), UV-vis diffuse reflectance spectroscopy (UV-vis DRS). N doping caused narrowing the band gap of the TiO<sub>2</sub> and a red shift in the absorption edge was observed toward visible light. Photocatalytic oxidative desulfurization of dibenzothiophene (DBT) in model fuel under visible light irradiation and air bubbling was investigated using the N-doped TiO<sub>2</sub> nanoparticles as photocatalyst. N-TiO<sub>2</sub> nanoparticles exhibited satisfactory photocatalytic activity for DBT oxidation under visible light illumination which can be attributed to the successful doping on nitrogen in the TiO<sub>2</sub> framework.

**Keywords:** N-doped TiO<sub>2</sub>, photocatalyst, nanoparticles, PODS.

### **Introduction**

Air pollution and acid rain caused by sulfur oxides (SO<sub>x</sub>) have drawn considerable research interest and societal responsiveness. The emission from vehicle engine is recognized as a main source of SO<sub>x</sub> which is formed by oxidizing sulfide existing in gasoline and diesel [1]. Hydrodesulfurization (HDS) has been widely used in removing sulfur species, which requires high temperature (320–380 °C), high pressure (3–7 MPa) and expensive hydrogen gas. In addition, it is difficult to meet the requirement for deep desulfurization (<50 ppm), since dibenzothiophene (DBT) and its derivatives such as 4,6-dimethyl dibenzothiophene (4,6-DMDBT) are strongly stable under hydrogenation [2].

Alternative methods including oxidative desulfurization (ODS), extractive desulfurization (EDS), biodesulfurization (BDS) and adsorption have been used to remove sulfur species from fuel oil. Among them, photocatalytic oxidative desulfurization (PODS) is considered to be one of the most promising desulfurization methods because of its mild reaction conditions and high efficiency. In PODS, refractory sulfur compounds are oxidized to their corresponding polar compounds (sulfoxides or sulfones), which can be easily removed from the fuel by solvent extraction or adsorption [3]. Hydrogen peroxide, air, and O<sub>2</sub> have been used as oxidant under ultraviolet (UV) irradiation with TiO<sub>2</sub> as photocatalyst for PODS [4].

TiO<sub>2</sub> has attracted massive research interests on photocatalytic reactions over the past decades. However, the process only works under UV light irradiation instead of sunlight due



to the wide band gap of TiO<sub>2</sub>. To utilize sunlight efficiently, TiO<sub>2</sub> photocatalysts must be responsive to visible light, which is the strongest output range of sunlight. Motivated by developing the photocatalyst that is capable of absorbing visible light, introduction of nonmetals (such as N, C, F, I, B, and S) into TiO<sub>2</sub> for narrowing its wide band gap and doping of metals (such as Fe, Mn, Cu, W, and V) into TiO<sub>2</sub> are the mainstream approaches. Compared to the other nonmetal elemental doping, N-doped TiO<sub>2</sub> materials exhibit a significant photocatalytic activity and strong absorption in the various reactions under visible light irradiation, where both of the N impurity and Ti<sup>3+</sup> act cooperatively to narrow the band gap of N-doped TiO<sub>2</sub> [5, 6].

In the present study, N-doped TiO<sub>2</sub> nanoparticles were synthesized via an impregnation method assisted by ultrasonic irradiation starting from the TiO<sub>2</sub>-P25 precursor and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) as nitrogen source. The prepared nanoparticles were used as photocatalyst for the PODS. The photocatalyst was characterized by XRD, FE-SEM, and UV-vis DRS. DBT oxidation in model fuel was investigated using the synthesized nanophotocatalyst under visible light irradiation and air bubbling as oxidant.

### ***Experimental materials***

Commercial TiO<sub>2</sub>-P25 was purchased from Degussa Evonik Company as TiO<sub>2</sub> source for preparation of N-doped TiO<sub>2</sub> nanoparticles. NH<sub>4</sub>NO<sub>3</sub> and DBT were supplied by Merck (Germany). *n*-decane was provided from Daejung Company. The deionized water was used for the catalyst synthesis.

### ***Catalyst preparation***

N-doped TiO<sub>2</sub> nanoparticles were prepared by ultrasonic assisted direct impregnation reaction of TiO<sub>2</sub>-P25. Certain amount of NH<sub>4</sub>NO<sub>3</sub> was dissolved in deionized water under magnetic stirring. Then, TiO<sub>2</sub>-P25 was added to the solution and vigorously stirred. Subsequently, the suspension was sonicated. The obtained stable suspension was dried at 100 °C in an oven for 24 h. Finally, it was crushed and calcined in air at 400 °C for 1 h. The obtained light yellow nanopowders were named N-TiO<sub>2</sub>. As prepared, N-TiO<sub>2</sub> nanoparticles were used for characterization and photocatalytic oxidative desulfurization.

### ***Characterization***

X-ray diffraction (XRD) patterns of the catalysts were obtained using Cu K $\alpha$  radiation ( $\lambda=1.541874$  Å) in the range of 10-80° for 2 $\theta$  angle at 40 kV and 30 mA (Equinox 3000, Inel, France). The crystalline structure of the nanoparticles were determined by XRD. The morphological study of the samples was carried out using field emission scanning electron microscope (FE-SEM, Hitachi S4160). The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was conducted using a Cary-50 Scan UV-vis spectrophotometer (Varian, USA) for the optical characterization of photocatalysts.

### ***Photocatalytic oxidative desulfurization***

Photocatalytic reaction was conducted in a pyrex reactor equipped with a circulating water jacket. Water circulation through the water jacket cooled the reaction media and kept the temperature at 25 °C. A xenon lamp was placed above the model fuel in the reactor as the visible light source. Air was introduced into the model fuel with a glass distributor to supply oxygen during photocatalytic reaction and to ensure perfect mixing. The diesel model fuel was made by dissolving DBT in *n*-decane with 300 ppmw DBT content. 25 mL of model fuel



and 75 mg of photocatalyst were placed in the reactor. The suspension was stirred in the dark for 1 h with magnetic stirrer to achieve adsorption-desorption equilibrium. Then the xenon lamp was turned on. The suspension was irradiated for 4 h under constant stirring and air bubbling. To determine the DBT concentration in the model fuel, the samples were collected and filtered using a 0.2  $\mu\text{m}$  membrane syringe. After filtering, the samples were analyzed by a gas chromatograph (Agilent 6890N, HP5 capillary column) with a flame ionization detector and helium gas as carrier.

### Results and discussion

Fig. 1 shows the XRD patterns of the synthesized N-TiO<sub>2</sub>. As shown in Fig. 1, both anatase and rutile phases exist in the N-TiO<sub>2</sub> while anatase is the dominant phase. It is reported that the presence of the mixed phases (anatase and rutile) in TiO<sub>2</sub> can prevent the recombination of photogenerated electrons and holes resulting in photocatalytic activity enhancement [7]. Therefore, the conformity of N-TiO<sub>2</sub> crystalline phase with TiO<sub>2</sub>-P25 can be beneficial for the N-TiO<sub>2</sub> photocatalytic activity. As shown in Fig. 1, the sharp peaks reveal the high crystallinity of N-TiO<sub>2</sub>. It seems the high crystallinity of this catalyst and its anatase dominant crystalline phase can make it suitable for photocatalytic activity.

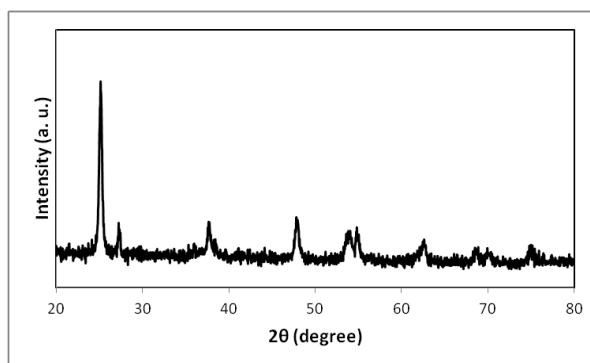


Fig. 1. XRD pattern of N-TiO<sub>2</sub>

The FE-SEM image of N-TiO<sub>2</sub> is illustrated in Fig. 2. It can be observed that doped TiO<sub>2</sub> display a spherical morphology and its particle size ranges between 30-70 nm.

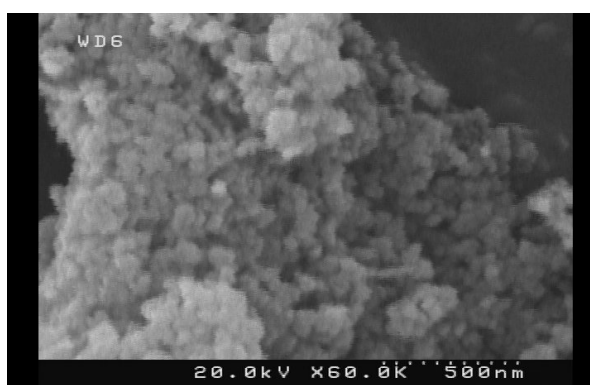


Fig. 2. FE-SEM image of N-TiO<sub>2</sub>

The optical absorption properties of the N-doped TiO<sub>2</sub> nanoparticles are investigated as the most important parameters in determining their photocatalytic activity in the visible light region. The UV-vis diffuse reflectance spectra of the N-TiO<sub>2</sub> shown in Fig. 3. The results



demonstrate that the absorbance for the N-TiO<sub>2</sub> is extended in the visible light region. The N-TiO<sub>2</sub> light absorbance in the visible light region is due to inclusion of the nitrogen in the TiO<sub>2</sub> lattice. The extension of absorption to the visible region is consistent with the light yellow color of the N-doped TiO<sub>2</sub>. In order to determine the band gap energy of the photocatalyst, reflectance [F(R)] spectra using Kubelka–Munk formalism and Tauc plot was employed for the photocatalyst. Using the Tauc plot of  $[F(R).hv]^n$  vs.  $hv$  where  $hv$  is the photon energy and  $n = \frac{1}{2}$  for direct band gap of the photocatalyst, the linear region of the plot was extrapolated to intersect on the photon energy axis to deduce the band gap energy of the photocatalyst [8]. The band gap energy was calculated as 2.85 eV. The band gap energy of N-doped TiO<sub>2</sub> is lower than that of TiO<sub>2</sub>-P25 (3.1 eV) [6]. For the yellow color N-TiO<sub>2</sub> nanoparticles with the band gap of 2.85 eV, the successful incorporation of nitrogen into the TiO<sub>2</sub> structure leads to a decrease in the band gap energy and increase in the absorbance of visible light, which is due to the formation of a new energy level above the valence band of TiO<sub>2</sub> [9]. Decrease in the band gap energy increases the absorbance in the visible region and indicates that the electron–hole pairs can be generated with N doping of the TiO<sub>2</sub>, which can increase the photocatalytic activity of N-doped TiO<sub>2</sub>.

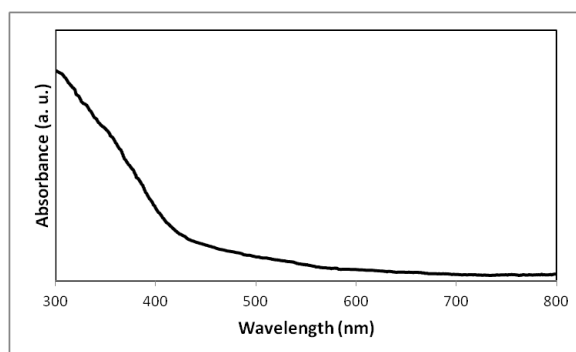


Fig. 3. UV–vis diffuse reflectance spectra of N-TiO<sub>2</sub>

The photocatalytic activity of the N-TiO<sub>2</sub> and TiO<sub>2</sub>-P25 nanoparticles for PODS of DBT were investigated. Photocatalytic activity of the TiO<sub>2</sub>-P25 and N-TiO<sub>2</sub> nanoparticles for DBT oxidation under visible light irradiation for 4 h are illustrated in Fig. 4. It is observed that the photocatalytic activity of N-TiO<sub>2</sub> for DBT oxidation is much higher than that of the TiO<sub>2</sub>-P25. The negligible activity of TiO<sub>2</sub>-P25 under visible light irradiation leads to a low DBT conversion. The DBT conversion using TiO<sub>2</sub>-P25 and N-TiO<sub>2</sub> after 4 h reaches 13.1% and 48.9%, respectively. It can be seen that DBT conversion with N-TiO<sub>2</sub> is about 3.7 times higher than that of TiO<sub>2</sub>-P25.

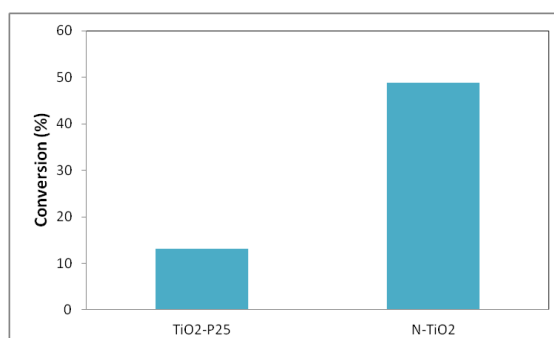


Fig. 4. DBT conversion under visible light irradiation



The effect of the nitrogen on enhancement of photocatalytic activity of the N-TiO<sub>2</sub> can be investigated by understanding the photogeneration of electron-hole pairs and their behavior in the photocatalyst. Nitrogen doping forms a new N 2p energy level above the valence band of the TiO<sub>2</sub> that increases the visible light absorption in the reaction suspension and promotes the generation of electrons and holes. Therefore, enhancement in the photocatalytic oxidation of DBT occurs under the visible light irradiation.

In the N-doped TiO<sub>2</sub>, electrons can be transferred from the N 2p energy level to the conduction band under visible light irradiation; therefore, electrons and holes are generated in the conduction band and N 2p state, respectively. The photoinduced holes in the N 2p state can be utilized for oxidation of the adsorbed DBT on the catalyst surface [10]. Meanwhile, the holes can oxidize hydroxyl groups on the catalyst surface to produce ·OH radicals. Hydroxyl radicals, as the principal oxidant in photo-oxidation reactions, have a decisive efficacy in the DBT oxidation. Therefore, the presence of more hydroxyl radicals is beneficial for photocatalytic performance [11]. The photoexcited electron can be trapped by adsorbed oxygen on the surface of catalyst which leads to produce superoxide anion radicals (·O<sub>2</sub><sup>-</sup>). superoxide anion radicals are important oxidant in DBT photocatalytic oxidation. The presence of oxygen not only leads to produce the hydroxyl and superoxide anion radicals, but it also results in preventing photogenerated charges recombination which causes a significant enhancement of the N-doped TiO<sub>2</sub> photocatalytic activity. The recombination of the photogenerated electron-hole pairs suppresses the generation of ·OH radicals which results in the decrease in DBT oxidation.

### **Conclusions**

N-doped TiO<sub>2</sub> nanoparticles were synthesized via a an impregnation method which was assisted by ultrasonic irradiation from TiO<sub>2</sub>-P25 and ammonium nitrate precursor. The absorbance for the N-TiO<sub>2</sub> is extended in the visible light region, which resulted in the enhancement of the visible light absorption. The N-TiO<sub>2</sub> photocatalyst exhibited efficient photocatalytic activity for DBT oxidation under the visible light irradiation compared with the TiO<sub>2</sub>-P25. Decrease in the band gap energy increases the absorbance in the visible region and indicates that the electron-hole pairs can be generated with N doping of the TiO<sub>2</sub>, which can increase the photocatalytic activity of N-doped TiO<sub>2</sub>.

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