Chemically Synthesized Mesoporous Nitrogen-Doped TiO_2 and its Application to High Efficiency Dye-Sensitized Solar Cells

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Abstract

Nanosize mesoporous nitrogen-doped TiO_2 (N-doped TiO_2) has been synthesized by the sol gel method. The Hydrolysis approach for N-substituted titanium isopropoxide precursors has been proved with incorporation of nitrogen into the TiO_2 matrix, which involves the direct binding of N to the central Ti ion. The light absorption onset shifts to the visible region at 550 nm with N-doped TiO_2. The substitution of oxygen sites with nitrogen atoms in the titania structure was confirmed by X-ray photoemission spectroscopy (XPS). A clear decrease in the band gap of N-doped TiO_2 (compared to Degussa P25) is deduced from the optical absorption spectroscopy results. Application of synthesized nanocrystalline N-doped TiO_2 to dye-sensitized solar cells resulted in 7.5% overall conversion efficiency, which was higher than the Degussa P25.

Keywords: dye-sensitized solar cells, N-doped, conversion efficiency

1. Introduction

Fossil fuels have supported the energy needs of our world. However, they pose several drawbacks since fossil fuels are nonrenewable, cause many environmental problems, and are likely not to continue to remain abundant for the next generations. Therefore, the search for alternative renewable energy technologies is of crucial importance for the sustenance and development of modern society [1]. One of the possible solutions to the energy challenge is to make efficient use of solar energy, which is abundant, long lasting, and clean. Solar cells are a large area of interest in solar energy utilization because they can directly convert solar energy to electricity.

A new type of solar cells developed by O’Regan and Grätzel in 1991, dye-sensitized solar cells (DSSCs), have been attracting much attention over the last decade as a potential low-cost alternative to commercial solar cells based on silicon, due to their ease of fabrication and high photoconversion efficiencies [2-5]. Despite low-cost, their system had a light-to-electricity conversion efficiency of around 12%, a level that is not easily obtained [6].

It is necessary to further improve the energy conversion efficiency in order to comercialize DSSC successfully. Many methods for improving the conversion efficiency of the DSSC have been attempted [7-10]. Some considerable efforts have been devoted to find the most efficient, dyes to increase the efficiency but effort to modify titania as the most efficient support for the dye has been overlooked.

Nanoparticle TiO_2 and thin film TiO_2 are easily produced, inexpensive and show good stability under illumination in most environments [11-13]. However, a major disadvantage for solar energy applications is that the bandgap energy, around 3 eV, only allows altraviolet (UV) absorption. To improve the photoelectrochemical efficiency of the material, it is desirable to red-shift the photoelectrochemical onset to also include the less energetic but more intense visible part of the solar spectrum. Traditionally, this has been achieved by anchoring organic dyes as sensitizers, which are usually Ru(II) complexes, to harvest the visible light [2,9]. Although this method broadens the range of the visible light response effectively, a problem appears with organic dyes. They can detach from the surface when employed in aqueous solution and the long term stability of many dyes can be questioned. In addition, the semiconductors usually use pure TiO_2 in which there is some oxygen deficiency in the crystal structure [14-17]. It is known that oxygen deficiency can create electron-hole pairs and that the oxidizing holes can either react with the dye or destroy it and/or it is scavenged by iodide ions [18], so the lifetime of the dye-sensitized solar cell may be shortened. Therefore, there is a need to increase the DSSC efficiency and stability by other approaches.

In this paper, we report a sol gel method for synthesizing nitrogen-doped (N-doped) TiO_2 and its application to the DSSC system to enhance the efficiency of the solar cell, due to the replacement of oxygen-deficient titania by visible-light-active N-doped TiO_2.

2. Experimental Section

2.1. Materials

Titanium Tetra Isopropoxide, Ti $(OPr)_4$, 97% and acetylacetone were purchased from Aldrich. Dodecylamine 98 % and TritonX-100 were purchased from Fluka. Ethanol absolute and CH_3COOH were obtained from Merck. All materials were used as received. Di-tetrabutylammonium cis-di(isothiocyanato)bis (2,2’-bipyridyl-4,4’-dicarboxylato) Ru(II) (N719 dye), Electrolyte EL-HSE, TEC 15 electrode glass plate, and Pt-coated counter electrode are commercial products of Dyesol (Australia).

2.2. Synthesis of N-doped TiO_2

For a typical synthesis of the N-doped TiO_2 powders, a mixture of 3 mL of $Ti(OPr)_4$, 5 mL dodecylamine, and 80 mL of ethanol absolute solution was stirred for 4 hours at 70°C to provide a clear solution. This precursor solution was then cooled to room temperature and 5 mL of CH_3COOH was added to neutralize the excess dodecylamine. The hydrolysis process was then achieved by adding 20 mL of distilled water dropwise into the solution under vigorous stirring. The solution was continuously stirred for 24 hours. The resulting yellowish precipitate was centrifuged and washed subsequently with distilled water and ethanol. Finally, the N-doped TiO_2 was vacuum-dried for 12 h. The surfactant from the as-made N-doped TiO_2 powders was removed by calcining at a heating rate of 2°C/min in air atmosphere for 4h at 200, 300, 400, 450, 600 and 800°C.

2.3. N-doped TiO_2 thin film preparation

N-doped TiO_2 powder (2g) was mixed with 4 mL deionised water, 10 μL of acetylacetone and 50 μL of Triton X-100 in stepwise addition into a porcelain mortar to make slurries. The mixtures were ground until no lumps were observed. Then, using Scotch adhesive tape (as the spacer) to make a 0.25 cm^2 active area, the slurries were deposited on electrode glass by a doctor blade technique. Before sintering at 400°C (heating rate of 20°C/min) for 30 min, the films were dried in air at room temperature for 10 min, and heated at 50°C for 10 min. For comparison a Degussa P-25 (Nippon Aerosil Co., Ltd.) thin film was made through a similar way.

2.4. Characterization

The structure of the N-doped TiO_2 powder was examined with an X-Ray powder diffractometer (XRD, Shimadzu) with Cu Kα radiation (λ = 0.15406 nm), X-ray photoelectron spectroscopy (XPS, PHI-5300), and N_2 adsorption-desorption measurements at 77 K (NOVA Quantachrome). UV-visible diffuse reflectance spectra were obtained for N-doped TiO_2 using a UV-visible spectrophotometer (UV-2550, Shimadzu).

2.5. DSSC fabrication

To fabricate the DSSCs, the N-doped TiO_2 electrodes were immerse in a 0.3mM solution of N719 dye in acetonitrile overnight. Cells were assembled by placing the Pt-counter electrode (CE) over the active area of N-doped TiO_2 working electrode. The electrolyte was introduced through a drilled hole on CE by capillary action, the hole was then sealed. For comparison, DSSCs based on Degussa P25 thin film working electrode were also fabricated under the same conditions.

2.6.Current-voltage Measurement

Current-voltage measurements were done using a 450 W Xe lamp that was focused to provide 1000 W/m^2, equivalent to one sun at AM 1.5, at the surface of the cells. The spectral output of the lamp was matched in the region 350 – 800 nm with the aid of a Schott KG-5 sunlight filter so as to reduce the mismatch between the simulated and the true solar spectrum to less than 2%. The current-voltage characteristics of the cells were determined by biasing the cells externally and measuring the generated photocurrents. The overall photoconversion efficiency η is calculated from the integral photocurrent density (J_{sc}), the open circuit photocurrent (V_{oc}), the fill factor of the cell (ff), and the intensity of incident light (I_s) using the formula:

$$\eta = J_{SC} V_{OC}\, ff / I_S \tag{1}$$

I_s = 1000 W/cm^2 at air mass (AM) 1.5, or under full sunlight. Fill factor (ff) is given by:

$$ff = V_{\max} I_{\max} / (J_{SC} V_{OC}) \tag{2}$$

2.7. Photodegradation of Methylene Blue

The photocatalytic activity of the N-doped TiO_2 was determined by measuring the decomposition of methylene blue (MB) under the irradiation with visible light (>400 nm). A 150 W high-pressure Xenon arc lamp was used as light source. The concentration of methylene blue (MB) was determined by measuring the absorbance of the MB solution in a Shimadzu UV-Vis spectometer. For comparison, a photocatalytic reaction was also carried out using commercial titania (Degussa P25) nanoparticles.

3. Result and Discussion

Nanocrystalline N-doped TiO_2 has been successfully synthesized through hydrolysis sol gel methods involving the direct binding of N to the central Ti ion. In the synthesis the nitrogen has been doped into the lattice and/or attached to the nanoparticle surface. However, at the same time, there is water and organic residue adsorbed on the surface and enclosed into the amorphous and porous N-doped TiO_2 powder. Appropriate sintering removes most of organic residues on the surface and retains sufficiently high N-doping levels in the resulting nanosize particles.

The crystal structures of the synthezised N-doped TiO_2 were studied by X-ray powder diffraction (XRD), as shown in Figure 1. It is found that N-doped TiO_2 nanoparticles are amorphous when sintered at temperatures below 400^{o}C. The XRD patterns of N-doped TiO_2 calcined at 400^{o}C correspond to the anatase TiO_2. The anatase phase has been transformed to rutile after increasing the calcination temperature to 600^{o}C. It can also be seen from the XRD patterns that the N-doped TiO_2 samples show a broad peak, which indicates the formation of nanoparticles. Following the Debye-Scherrer formula, it is calculated that the particle size is around 7–10 nm.

The above results show that the properties of the N-doped TiO_2 change with calcining temperatures. The substitution of the oxygen sites with nitrogen atoms in the titania structure was confirmed by X-ray photoemission spectroscopy (XPS), as shown in Figure 2. The nitrogen 1s core level of N-TiO_2 shows three peaks at 396.0, 399.4 and 400.5 eV, which is consistent with the reported results for N-TiO_2. The two peaks at higher binding energies may be attributed to molecularly adsorbed nitrogen species, whereas the peak at 396 eV was assigned to the substitutionally bound N^- species in the TiO_2 lattice [19]. Irie *et.al.* [20,21] and Diwald *et.al.* [22,23] reported that the peak at 396 eV in the XPS spectra was attributed to a chemically bound N^- species within the crystalline TiO_2 lattice. Most N species in the N-TiO_2 exist in the form of nitrides such as N in the O-Ti-N linkage, corresponding to the binding energy (BE) of 399.4 eV, while only small amounts of N are present in the form of surface adsorbed ammonia, with the BE located at 396.0 eV.

Figure 3 shows the typical nitrogen isotherm of N-doped TiO_2 spheres. It exhibits a type-IV isotherm curve with an H2 hysteresis loop according to IUPAC classification [24], which means the spheres have mesoporous structure. The N-doped TiO_2 shows a high BET surface area of $142m^2/g$ because of the mesoporous structure and the large amount of nanometer crystallites.

The optical absorbance and reflectance was used to study the capability to photosensitize the TiO_2 nanoparticles. The absorbance shift of the N-doped TiO_2 NPs can be observed from the reflectance spectra of undoped (Degussa P25) and N-doped TiO_2 NPs in Figure 4. The yellowish N-doped TiO_2 sphere powders show good absorbance of visible light. It can be seen from Figure 5 that the visible light absorption is high and extended up to 550 nm in the case of N-doped TiO_2 calcined at 450^{o}C, compared to that of pure TiO_2 which could only absorb light in the UV range. It may be because nitrogen species occupy some of the oxygen positions in the lattice. This also rules out the occupancy of N in any other positions such as interstitial sites, which should give rise to a mid gap band/level between valence and conduction bands.

Figure 5 shows the current-voltage curves of the open cells based on the N-doped TiO_2 and Degussa P25 photoelectrodes. A pronounced increase in the photocurrent for the DSSC, based on the nitrogen-doped titania was observed. The performance properties of the DSSCs are summarized in Table 1. A high-energy conversion efficiency of 7.5% was achieved, which was 25% higher than that of the P25, The high number of Voc indicated that the instruments needed to be more accurately calibrated.

It is assumed that occurrence of visible light absorption due to the nitrogen-doped titania support intrinsically increases the efficiency value, due to the photoresponse of N-doped TiO_2 in the visible light region, which is also supported by the results reported by Lindgren *et al.* [19]. They have demonstrated that the photo-induced current due to the visible light activity of the best nitrogen-doped titania electrode, prepared by reactive DC magnetron sputtering, can be increased significantly by approximately 200 times over those of the undoped titania electrodes. On the basis of these results, it can be expected that the optimization of the amount of nitrogen doping in titania nanoparticles and electrode can further improve the performance of the DSSCs.

The photocatalytic activity of N-doped TiO_2 and Degussa P25 samples have also been studied by measuring the percentage decomposition of methylene blue (MB) aqueous solution. It can be seen from Figure 6 that the photocatalytic activity of N-TiO_2 (calcined at 450^oC) sample shows higher activity to that of Degussa P25 catalyst in the visible region. The enhanced photocatalytic activities of N-TiO_2 in the visible region may be due to the increase of the surface deficiency after the introduction of nitrogen into the TiO_2 structure [15], which could be the evidence to confirm the role of nitrogen in the lattice for improvement of the visible-light response of N-TiO_2 (Figure 4).

4. Conclusion

N-doped TiO_2 nanocrystalline materials were successfully synthesized by a novel sol gel method. Three binding energy peaks were observed at 396.0, 399.4 and 400.5 eV in the N 1s region of the XPS. A new absorption edge was observed for the UV-vis spectrum of the nitrogen-doped TiO_2 in the visible light region. The action spectrum of the DSSC based on the N-doped TiO_2 was in agreement with the corresponding optical spectrum. A high energy conversion efficiency was achieved successfully for the DSSC, based on the N-doped nanocrystalline titania electrode.

5. Acknowledgement

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6. References

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Table 1: Performance properties of the DSSCs, based on N-doped TiO_2 and Degussa P25

Performance Measure	N-doped TiO_2 DSSC	Degussa P25 DSSC
J_{sc} (mA/cm^2)	12.8	10.86
V_{oc} (V)	0.95	1.1
I_{max} (mA/cm^2)	11.4	8.4
V_{max} (V)	0.74	0.82
Ff (%)	0.61	0.58
η (%)	7.5	6.8

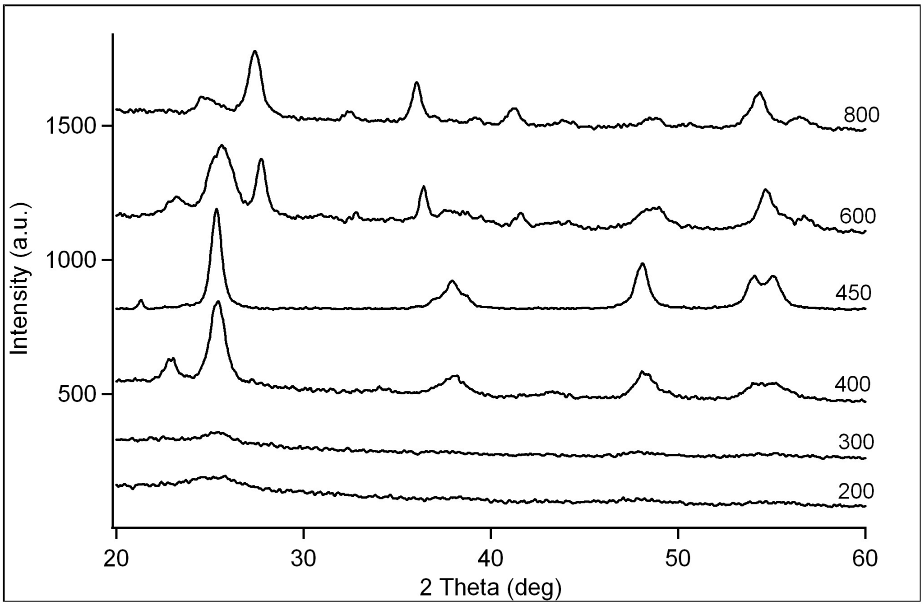

Figure 1 XRD Spectra of N-doped TiO_2 after calcination at (a) 200; (b) 300; (c) 400; (d) 450; (e) 600 and (f) 800 °C

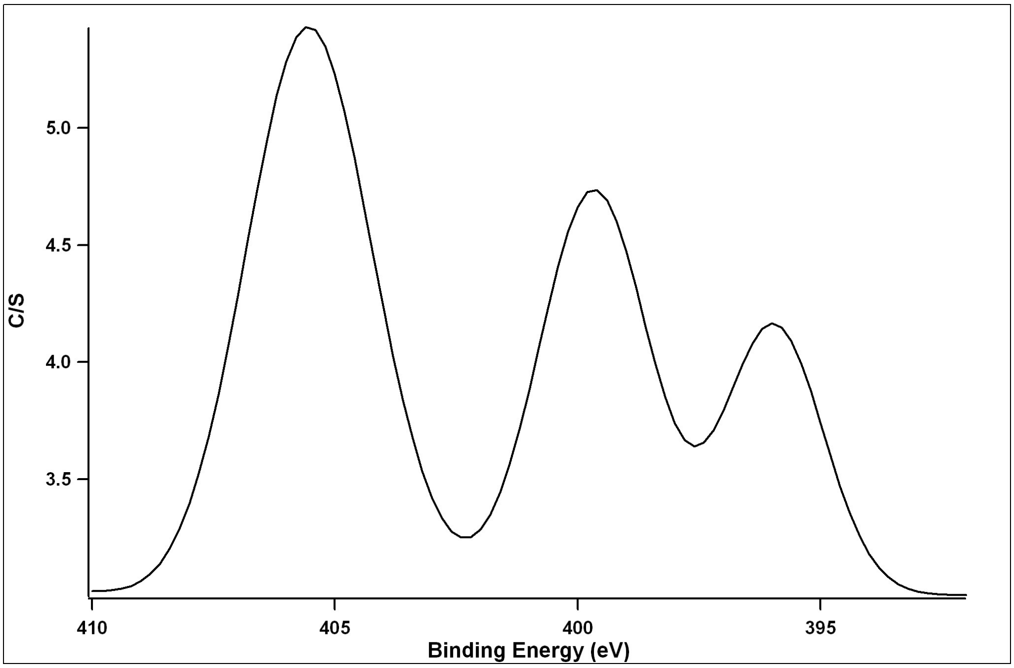

Figure 2 Nitrogen 1s XPS of N-doped TiO_2 calcined at 450 ^{o}C

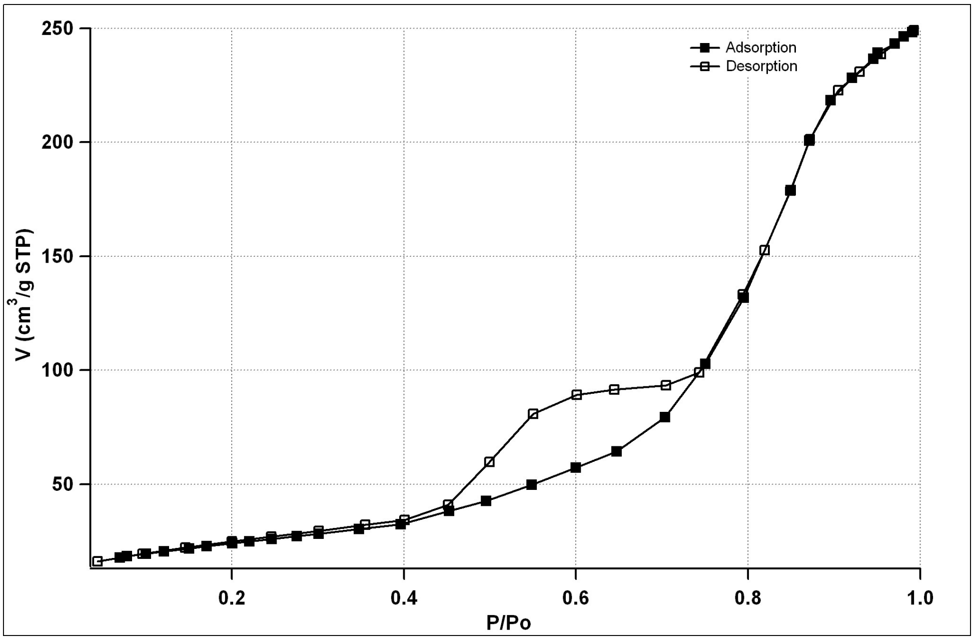

Figure 3 Isotherm curve of N-doped TiO_2

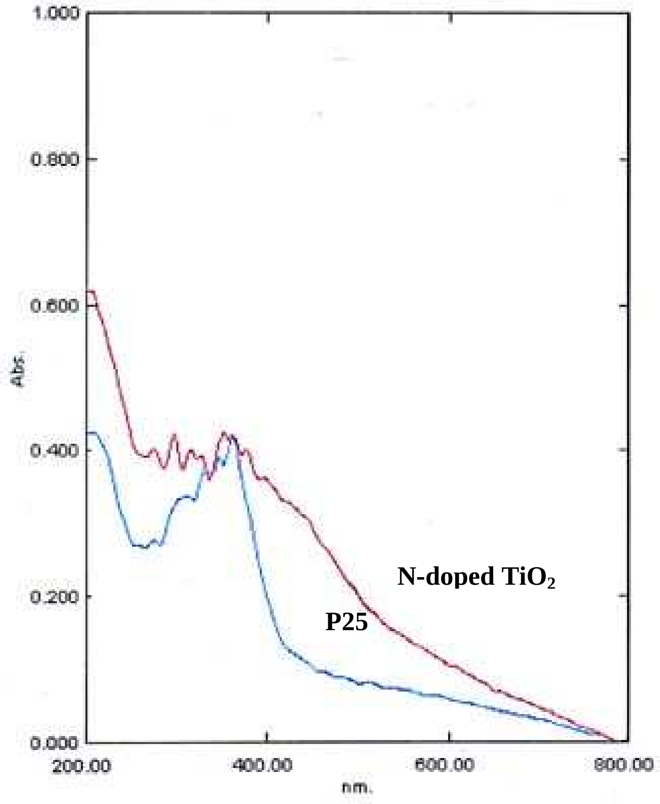

Figure 4 DRUV Spectra of N-doped TiO_2 compared to Degussa P25

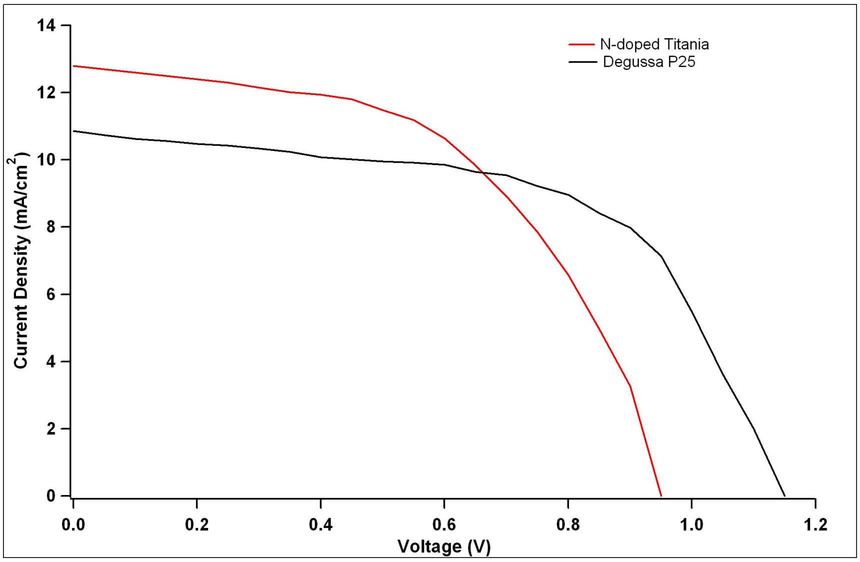

Figure 5 Current-voltage curves of the dye-sensitized cell, based on the N-doped TiO_2, and Degussa P25

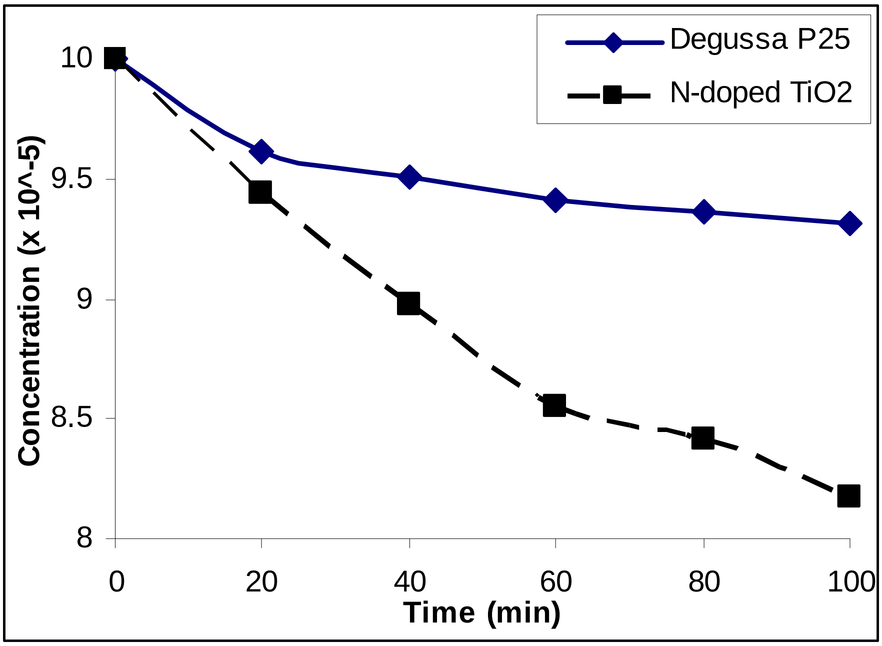

Figure 6 Photodegradation of Methylene Blue