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RESEARCH ARTICLE

Environmental Application of Photochemical Method for the Degradation of Rhodamine B Dye in Aqueous Media Using Modified Titania

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Abstract: The development of semiconductor photocatalysis for a wide range of environmental and energy applications. One of the most significant and commercial advances has been the development of visible light active TiO_2 photocatalytic materials. In the present study, a visible light active TiO_2 photocatalyst was prepared through Nitrogen doping by using Ammonia as Nitrogen source. Preparation was performed by a sol-gel method at various temperatures such as 400 ℃, 600 ℃ and 800 ℃. The resulting photocatalyst was characterized by XRD, SEM, EDAX. The decrease in concentration of rhodamine B was monitored by UV-Visible spectroscopy. The characterizations found that the photocatalyst possessed a high surface area and a crystalline size is about-19 nm, 28 nm and 52 nm respectively. On the degradation of rhodamine B in water under visible light irradiation [λ= 554 nm]. The photocatalytic activity increased with decrease in concentration of catalyst and increase in light intensity.

Keywords: Photocatalyst, Titanium dioxide, Nitrogen doping, Rhodamine B, Visible light

Introduction

Foreign substances either from natural or anthropogenic sources, contaminated with water supplies, may be harmful to life because of their toxicity, reduction of normal oxygen level to water, aesthetically unsuitable and spread epidemic diseases. About 1-20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents[1]. The release of those coloured wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis or other chemical reactions taking place in the waste water phase. It must be noted that dyes can present toxic effects and reduce light penetration in contaminated waters[2].

Traditional physical methods such as ultrafiltration, reverse osmosis, coagulation by chemical agents, ion-exchange methods, adsorption of activated carbon or charcoal have been used for the removal of dye pollutants. These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution.

The application of titanium dioxide as heterogeneous photocatalyst is altering considerable attention for water and air purification and remediation[3-7]. Because of its large band gap of 3.2 eV it can be activated only under UV light irradiation of wavelength <387 nm. However, UV light constitutes only a small fraction about 3-5% of the solar spectrum, it will have a positive effect for improving the photocatalytic efficiency of TiO_2 by shifting its optical response to the visible range. So scientists are exploring methods to modify titanium dioxide to absorb visible light. Most of these investigations had been made to convert the TiO_2 absorption from the ultraviolet to the visible region to dope TiO_2 with transition metals such[8-13] as Cr, Fe, Mn, V *etc*. However, the photocatalytic activity of transition metals doping is poor because of their thermal instability[8]. Recently, doping TiO_2 with nonmetal atoms has received much attention. For example, doping of nitrogen[14-19], carbon[20-25], sulphur[26-28] and iodine[29] in TiO_2 can lower its bandgap and shift its optical response to the visible region and also completely mineralize the target pollutants[30].

In a semiconductor with a large bandgap, electrons in the valence band cannot jump up to the conduction band. However if energy is applied externally, electrons in the valence band can rise to the conduction band. Consequently as many electron holes as the number of excited electrons are created in the valence band. This is equivalent to the movement of electrons from the bonding orbital to the antibonding orbital. In other words, the photoexcited state of a semiconductor is generally unstable and can easily break down. Titanium oxide on the otherhand, remains stable even when it is photoexcited. This is one of the reason that TiO_2 makes an excellent photocatalyst.

Rhodamine B is used as model organic dye, as it is most important Xanthene dye and dye pollutants from the textile industry are an important factor in environmental pollution and its degradation mechanism had been studied quite well[30-32]. The photodegradation of rhodamine B in aqueous solution was investigated by UV-Vis spectroscopy.

Experimental

Various methods are available for the preparation of TiO_2-based photocatalysts, such as electrochemical[33-38], thin films and spin coating[39-41] precipitation[42-46], hydrothermal and solvothermal[47-52], solvochemical and chemical vapour decomposition[53-55], Although, the benefits derived from preparing N-TiO_2 (NT) by sol-gel method which include synthesis of nanosized crystallized powder of high purity at relatively low temperature, possibility of stoichiometry controlling process, preparation of composite materials, and production of homogeneous materials have driven many researchers to the use of the method in preparing TiO_2-based photocatalysts.

Nitrogen doped TiO_2 photo catalyst was prepared by sol-gel method using TTIP (titanium tetra isopropoxide) as the precursor of titanium and ammonia water as the source of nitrogen. 12.00 g of TTIP liquid was mixed with 5 cm^3 of absolute ethanol unit, the homogeneous solution was given. Ammonia water is added drop by drop into TTIP under constant stirring, white precipitate was given immediately. Solution with white precipitate was stirred 30 min. and stand 18 h for aging. After aging white solid was filtered and calcined at 400 °C, 600° C and 800 °C.

Phocatalytic study

0.1 g of Photocatalyst was suspended in 100 mL aqueous RB-base dye solution in a 250 mL beaker. The suspension was stirred for 30 minutes in dark and irradiated under visible light. Samples were taken each 30 minutes, centrifuged and analysed for the degradation of Rhodamine B dye using UV-Visible spectrophotometer (Figure 1a & 1b). Rhodamine B dye has the maximum absorbance at 554 nm.

Absorbance of rhodamine B against time is recorded with same amount of catalyst with three different calcination temperatures is shown in the Figure 2(a-c). Absorbance is maximum using 0.2 g nitrogen doped TiO_2 at 600˚C and above a mixture of anatase and rutile phase of the sample were formed and hence absorbance somewhat decreases. The photocatalytic percent degradation of rhodamine B against time shown in Figure 3. Results show that all the modified catalysts give a linear relationship with time *i.e.,* up to 120 minutes, after 30 to 35 minutes 0.2g NT 600 has better photocatalytic degradation than that of 0.2g NT 400 and 0.2NT 800. This indicates that the photocatalytic activity of the prepared photocatalyst reached maximum at 600˚C. Further increase in the calcination temperature from 600 to 800˚C resulted in lower photocatalytic activity of the prepared photocatalyst. The reason given for this is that the increase in calcination temperature beyond 600 ˚C can promote the transformation of anatase to a mixture of anatase and rutile phase, which has little photocatalytic activity.

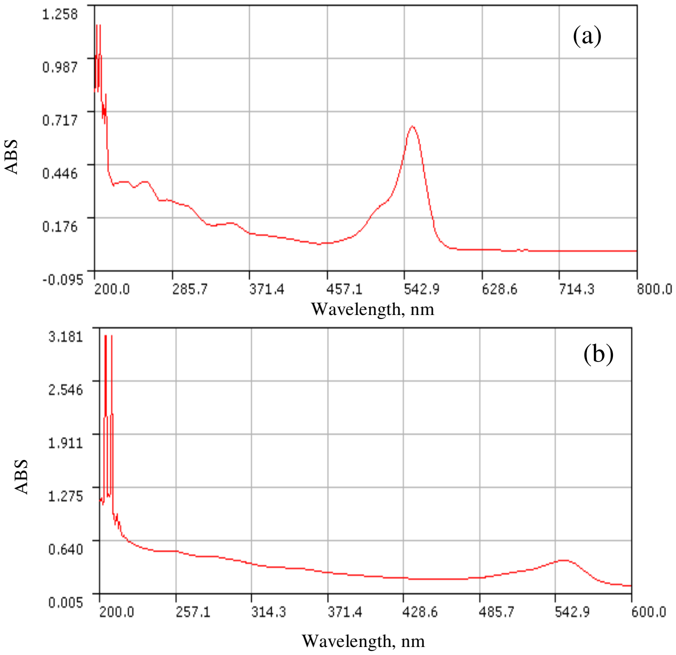
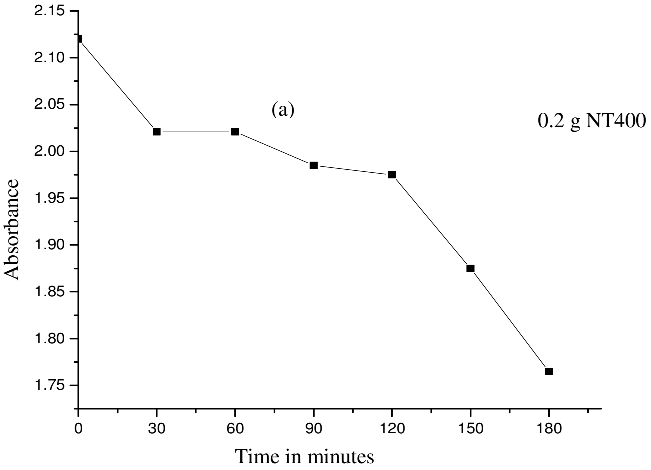


Figure 1. (a) UV of RB Dye (b) UV of RB dye degraded in the presence of $NTiO_2$



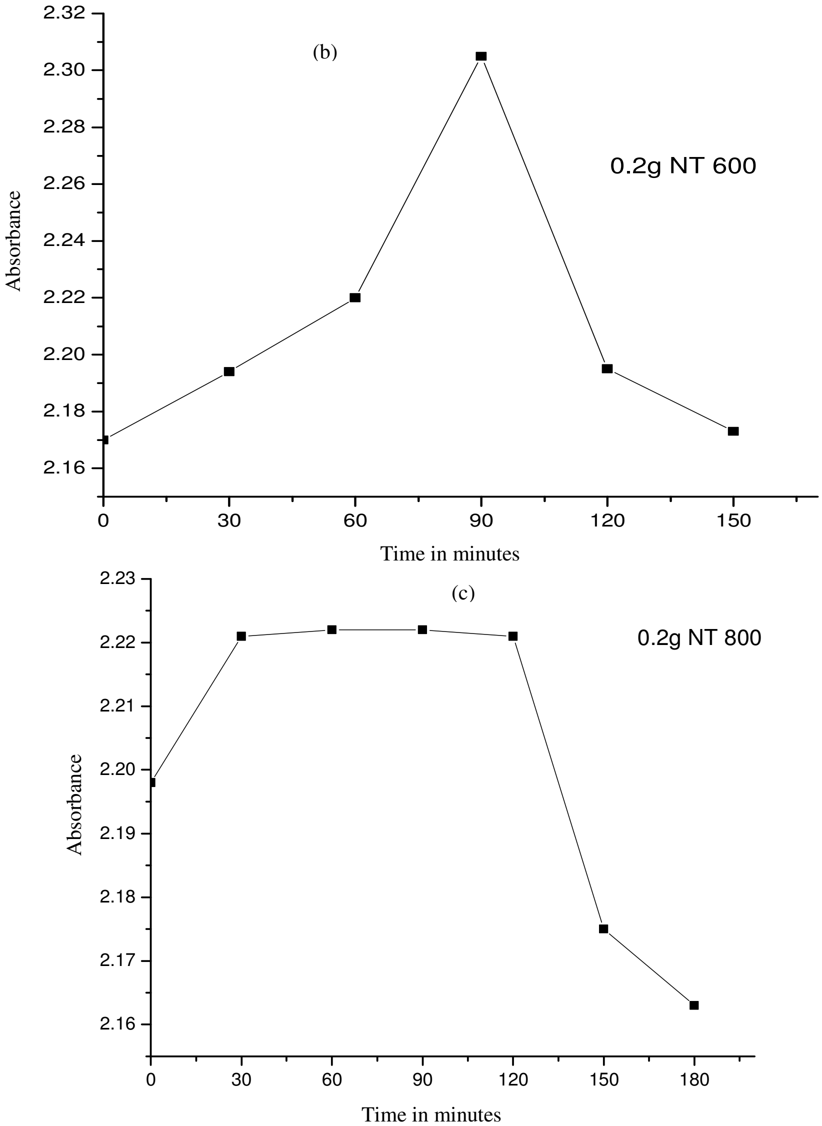


Figure 2. (a) 0.2 g NT 600 (b) 0.2 g NT 400 (c) 0.2 g NT 800

Results and Discussion

SEM analysis

The following Figure 4 shows surface morphology of microparticles with high-resolution images of the sample. The as-prepared N-TiO_2 has the small particle size and a good dispersion. A good dispersion of small particles could provide more activated sites for the reactants than the aggregated particles. TiO_2 doped with nitrogen gave more porous structure this may be attributed to prevention of TiO_2 agglomeration.

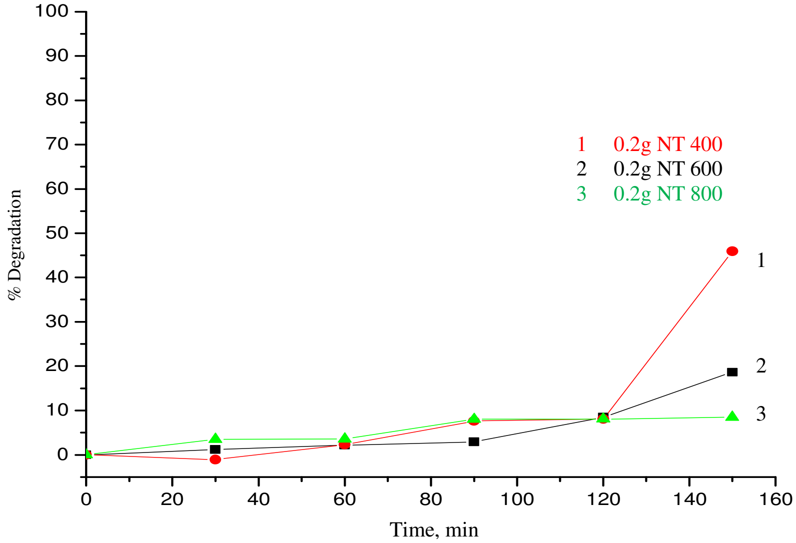
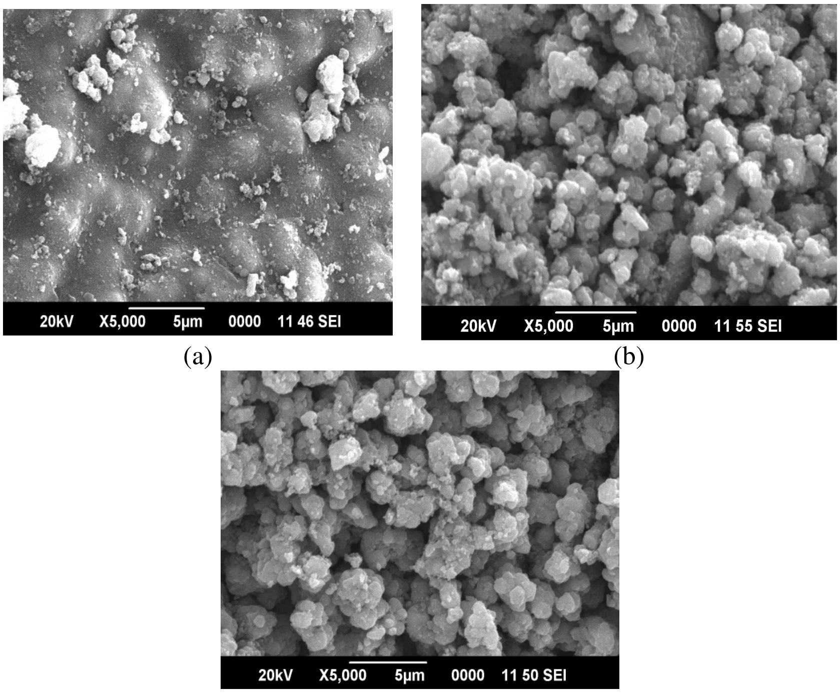


Figure 3. % Degradation of NT 400, NT 600, NT 800



(a) (b)

(c)

Fiigure 4. SEM of (a) NT 400 at 5 µm (b) NT 600 at 5 µm (c) NT 800 at 5 µm

XRD analysis

XRD was used to find the crystallographic structure of the inorganic component of the photocatalyst. Figure 5 shows the x-ray diffraction patterns of *N*-doped TiO_2 prepared with different calcinations temperature. All the as-prepared N-TiO_2 materials have single phase, crystalline, anatase TiO_2 (JCPDS no. 89-4921) except NT 800 sample, which is poorly crystalline anatase together with a small amount of rutile N-TiO_2. No new diffraction peaks are observed in the N containing phase.

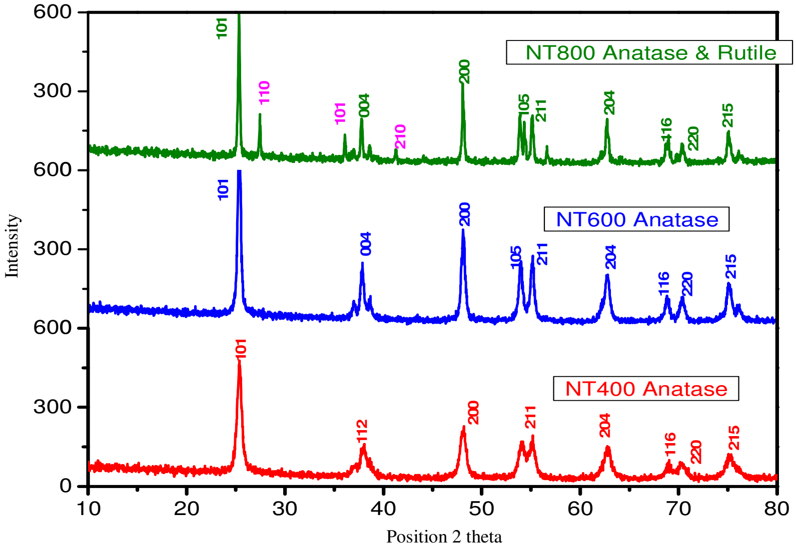


Figure 5. XRD patterns of N-doped TiO_2 with calcination temperatues

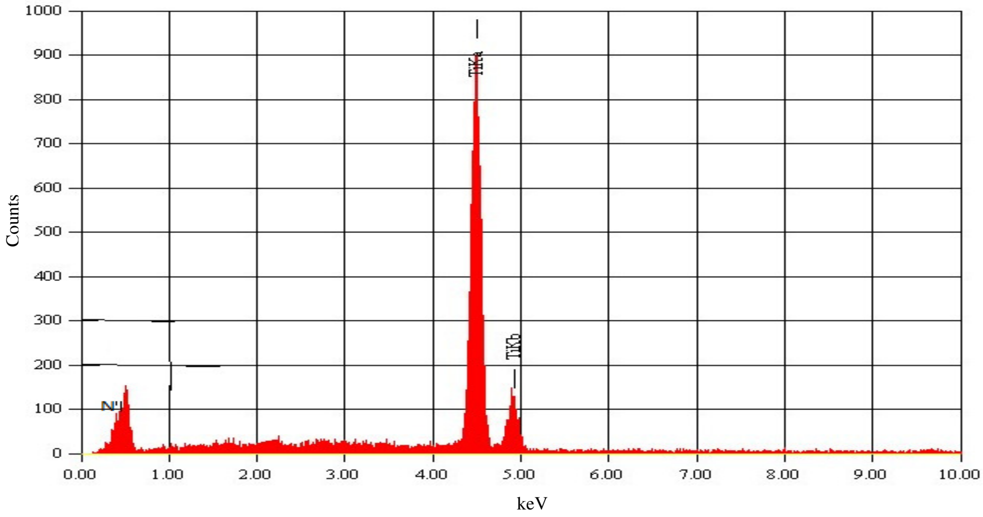


Figure 6. EDAX of $NTiO_2$

Table 1 lists the crystal size of N-doped TiO_2 with different calcinations temperature which were calculated by Scherrer equation[56]. It is well known that particle sizes play a vital role in photocatalytic activity since smaller crystals offer greater surface area to volume ratios and thus induce better surface absorbability of hydroxyl/water, which in-turn acts as an active oxidizer in the photocatalytic reaction. In addition, the increase of nominal nitrogen content and increase the calcination temperature leads to an increase of the average crystal size of N-doped TiO_2. It can therefore be concluded that the level of nitrogen doping has a significant effect on the particle size of TiO_2 grown during the doping process.

Table 1. Crystalline size and phase composition of *N*-doped TiO_2 (NT) with different calcination temperature

NT at difference calcinations temperature, ^{0}C	Phase Composition	Average Crystalline Size/nm
400	Anatase	19
600	Anatase	28
800	Anatase, Rutile	52

EDAX analysis

EDAX patterns of N-TiO_2 indicated Titanium and Oxygen as the major elements in the photocatalyst. The Figure 6 confirms the presence of dopant nitrogen in TiO_2.

Conclusion

This study examined the preparation, characterization and photocatalytic study of Nitrogen doped titania photocatalyst. TiO_2 nanoparticles were prepared by sol-gel method. From the SEM-EDX, UV-Vis results, it was confirmed that the incorporation of N in TiO_2 decreases the grain size and hence increases the photocatalytic degradation of Rhodamine B dye under visible light irradiation. Overall, Nitrogen doped TiO_2 photocatalysts revealed it's potential for rapid degradation of RB dye in wastewater using visible light. N doped TiO_2 possesses the highest visible light absorption and the best photocatalytic activity.

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