Synthesis, Characterization and Photo-Catalytic Activity of Nitrogen-Doped and Undoped Tio_2 Nanoparticles

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Abstract

Un-doped and nitrogen (N) doped titanium dioxide (TiO_2) nano-particles (NPs) were synthesized by the sol-gel method at room temperature (RT) using titanium tetra-isopropoxide as the precursor material of TiO_2. The TiO_2 and N- TiO_2 NPs were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL), FTIR and Raman studies. The crystallite sizes were estimated by the XRD and SEM analysis after annealing of the samples. FTIR, PL and Raman studies confirmed the incorporation of nitrogen in anatase TiO_2. The effect of nitrogen doping on photo-catalytic activity of TiO_2 nano-particles for the degradation of Rhodamin B under visible light was studied. The photo-catalytic activity was also studied under UV light after annealing the TiO_2 samples at different temperatures in air.

Key Words: N-TiO_2, sol-gel, nano-structures, PL, Raman spectra, photo-catalyst.

Introduction

Metal oxide semiconductor based photo-catalytic degradation process is one of the most studied research areas in environmental and industrial applications, particularly in the conversion of solar energy into hydrogen energy by splitting of water and purification of water and air by the decomposition of toxic organic and inorganic pollutants, antibacterial activity and deodorizing agent etc [1-4]. Among other metal oxides, titanium dioxide (TiO_2) received more popularity because of its excellent physical and chemical properties such as non-toxicity, photo-catalysis, sensor, thermal stability and high oxidative power [5-7]. However, pure TiO_2 NPs are only active under UV light irradiation due to their wide band gaps (3.0-3.2 eV). In order to eliminate this drawback of TiO_2 and enhance the absorption in visible region, many techniques such as doping TiO_2 with transition metal atom or non-metal anionic species, are improved by researchers [8-10]. The band gap energy of metal oxide nano-materials can be altered by varying the annealing temperature [11] and concentration of dopants [12]. The sol-gel method is a cost effective method for the preparation of TiO_2 nanomaterial [13, 14]. Magesh et al. [15] reported the photo-

catalytic degradation of methylene blue by CeO_2-TiO_2 system under visible light. Lijun Zhou. [16] reported the highest photo-catalytic activity of Ti/Si= 1:1 ratio of TiO_2-SiO_2 composite thin films prepared by the sol-gel method. In this article, we have reported the effect of nitrogen doping and annealing temperature on the structure, morphological and photo-catalytic activity of TiO_2 NPs prepared by the sol-gel method.

Materials and Methods

Titanium tetra-isopropoxide and ammonium chloride were used as precursor materials of TiO_2 and N, respectively. Titanium tetra-isopropoxide and ethanol were mixed with the volume ratio of 1:7.5. The solution was refluxed at 60^{o}C with constant stirring for 1 h. The de-ionized water was added drop wise and the milky colored precipitate obtained was filtered using Whatman filter paper. After washing with organic solvents, the precipitate was dried and annealed in a hot air oven maintained at 80^{o}C for 20 min. Then the white powder obtained was annealed in a furnace at different temperatures for 2 h in air. N-doped TiO_2 NPs were prepared by the addition of desired amount of ammonium chloride (0.5 M) dropwise into a solution containing titanium tetra-isopropoxide and ethanol and the same procedure was repeated. The resultant TiO_2 and N-TiO_2 nano-powders were subjected to structural and micro-structural characterization. The structural characterization was performed by x-ray diffraction (XRD) using Cu-Kα radiation. The micro-structural characterization was carried out using sirion scanning electron microscope (SEM). Spectroscopic analysis of N-TiO_2 and TiO_2 samples were performed using Agilent Technologies Cary 630 FTIR spectrometer. The photoluminescence (PL) and Raman spectra were also studied for un-doped and N-doped TiO_2 NPs, then subjected to photo-catalytic degradation of Rhodamin B dye under UV and visible light.

Photo-catalytic studies

Photo-catalytic degradation of Rhodamin B dye in UV and visible light was carried out in two different glass reactors (15cm x 5cm and 9cm × 3cm) with an outer jacket for cold water circulation. A sample of 100 mg of the catalyst (TiO_2 or N-TiO_2 NPs) was poured in to a 100 ml glass beaker filled with 10 ppm aqueous Rhodamin B (100 ml) solution and stirred using a magnetic stirrer. The solution was stirred in dark for 1h to attain the adsorption-desorption equilibrium and then it was irradiated using a UV and Xenon lamps. The irradiation was carried out for testing the photo catalytic activity of the samples after every 1h. The degradation of the Rhodamin B dye was measured from the absorption spectra using UV-VIS-NIR spectrophotometer (Ocean Optics, USA).

Results and Discussion

Fig. 1 (a) and (b) show the XRD patterns of TiO_2 and N-TiO_2 NPs, respectively annealed at 550^{o}C for 2 h in air. It is clear from the figure that the TiO_2 exhibits anatase polycrystalline phase with diffraction peaks in (101), (004), (200) and (211) orientations. It has already been reported that as-

prepared TiO_2 NPs/films are amorphous in nature and anatase phase exists after annealing at 300°C and higher temperatures [11]. It has been observed that the full width half maxima of the peaks were reduced with the incorporation of nitrogen in TiO_2. The crystallite sizes of the anatase phase are calculated by the Scherrer's formula [17],

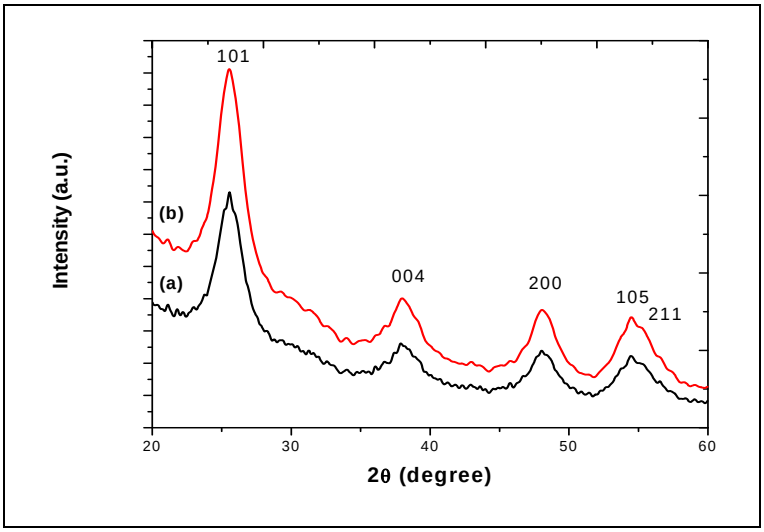

Figure 1. XRD patterns for (a) TiO_2 and (b) N-TiO_2 NPs annealed at 550°C under investigation.

$$D=0.9\,\lambda / [\beta\,\mathrm{Cos}\theta] \quad (1)$$

where λ is the wavelength of the x–ray radiation, β is the full width at half maximum peak position and θ is the diffraction angle. The crystallite sizes estimated for the peak (101) of TiO_2 and N-TiO_2 NPs are found to be 4.43 and 4.99 nm, respectively. Similarly for (200) peak, the crystallite sizes are estimated to be 4.49 and 4.74 nm, respectively. This depicts the increase of crystallite size of TiO_2 with the doping of N_2.

Fig. 2 shows the SEM images of the TiO_2 and N-TiO_2 NPs annealed at 550°C under ambient air. It is clear from the Fig. 2 that, the grain size of TiO_2 NPs is in the range of 4-5 nm for un-doped TiO_2 NPs and 5-6 nm for N-doped TiO_2 NPs. This is in agreement with crystallite size estimated by Scherrer's formula. The agglomeration of large number of grains was observed in the figure.

Fig. 3 (a) and (b) show the FTIR spectra of N-TiO_2 NPs annealed at 350 and 550°C, respectively for 2 h in air. The spectra present the presence of nitrogen ions in the anatase phase of TiO_2 sample. The band at 1430 cm^{-1} corresponds to the asymmetric bending modes of NH_4^+. The strong band at 3130 cm^{-1} is attributed to the N-H molecular stretching of NH_4^+. The broad band at 3350 cm^{-1} is ascribed to the –OH stretching vibration of H_2O and the peak at 1615 cm^{-1} corresponds to the bending vibrations of –OH [18]. With the increase of annealing temperature, the peaks corresponding to –OH and NH_4^+ reduced simultaneously and the bands become weak. After annealing the samples at 550°C, -OH band was completely vanished. Fig. 3 (c) shows the FTIR spectra of un-doped TiO_2 NPs. All the samples (TiO_2 and N-TiO_2) showed strong absorption bands of the stretching vibration of Ti-O-Ti bonds in the range 750-500 cm^{-1}. These characteristic absorption bands indicate the anatase phase of TiO_2 [19].

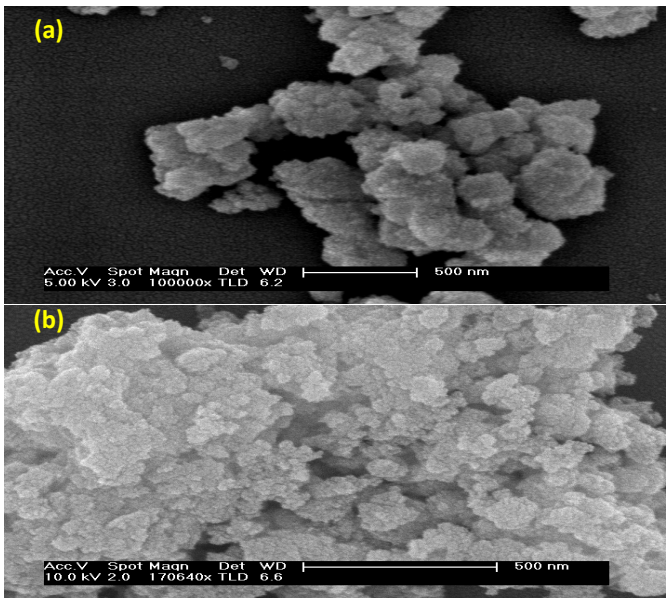

Figure 2. SEM images of (a) TiO_2 and (b) N-TiO_2 NPs annealed at 550^oC for 2 h in air.

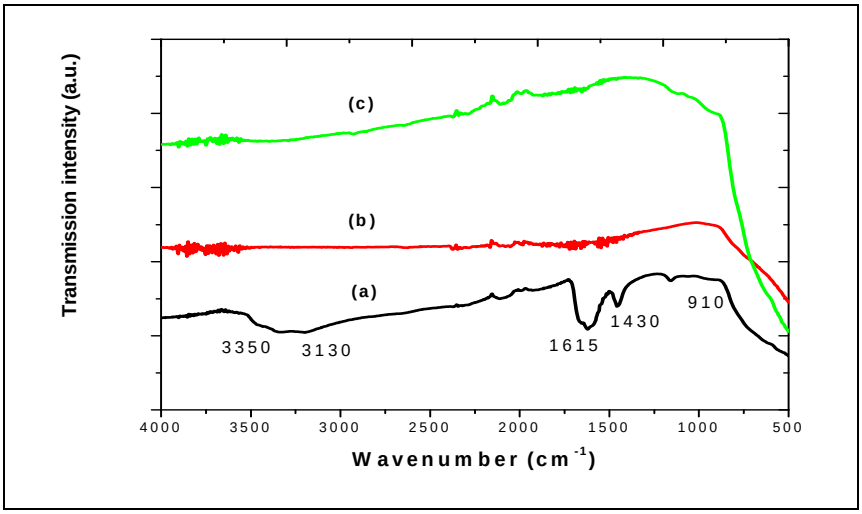

Figure 3. FTIR spectra of (a) N-TiO_2 NPs annealed at 350^oC, (b) N-TiO_2 NPs annealed at 550^oC and (c) TiO_2 NPs annealed at 550^oC for 2h in air.

Fig. 4 depicts the Raman spectra of TiO_2 NPs annealed at 450 and 550^oC and N-TiO_2 NPs annealed at 450, 550, 650 and 800^oC for 2 h in ambient air. It is clear from the Fig. 4 that, the Raman peak at 142.0 cm^{-1} for TiO_2 NPs has been shifted to 146.6 cm^{-1} with increase of annealing temperature from 450 to 550^oC, respectively. While the Raman peak intensity for N-TiO_2 NPs annealed at 450, 550, 650 and 800^oC were found to be 145.0, 143.21 and 142.78 cm^{-1}, respectively. Hence the peak position has been shifted with increase of annealing temperature. The observed peaks correspond to the characteristics of anatase phase of TiO_2 [20]. The peaks of anatase phase were disappeared completely and that of rutile

phase were appeared when the sample was annealed at 800°C as shown in the Fig. 4. This signifies the conversion of TiO_2 from anatase to rutile phase after annealing at 800°C.

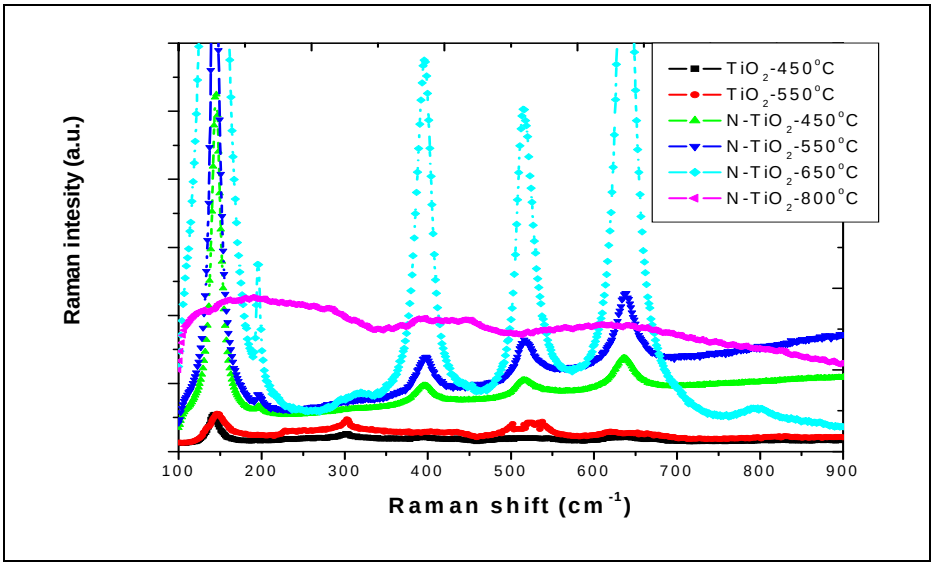

Figure 4. Raman spectra of TiO_2 and N-TiO_2 NPs annealed at different temperatures in air.

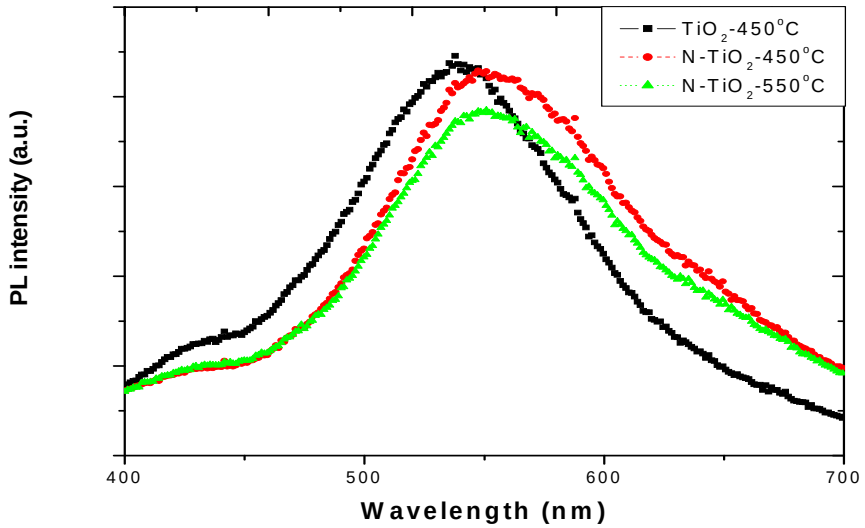

Figure 5. PL spectra of TiO_2 and N-TiO_2 NPs annealed at different temperatures in air.

Fig. 5 shows the photoluminescence (PL) spectra of TiO_2 and N-TiO_2 NPs with an excitation wavelength of 325 nm annealed at 450 and 550°C for 2 h in air. It can be seen that, both TiO_2 and N-TiO_2 NPs exhibit predominant green emission. The wavelength corresponding to maximum PL intensity position of TiO_2 NPs annealed at 450°C is 540.5 nm while for the N-TiO_2 NPs annealed at 450 and 550°C

are 548 and 552 nm, respectively. Hence the red shift was observed with the doping nitrogen and increase of annealing temperature.

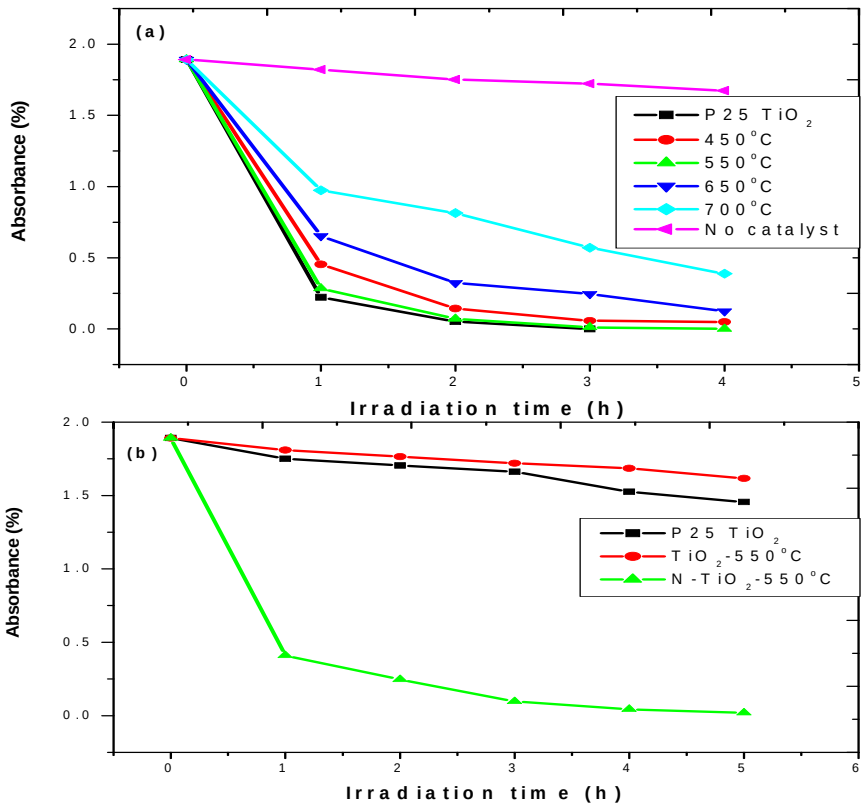

Figure 6. Photo-catalytic activity of (a) TiO_2 NPs annealed at different temperatures under UV irradiation and (b) TiO_2 and N-doped TiO_2 NPs annealed at 550^{o}C obtained from the kinetics of the Rhodamine B degradation under visible light.

The red shift in PL intensity is due to the increase of crystallite size of TiO_2. The increase in particle size decreases the surface energy which may be ascribed to the quantum confinement effect. The predominant green emission is due to transition of electrons from the donor levels of the oxygen vacancies [20].

Fig. 6 (a) shows the absorbance spectra measured at 553 nm to present the photo-catalytic degradation of Rhodamin B dye using TiO_2 NPs, annealed at different temperatures under the UV irradiation (360 nm). The photo-catalytic activity was compared with commercially available TiO_2 nano-powder (Degussa, P-25). It has been observed that, the photo-catalytic activity is maximum in TiO_2 NPs annealed at 550^{o}C which is almost equal to P-25. The photo-catalytic activity was decreased with increase of annealing temperature. This may be due to the fact that, with increase of annealing temperature to 700^{o}C and higher, simultaneous phase transformation occurs from anatase to rutile phase. Therefore rutile TiO_2 is not an efficient photo-catalyst as compared to anatase TiO_2.

Fig. 6 (b) shows the absorbance spectra measured at 553 nm for the comparison of photo-catalytic activity of TiO_2 and N-TiO_2 NPs annealed at 550^oC for 2 h in air under visible light. It has been observed that, N-doped TiO_2 NPs exhibit very high photo-catalytic activity compared to TiO_2 NPs in visible light. The photo-catalytic activity was enhanced with N-TiO_2 NPs due to decrease in the band gap of TiO_2 [21]. The un-doped TiO_2 NPs and commercial TiO_2 NPs (P-25) showed very low photo-catalytic activity in the visible light.

Conclusions

The XRD and SEM results revealed the increase of crystallite size with the doping of nitrogen in TiO_2 NPs. Raman studies proved the shifting of Raman peaks corresponding to anatase phase with the doping of nitrogen in TiO_2. Photoluminescence spectra showed the predominant green emission with red shift by the doping of nitrogen. The photo-catalytic activity was enhanced in TiO_2 NPs annealed at 550^oC. The photo-catalytic activity of TiO_2 NPs was improved in the visible light by the doping of nitrogen.

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