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Synthesis, Characterization, Electronic Structure, and Photocatalytic Activity of Nitrogen-Doped TiO_2 Nanocatalyst

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Nitrogen-doped TiO_2 (N−TiO_2) nanocatalyst with spherical shape and homogeneous size has been synthesized through a chemical method using $TiCl_3$ as precursor. The light absorption onset shifts from 380 nm on pure TiO_2 to the visible region at 550 nm with N−TiO_2. A clear decrease in the band gap and the nitrogen 2p states on the top of the valence band on N−TiO_2 (compared to TiO_2) is deduced from the optical absorption spectroscopy results. The chemical nature of N has been evolved as N−Ti−O in the anatase TiO_2 lattice as identified by X-ray photoelectron spectroscopy (XPS). Photocatalytic decomposition of methylene blue has been carried out both in the UV and in the visible region and N−TiO_2 shows higher activity than the Degussa P25 TiO_2 photocatalyst in the visible region.

1. Introduction

Recently, the anion-doped TiO_2 has attracted considerable attention due to its photocatalytic activity in the visible region.[1,2] Even though TiO_2 is a promising photocatalyst for the wastewater purification,[3] exploitation for practical circumstances has not been achieved as expected, due to its poor light absorption in the visible region. Attempts have been made to improve the utility of TiO_2, by shifting its onset absorption from the UV to the visible region. Various noble/transition metal (or) metal ions have been doped into the TiO_2 lattice and the photocatalytic activity has been studied,[4,5] but none of them gave satisfactory results. Even though the visible light response of anion-doped TiO_2 was discovered in 1986 by Sato,[6] the recent work by Asahi et al.[7] has rekindled a great interest in TiO_2 as a visible light photocatalyst. Consequently, in recent years, a few preparation methods have been reported in the literature for N-, S-, P-, F-, and B-doped TiO_2 catalyst.[7−11] In parallel, some theoretical calculations have also been performed to suggest that anion doping of TiO_2 has considerable effect on the band gap alteration.[7,9,12] Subsequently, N-doped TiO_2 (N−TiO_2) has been prepared by a variety of methods such as sputtering, ion implantation, chemical vapor deposition, sol−gel, oxidation of TiN, and decomposition of N-containing metal organic precursors.[13−24] The photocatalytic activities of such N-doped systems have been studied.[18−20]

Considerable success has been achieved in increasing the photocatalytic activity by decreasing the band gap with N−TiO_2,[6,7,11,13−24] due to either mixing of nitrogen 2p states with O 2p states on the top of the valence band or a creation of N-induced mid-gap level. The success in producing N−TiO_2 provides good opportunities for various applications such as oxidation of CO, ethanol, acetaldehyde, and NO_x removal at room temperature as well as the decomposition of dyes such as methylene blue.[7,13,22] However, there seems to be no consensus among the reports[7,11,13,17,21−24] about the

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state of doped nitrogen in the N−TiO_2 lattice and hence the mechanism of band gap reduction. XPS analysis of N−TiO_2 shows the N 1s core level at a binding energy (BE) between 396 and 397 eV and claimed the state of nitrogen to be either nitrogen anion (N^-)[17] or atomic β N atoms,[7,13,21] as explained in the oxidation of TiN.[25] Additional N 1s peaks on N−TiO_2 were observed at 400 and 402 eV and are attributed to chemisorbed N_2 or adsorbed organic impurities.[7,13,25] Sakthivel and Kisch[11] observed no anionic-like nitrogen species around 396 eV, rather a N 1s peak at 404 eV attributed to hyponitrite type nitrogen. Valentin et al.[23] recognized the above controversy in the assignment of N 1s XPS results. They observed N 1s core level at 400 eV and hinted at a lower valence state for N. However, recently, Burda et al.[22] observed a N 1s core level at 401.3 eV from the detailed XPS investigations of nano N−TiO_2 and suggested that there is N−Ti−O bond formation due to nitrogen doping and no oxidized nitrogen is present. It is to be noted that the preparation procedure adopted was different in the above cases and this could lead to the different observations in XPS. In this paper, a simple and new chemical preparation method for N−TiO_2 has been adapted and its photocatalytic activity in the decomposition of methylene blue under UV and visible radiation has been studied. The results are compared with that of Degussa P25 catalyst and pure anatase TiO_2. Clear N 2p states on the top of the valence band could be identified and the consequent band gap reduction. The state of N to be more like an anion is demonstrated in the XPS results.

2. Experimental Section

For the typical synthesis of the N-doped TiO_2 powders, 50 mL of 15% titanium trichloride (48.6 mmol) was mixed with 50 mL of Na_2S solution (51.2 mmol). The pH of this acidic solution was adjusted to 8.5 by slow addition of diluted NH_3 solution. The precipitate formed at this pH was continuously stirred for 4 h. The precipitate was filtered and washed with double distilled water until the filtrate was free from chloride and sulfide ions. The oxide was calcined at different temperatures, viz., 400, 500, and 600 °C, for 4 h in air. Pure TiO_2 was also prepared by a similar procedure without the addition of Na_2S solution.

UV−visible absorption spectra were recorded using a Cary 5E UV−Vis−NIR spectrophotometer in the spectral range of 200−800 nm. The absorption spectra for the samples were recorded as a Nujol paste. Powder X-ray diffraction patterns of the TiO_2 samples were recorded in a Shimadzu XD-D1 diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). The chemical nature of N in TiO_2 has been studied using X-ray photoelectron spectroscopy (XPS) in a VG Microtech Multilab ESCA 3000 spectrometer with non-monochromatized Al Kα X-ray ($h\nu = 1486.6$ eV). The catalyst pellet surface was scraped in situ to remove any surface contamination that could arise from atmospheric components such as water and CO_2. The energy resolution of the spectrometer was set at 1.1 eV at a pass energy of 50 eV. BE was calibrated with respect to Au $4f_{7/2}$ core level at 83.9 eV.[26] Specific surface area and pore volume of the samples were estimated from N_2 adsorption at 77 K using a SORPTOMETRIC (Model 1990) instrument. Prior to adsorption of N_2, the samples were degassed at 423 K for 12 h. Transmission electron micrographs (TEM) were recorded with a JEOL-JEM 100SX microscope, working at a 100 kV accelerating voltage.

Photocatalytic decomposition of methylene blue was performed on these materials using a quartz reactor with a water circulation facility at the outer wall of the reactor and with the specific outlet for the sample collection. For a typical photocatalytic experiment, 25 mg of catalyst was added to 25 mL of aqueous solution containing ∼110 ppm methylene blue solution and the solution was irradiated using a 400 W Hg lamp (ORIEL Corporation, USA). The experiments were carried out separately, at four different wavelengths, namely, 365, 405, 436, and 546 nm, using the monochromatic filters (Oriel) for 30 min duration. After recovering the catalyst by centrifugation, the light absorption of the clear solution was measured at 662 nm (λ_{max} for MB). The photocatalytic activity was compared with those using Degussa (P25) and pure TiO_2 (anatase) prepared in the laboratory.

3. Results and Discussion

The addition of Na_2S solution during the catalyst preparation is essential for N-doping in the TiO_2 lattice. The addition of Na_2S solution increases the ionic strength of the medium and it also induces an in situ formation of transient $(NH_4)_X$-TiS_X complex, which on slow hydrolysis results in the N−TiO_2 nanoparticles. In addition, the presence of Na_2S might be effective in purging any dissolved oxygen by H_2S and thereby contributing to the N-doping in a reductive solution atmosphere. It has been confirmed by the blank experiments, by following the above procedure, but without Na_2S addition the resultant material is pure TiO_2 after calcination at 400 °C for 4 h in air. This sample showed no absorption of light in the visible region, as explained below (vide infra, Figure 1).

The UV−visible light absorption spectra of N−TiO_2 as a function of calcination temperatures and pure TiO_2 prepared in our laboratory are shown in Figure 1. The inset in Figure 1 shows the optical absorption edge (in eV) and hence band gap narrowing for N−TiO_2 calcined at 400 °C compared to that of TiO_2. Pure TiO_2 spectrum is provided for comparison. It can be seen from Figure 1 that the visible light absorption is high and extended up to 550 nm in the case of N−TiO_2[7,13,22] calcined at 400 °C compared to that of pure TiO_2. Nevertheless, the light absorption of N−TiO_2 in the visible region decreases very significantly as the calcination temperature increases above 400 °C. It may be due to the fact that there is a decrease in the amount of N doping on the TiO_2 lattice with an increase in calcination temperature. It has also been observed in an earlier report[27] that an increase in the calcination temperature decreased the amount of heteroatom doping in TiO_2. The inset in Figure 1 shows a clear-cut shift in the optical absorption edge toward the visible region by 0.13 eV on N−TiO_2 at 3.26 eV (orange arrow) compared to 3.39 eV (wine red color arrow). The above shift of 0.13 ± 0.01 eV suggests the localized nature of nitrogen species in the TiO_2 lattice. These 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/

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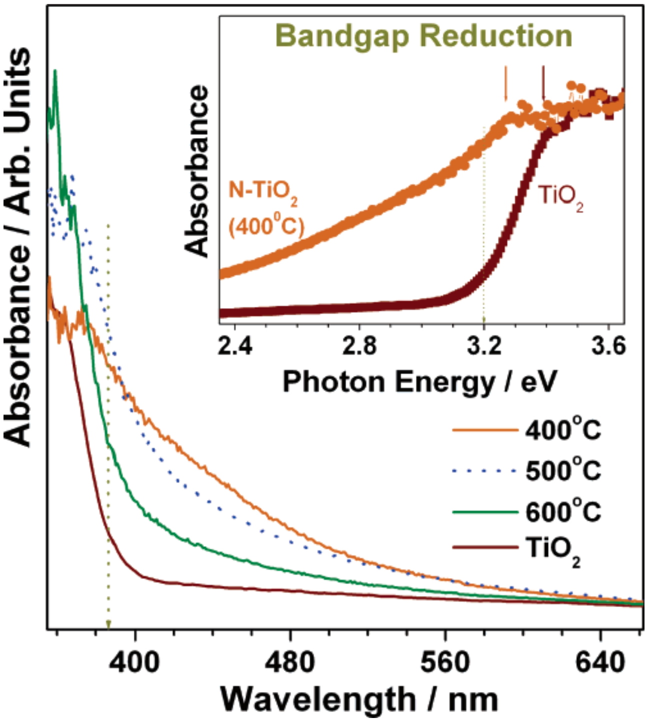

Figure 1. UV−visible absorption spectrum of N-doped TiO$_2$ at different calcination temperatures and pure TiO$_2$. Inset shows a shift in the absorption edge toward the visible region on N−TiO$_2$ compared to TiO$_2$ and hints at the localized nature of nitrogen. Orange and wine red arrows indicate the band gap energy. A dotted arrow is placed at the same energy in both figures for reference.

level between valence and conduction bands. It is to be pointed out here that there is an excellent agreement between the energy width of the localized N states observed above and the calculated one to be 0.14 eV from the density functional theory by Valentin et al.[23] and, in general, by Asahi et al.[7] Recent N-induced mid gap levels suggested by Nakamura et al.[24] and oxygen vacancy induced state below the conduction band suggested by Ihara et al.[28] for N−TiO$_2$ is in contradiction with the present results. It is to be noted that the evidence to show the presence of nitrogen is not direct and the average particle size is close to 1 μm in ref 24. It is also likely possible that the electronic structure changes with particle size and is worth investigating further on this line. Further, the amount of nitrogen was found to be too small and the preparation methods are also different in both the references 24 and 28 compared to those of the present method.

In Figure 2, the XRD patterns of different TiO$_2$ samples are provided. The presence of anatase phase is observed for the N−TiO$_2$ sample calcined at 400 °C. The anatase phase has been retained without phase transformation to rutile even after increasing the calcination temperature to 600 °C. It can also be seen from the XRD patterns that the N−TiO$_2$ samples show peak broadening compared to pure TiO$_2$, which indicates the formation of nanoparticles. The crystallite size of the N−TiO$_2$ particle was calculated using the Debye−Scherrer equation[29] and the values are given in Table 1 along with other physical characteristics. It can be seen from Table 1 that as the calcination temperature increases, the particle size also increases caused by an agglomeration of particles at high temperatures. In addition to this, there is no change in the "d" space values, which implies that, in N−TiO$_2$ samples, N has been introduced into the lattice without changing the average unit cell dimension. A good correspondence between the XRD and the optical absorption results of TiO$_2$ and N−TiO$_2$ calcined at 600 °C hints at the progressive loss of N due to heat treatment and movement toward N-free TiO$_2$. The samples calcined at 400 °C show higher surface area of 73 m^2/g and an increase in calcination temperature results in the decrease of the values of specific surface area (Table 1). Thus, with increase in temperature, agglomeration of particles can be seen. It is further confirmed from the transmission electron microscopy (TEM) results given in Figure 3 that uniform size (14 ± 2 nm) of spherical type particles have been observed for the N−TiO$_2$ calcined at 400 °C. TEM of N−TiO$_2$ calcined at ≥500 °C shows significantly larger particles (not given here).

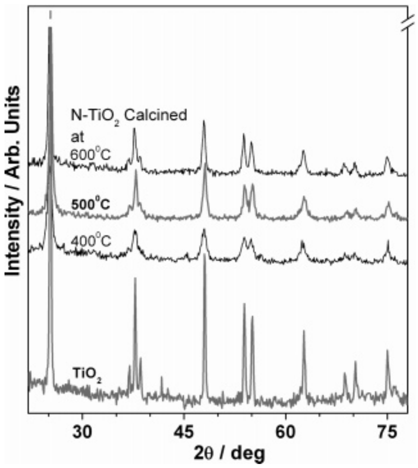

Figure 2. X-ray diffraction pattern of N-doped TiO$_2$ calcined at various temperatures and pure TiO$_2$ (anatase). There is an increase in crystallite size with increasing calcinations temperature, but no phase change ≤600 °C on N−TiO$_2$.

Table 1. Specific Surface Area, Particle Size, and Crystalline Phase for N-Doped TiO$_2$ at Different Calcination Temperatures and Pure TiO$_2$

sample	calcination temperature (°C)	specific surface area (m^2/g)	crystallite size (nm)	anatase crystalline phase (%)
N−TiO	400	73	12	100
N−TiO$_2$	500	66	15	100
N−TiO$_2$	600	37	20	100
pure TiO$_2$	400	14	35	100

The XPS spectra of TiO$_2$ and N−TiO$_2$ samples recorded are shown in Figure 4 for Ti 2p, N 1s, and O 1s core levels. It is to be noted that the above results are after in situ scraping of the pellet surfaces of both the catalysts within the ESCA spectrometer under ultrahigh vacuum conditions, mainly to remove any contribution from the atmospheric degradation. It is to be mentioned here that Ar$^+$ sputtering might lead to preferential removal of lower atomic weight elements first and hence an artifical reduction of cations on the surface. However, physical scrapping does not alter the oxidation state of any element on the surface. Indeed, the unscraped surface displays high carbon (some carbonate also) content along

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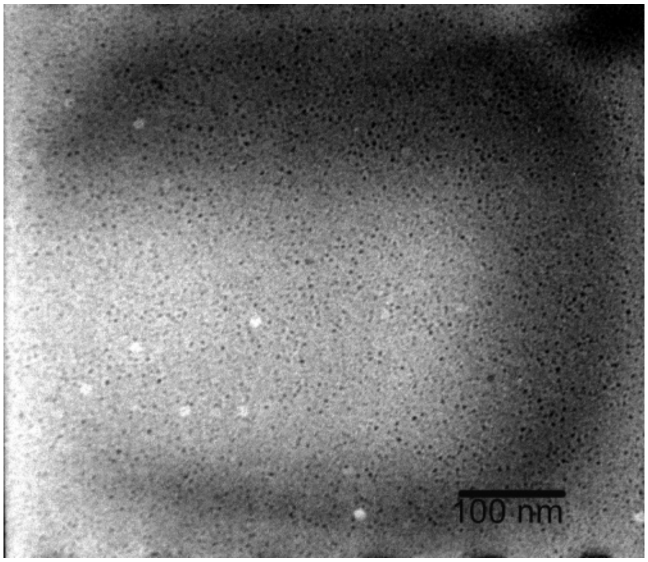

Figure 3. TEM image of N-doped TiO_2 calcined at 400 °C.

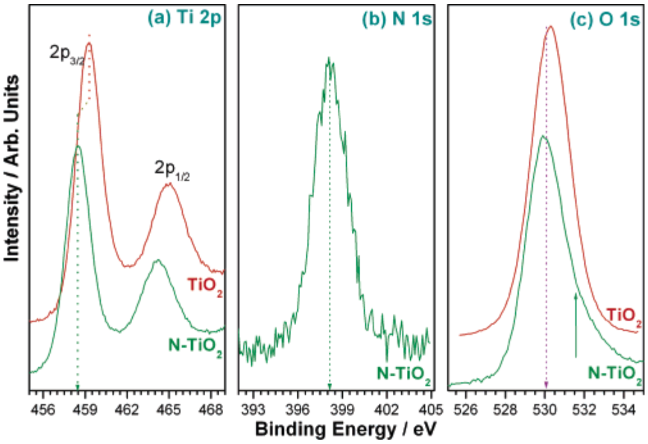

Figure 4. X-ray photoelectron spectral details collected from TiO_2 and $N-TiO_2$ samples: (a) Ti 2p, (b) N 1s, and (c) O 1s core levels. Note the shift in Ti 2p binding energy after the introduction of N into the TiO_2 lattice.

with a relatively low intensity Ti 2p peak (not shown). However, carbonate and hydroxide contamination was fully removed by scraping the catalyst surface and that enhances all intrinsic features intensity. Ti $2p_{3/2}$ core level appears at 459.3 and 458.5 eV for TiO_2 and $N-TiO_2$ calcined at 400 °C, respectively. Lower BE of Ti 2p in $N-TiO_2$ shows that the electronic interaction of Ti with anions is considerably different than on TiO_2. This suggests that TiO_2 lattice is considerably modified due to N-substitution. Lower BE of Ti 2p in $N-TiO_2$ can also be explained on the basis of covalency between the Ti and nitrogen bond. It is known that if the electronegativity of the anion decreases, the percentage ionicity will decrease;[30] as a result, the electron density around the anion decreases, resulting in the increase in electron density around the cation. Our results on Ti 2p core levels are consistent with that of Burda et al.[22] and Saha et al.[25] Oxygen 1s core level peak appears around 530 eV in both cases, indicating the nature of oxygen to be similar. Nonetheless, a broadening on the higher BE side at 531.5 eV (indicated by an arrow) is clearly visible in the case of the $N-TiO_2$ sample. This indicates the presence of another type of oxygen due to the more covalent nature of $N-TiO_2$. This might be due to the presence of oxygen and nitrogen from the same lattice units in TiO_2. However, a small amount of contamination that might remain on the surface cannot be ruled out.

Nitrogen 1s core level from $N-TiO_2$ shows a single peak at 398.2 eV. We attribute the above N 1s peak to the anionic N^- in O−Ti−N linkages. Nitrogen from simple chemisorbed nitrogen or TiN should appear at ≤397.5 eV and NO or NO_2 type species appear above 400 eV.[25,31−36] Additionally, few nitrogen in the TiO_2 lattice also might reduce the electron density on nitrogen due to the high electronegativity of oxygen and hence a relatively higher BE observed compared to TiN. However, the observation of a N 1s core level at 398.2 eV after high-temperature calcination at 400 °C supports the conclusion that the nitrogen should be from the TiO_2 lattice as N−Ti−O linkages. Any significant interaction between N and O within the lattice would increase the BE of the N 1s level and hence any direct interaction between N and O within the lattice is ruled out. It is further supported by the low BE of Ti 2p compared to that of pure TiO_2. A mixed phase of TiO_2-TiN is also ruled out due to the absence of two different Ti peaks in the Ti $2p_{3/2}$ core level at ∼459.5 eV (TiO_2) and 455 eV (TiN).[25,35] From the above observations it can be concluded that the peak observed in the present study at 398.2 eV is due to the N^- anion incorporated in the TiO_2 as N−Ti−O structural feature. It is relevant to point out here the contradiction between the recent XPS findings by Chen and Burda[22] on $N-TiO_2$ and the present results. It has been reported that the N 1s feature appears at 401.3 eV and was interpreted to be due to N−Ti−O linkages.[22] However, an overall view from the BE of N in different environments[25,32−37] hints that the presence of oxidized nitrogen such as Ti−O−N and/or Ti−N−O linkages should appear above 400 eV. It might also be due to a different preparation procedure followed by Burda et al.[22]

It is clear from the above discussion that if the N atom is subtitutionally doped into the TiO_2 lattice, it is not likely to have significant interaction with nearby oxygen atoms too. However, an interstitial N-doping in the anatase lattice is likely to have some strong interaction with nearby oxygen and hence a change in effective charge on the nitrogen species and hence a shift in the BE. Present results on N 1s BE at 398.2 eV suggests that it is comparable to N 1s BE (398.8 eV) in NH_3.[36,37] However, a lower BE results from some partial negative charge on N in $N-TiO_2$ and also supports substitutional N-doping. It is highly likely that the interaction between N and O is strong for interstitial N

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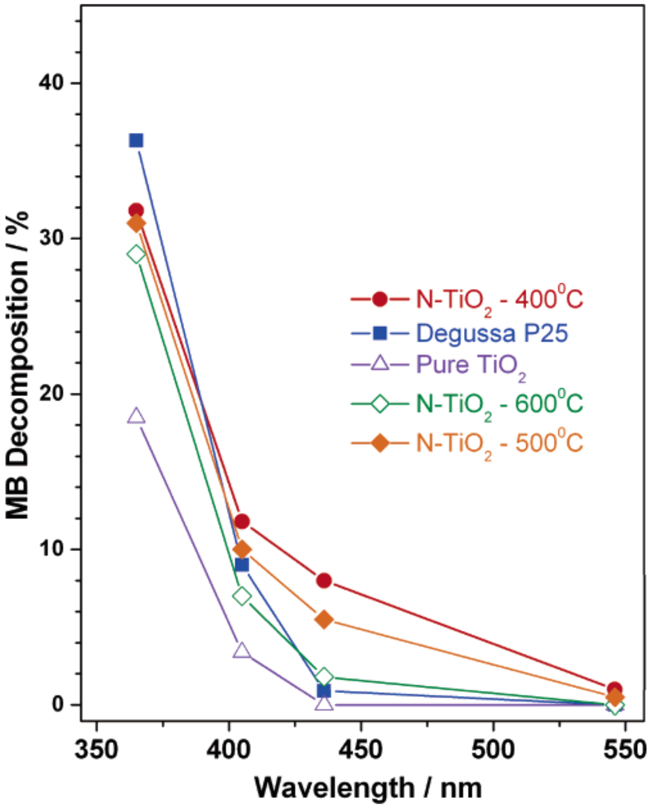

Figure 5. Photocatalytic decomposition profiles of methylene blue over N−TiO_2 calcined at different temperatures, pure TiO_2, and Degussa (P25) at different wavelengths. A significant photocatalytic activity of N−TiO_2/400 °C in the visible region is to be noted.

doping, as in NO type species.[34] The reported BE of >400 eV for N 1s core level by other investigators indicates either possible O−N−Ti linkages[11,22] or some surface oxidation. The above controversies involved in the interpretation of XPS results of N−TiO_2 remain to be clearly answered.[38]

The photocatalytic activity of N−TiO_2, pure TiO_2, and Degussa (P25) samples have been studied by measuring the percentage decomposition of methylene blue (MB) aqueous solution. It can be seen from Figure 5 that the photocatalytic activity of N−TiO_2 sample shows comparable activity to that of Degussa P25 catalyst in the UV region, whereas when compared to pure TiO_2, the N-doped TiO_2 shows better activity. In the visible region, the N−TiO_2 samples (calcined at 400 and 500 °C) show higher activity than the Degussa and pure TiO_2 samples. Nevertheless, the activity further decreases as the calcination temperature is increased to 600 °C. The calcination temperature is found to have an influence on the activity of the titania in the visible region only, whereas in the UV region there is no perceptible influence. In the visible region, it can be seen that as the temperature of calcinations is increased from 400 to 600 °C, the photoactivity is found to decrease. This decrease in activity may be attributed to the removal of the nitrogen from the TiO_2 matrix. This is evident from the shift in the absorption edge to lower wavelength (Figure 1). It is also to be mentioned that the above shift is not due to the change in the particle size of the catalyst. Indeed, the observed change in the particle size is expected to shift the absorption edge to the visible region.

An attempt has been made to compare the photocatalytic activity of our N−TiO_2 with the literature reports on S-doped TiO_2[39] and carbonate-doped TiO_2.[40] Even though the experimental parameters, like the intensity of light (a major factor), initial concentration of the MB, experimental time, temperature, and the amount of catalyst used, are very different, the present N−TiO_2 sample is (after normalizing for the variables) about 10 times more active compared to the carbonate-doped sample[40] and roughly 50% active compared to S-doped TiO_2.[39] The lower activity of N-doped TiO_2 in the present study compared to the S-doped TiO_2 reported in the literature may be due to the difference in the light intensity. Our experiments were measured at a monochromatic wavelength by using monochromatic filters with a 400 W Hg lamp, whereas in the literature cut-off filters have been used with a 1000 W Xe lamp as the light source, which provides higher intensity of light when compared to our experimental conditions.

4. Conclusion

N-doped TiO_2 nano-photocatalyst with a homogeneous size (14 nm) and spherical shape has been prepared by a simple chemical route and calcined at 400 °C. The light absorption onset of N-doped sample in the visible region (550 nm) is clearly observed. The advantages of this method over other methods of preparation are (i) use of inexpensive chemical precursors for the synthesis of N-doped TiO_2 and (ii) formation of TiO_2 as uniformly sized nanoparticles. Optical absorption studies clearly identified the substitutional N-doping and localized N-states in the TiO_2 lattice. XPS results indicate the status of N to be anion-like (N^-) and the chemical environment of N is as in N−Ti−O in the TiO_2 lattice. A higher photocatalytic activity for the decomposition of methylene blue in the visible region has been obtained for the N−TiO_2 sample compared to Degussa P25 and pure TiO_2.

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