Appl Nanosci (2015) 5:229–234
DOI 10.1007/s13204-014-0310-9

ORIGINAL ARTICLE

Photocatalytic removal of hazardous Ponceau S dye using Nano structured Ni-doped TiO_2 thin film prepared by chemical method

Sunil D. Marathe · Vinod S. Shrivastava

Received: 9 April 2014 / Accepted: 19 April 2014 / Published online: 5 May 2014

Abstract Many attempts have been made by researchers for the removal of various dyes using nano structured Ni-doped TiO_2; however, removal of 'hazardous Ponceau S dye' using nano structured Ni-doped TiO_2 has been not studied yet. In the present work, environmental application of Nano structured Ni doped TiO_2 has been studied. Nano structured Ni-doped TiO_2 thin films were deposited by the chemical method on a glass substrate. The prepared thin film was characterized by XRD, SEM, and EDX. The crystal size calculated from XRD is about 26.2 nm. The SEM analysis reveals nano spherical morphology of average particle size about 92 nm. The optical analysis was carried by using UV–visible spectroscopy. The band gap estimated from absorbance spectra for thin film was around 3.5 eV, making suitable Ni-doped TiO_2 for photocatalytic removal of hazardous Ponceau S dye. In photocatalytic application different parameters like dye concentration, contact time, pH, UV light and sunlight were optimized for the removal of Ponceau S dye, respectively. The change in chemical oxygen demand after photo catalytic treatment was also studied.

Keywords Nanocrystalline TiO_2 · Ponceau S dye · Photocatalytic removal

Introduction

Textile industries use large amounts of dyes for the purpose of coloring, causeing serious environmental issues when these dyes come in contact with water bodies (Chen et al. 2005). The discharge of effluents containing modern synthetic dyes of high stability to water bodies cause harm to aquatic life (Denizil et al. 2000; Acosta et al. 2005). Ponceau S is a red colored dye and belongs to the family of azo dyes. Being an azo dye, it may elicit intolerance in people allergic to salicylates (aspirin), it is a histamine liberator, and may intensify symptoms of asthma.

Different methods have been developed to control the pollution due to textile dyes. Among these methods like coagulation, filtration and adsorption with carbon were conventional methods. Since last few years, the photocatalytic decomposition of organic pollutants wastewater using semiconductors as photocatalyst has been a promising technique (Bahanmann et al. 1991; Hermann 1999; Hoffmann et al. 1995; Mills and Hunte 1997; Blake 1999; Boye et al. 2002).

Now a days researchers have focused on the method of photocatalysis by employing the nanosized semiconductor materials as catalyst for water purification; this method is also known as an advanced oxidation process (AOP). The AOP is initiated upon absorption of UV radiation having energy greater than band gap energy by semiconductor photo catalyst with the formation of electron–hole pair (e^-/h^+). After reaction with water, these holes can produce hydroxyl radicals with high oxidizing potential (Fijushima et al. 2000).

The titanium dioxide (TiO_2) is most widely used semiconducting material for semiconductor photocatalysis because it is non-toxic, non-expensive and efficient photocatalyst for this purpose (Linsebigler et al. 1995; Kansal et al. 2007). The TiO_2 has gained much attention because of strong photocatalytic abilities to purify pollutants in air and water under irradiation (Konstantinou et al. 2001; Buechler et al. 1999). TiO_2 thin films can be prepared by various methods (Ghorai et al. 2007; Zhang et al. 2005).

S. D. Marathe · V. S. Shrivastava (✉)
Nano Chemistry Research Laboratory, GTP College, Nandurbar 425412, India
e-mail: drvinod_shrivastava@yahoo.com

S. D. Marathe
e-mail: sunilmarathe86@gmail.com

Experimental and instrumentation

Materials and methods

All the chemicals were of analytical grade. For photo catalytic study the water soluble Ponceau S dye (M F $C_{22}H_{12}N_4O_{13}S_4Na_4$ and M W 760.56 g) and nanosized Ni doped TiO_2 thin film prepared by chemical bath deposition (CBD) method were used. The structure of Ponceau S dye is shown in Fig. 1. A stock solution of 100 ppm of Ponceau S dye was prepared in distilled water. Different concentrations (10, 20, 25, 30, 40 and 50 ppm) of Ponceau S dye were prepared from stock solution. The pH of Ponceau S dye solution was adjusted by adding HCl and NaOH. The rate of photocatalytic degradation was followed by measuring the absorbance of sample after different intervals of time by using UV–Visible spectrophotometer (Systronics-2203) using quartz cell of 1 cm path length at max 519 nm.

Instrumentation

X-ray diffraction measurements were performed on D8 ADVANCE (BRUKER) model X-ray diffractometer using Cu Kα1 radiation of wavelength 1.54060 Å as X-ray source. The XRD was recorded over 2θ range of 10°–80°. The scanning electron microphotographs of Ni-doped TiO_2 thin film was obtained using Hitachi s-4800 FE-SEM equipment.

The photocatalytic degradation of Ponceau S dye was carried out in a Photocatalytic reactor with a 400 W medium pressure Mercury lamp with nominal wavelength range 220–1,400 nm. The reactor consists of a cylindrical Pyrex glass reactor, a double-walled quartz cooling water jacket to maintain the temperature and prevent the reactor from excessive heating. The reaction solution was stirred with magnetic stirrer at a constant speed. The changes in dye concentration are followed using spectrophotometer (Systronics 2203). The pH measurements are carried out using an equiptronics digital pH meter (Model-E610).

Thin film preparation

The chemicals used were of analytical grade and solutions were prepared in double distilled water. In preparation of Ni-doped TiO_2 thin film by chemical bath deposition method $TiCl_4$, ethanol and nickel nitrate were used as starting materials. The thin film was deposited on previously cleaned glass substrate. The chemical bath was prepared by slow addition of $TiCl_4$ to ethanol; the solution was heated on water bath at 75 °C for 2 h after adding nickel nitrate by dipping glass substrate in it. The glass slides were removed from the bath, washed and dried in air. The prepared thin film of TiO_2 was annealed at 450 °C for 2 h.

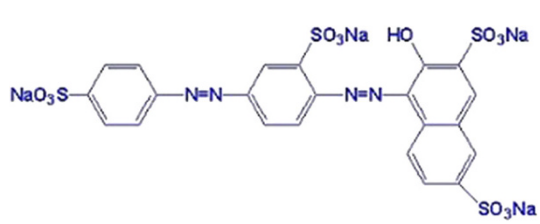

Fig. 1 Structure of Ponceau S Dye

Results and discussion

Structural analysis

Phase and purity of as-deposited Ni-doped TiO_2 thin films have been analyzed by XRD. The XRD pattern for Ni-doped TiO_2 thin films annealed at 450 °C for 2 h are as shown in Fig. 2. The defined peaks reveal the nanocrystalline nature of deposited material.

Surface morphology

Figure 3 shows SEM images of nano crystalline Ni-doped TiO_2 thin film. SEM images show the dense, uniform nanosperes of nano crystalline TiO_2 of average diameter around 90–92 nm.

Energy dispersive X-ray spectrometry

Elemental analysis was performed with the help of energy dispersive X-ray spectrometry (EDX). Figure 4 shows EDX images for Ni-doped TiO_2 which shows peaks for Ti, O and Ni. Thus, confirms the doping of Ni over TiO_2 thin film.

Optical studies

The UV–visible spectra of Ni-doped TiO_2 thin films were recorded in the range 300–800 nm. Figures 5 and

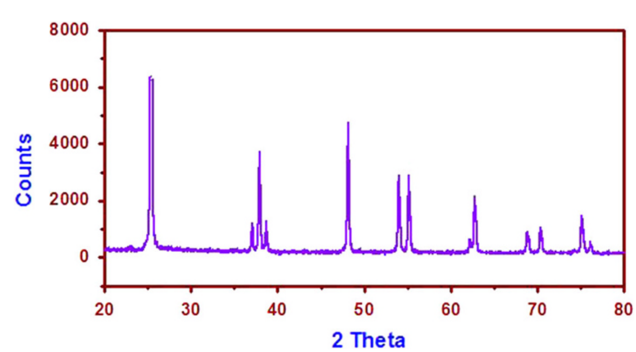

Fig. 2 X-ray diffraction patterns of Ni doped TiO_2 thin films

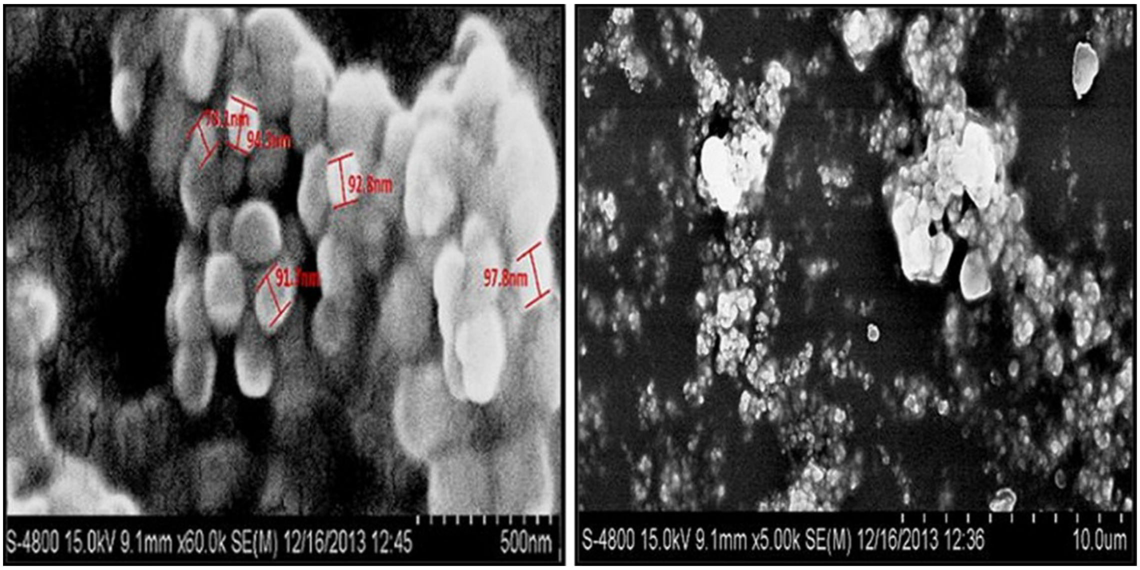

Fig. 3 Scanning electron micrographs of Ni doped TiO_2 thin films

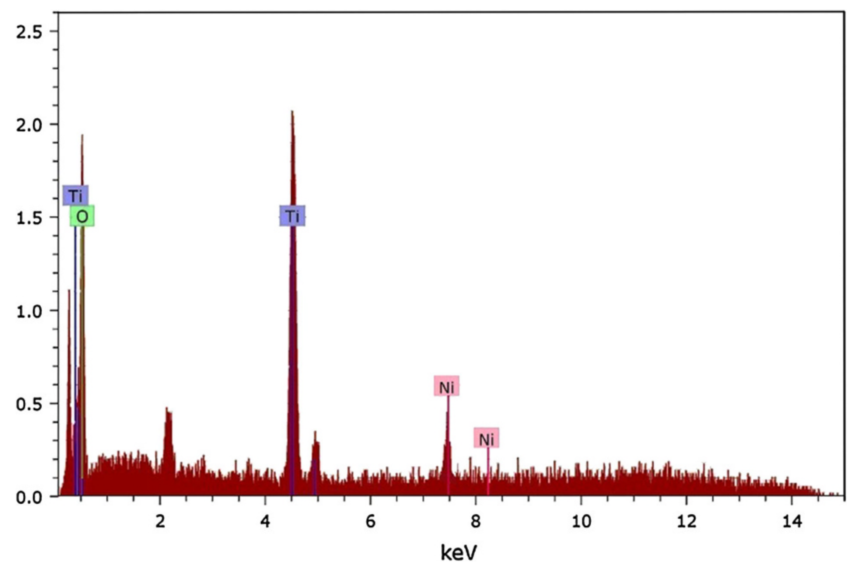

Fig. 4 EDX patterns of Ni doped TiO_2 thin films

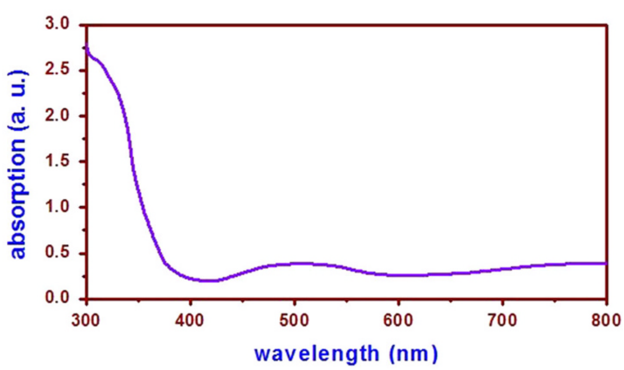

Fig. 5 UV-visible absorption spectra of Ni doped TiO_2 thin films

6 show the wavelength-dependent absorption and transmission spectra of Ni doped TiO_2 thin film, respectively. Transmittance spectra of Ni doped TiO_2 thin film shows that film is highly transparent in the visible wavelength region, with an average transmittance of about 55 %. The optical band gap E_g for Ni doped TiO_2 thin films was estimated from absorption spectra. Figure 7 shows plot of (absorbance) ^{2} versus photon energy ($h\upsilon$), when extrapolated to zero the absorption provides the value of energy band gap (E_g) about 3.5 eV, making it suitable for photocatalytic removal purpose.

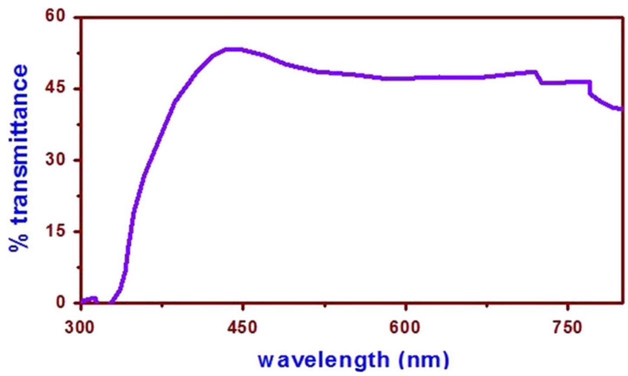

Fig. 6 UV-visible transmittance spectra of Ni doped TiO_2 thin films

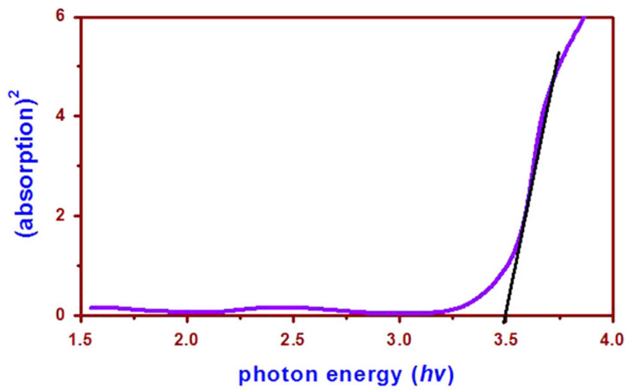

Fig. 7 Energy band gap determination of Ni doped TiO_2 thin films

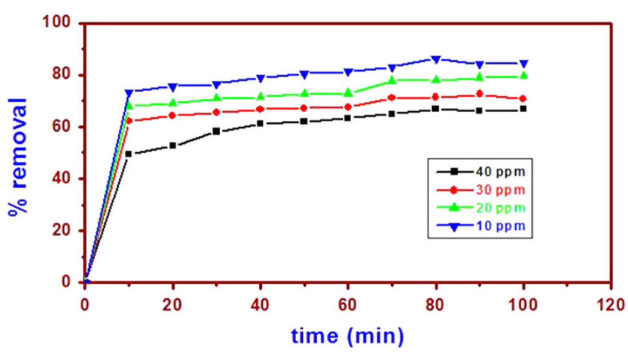

Fig. 8 Effect of initial dye concentration on removal percentage of Ponceau S dye using Ni doped TiO_2 thin films at pH 9

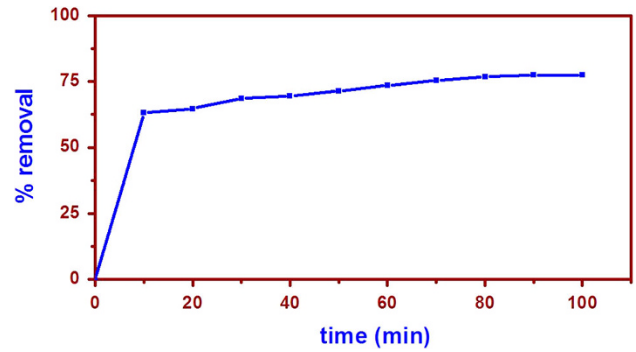

Fig. 9 Effect of contact time on removal percentage of Ponceau S dye using Ni doped TiO_2 thin films with initial dye conc. 25 ppm

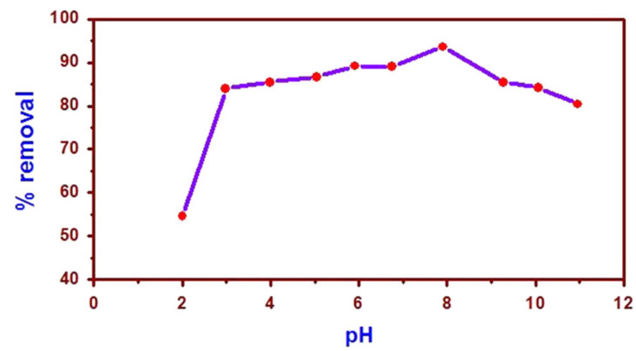

Fig. 10 Effect of pH on removal percentage of Ponceau S dye using Ni doped TiO_2 thin films with 75 min contact time and initial dye conc. 10 ppm

Photocatalytic behaviours

Effect of initial dye concentration

A series of experiments were performed to optimize the initial dye concentration. The effect of initial dye concentration on the rate of removal of Ponceau S dye was studied by carrying out a series of experiments with different initial dye concentration (10, 20, 30 and 40 ppm) at constant pH of 9. The results are shown in Fig. 8. It was observed that the percentage removal decreases with increasing initial concentration of dye.

Effect of contact time

The effect of contact time on removal percentage of Ponceau S dye is shown in Fig. 9. The effect of contact time was studied with 25 ppm initial dye concentration. The percentage removal increases with increasing time. The removal rate increases rapidly in the start and then increases slowly.

Effect of pH

The pH of the dye solution plays an important role in the whole process of photocatalytic degradation. Using Ni doped TiO_2 thin films as photocatalyst the degradation of Ponceau S dye was studied in pH range 3–11. It was observed that the rate of removal of Ponceau S dye increases with increasing pH up to 8 and then slightly drops. The effect of pH on removal percentage is shown in Fig. 10.

Chemical oxygen demand

The chemical oxygen demand test is a technique to measure the organic strength of wastewater. The test allows

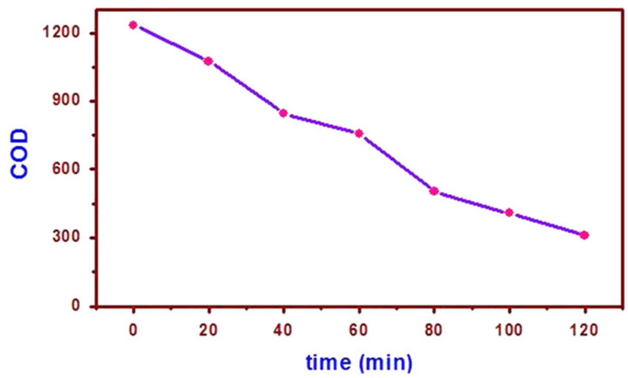

Fig. 11 Effect of photocatalytic treatment on chemical oxygen demand

Table 1 Effect of photo catalytic treatment on chemical oxygen demand

Conditions	UV light	Catalyst + UV light (%)	Sun light (%)	Sun light + catalyst (%)
Removal percentage	10.2	73.82	4.3	42.13

measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic material to CO_2 and water. The present work results of chemical oxygen demand were taken as one of the parameters to judge the feasibility of the photochemical process for the degradation of Ponceau S dye solution. In this work Ponceau S dye after measurement of initial COD was irradiated with UV light in photocatalytic reactor and the changes in COD with increasing time were measured by withdrawing few milli literes of sample at regular interval from the reactor. The results are shown in Fig. 11.

Effect of UV light and sun light

The effect of artificial UV light condition in a laboratory and sunlight on the removal percentage of Ponceau S dye using Ni doped TiO_2 thin film was also studied. The results are shown in Table 1. The results reveal that greater removal is obtained in the presence of UV light than sunlight. In the presence of a catalyst the removal percentage is very high than that in the absence of catalyst for both UV light and sunlight conditions.

Conclusion

Nano structured Ni doped TiO_2 thin film was successfully prepared by chemical bath deposition from $TiCl_4$, ethanol and nickel nitrate. The prepared thin film was successfully applied for the removal of hazardous Ponceau S dye from aqueous medium. The removal rate was found to be increased significantly with increasing irradiation time while on increasing initial dye concentration the removal rate drops. The removal rate increases from acidic to alkaline region, and maximum removal was obtained at the pH 8, after that removal rate drops slightly. The chemical oxygen demand of aqueous dye solution decreases when exposed photocatalytic treatment.

Acknowledgments The Authors are gratefully acknowledged to North Maharashtra University, Jalgaon for XRD, SEM and EDX. The Authors are also thankful to the Principal G.T.P. College, Nandurbar for providing necessary laboratory facilities.

References

Acosta DR, Martinez AI, Lopez AA, Magana CR (2005) Titanium dioxide thin films: the effect of preparation method in their photocatalytic properties. J Mol Catal A 228:273–283

Bahanmann DW, Pelizzetti E, Schiavello M (eds) (1991) Mechanisms on organic transforms on semiconductor particles. In: Pellezzetti E, Schiavello (Eds) Photochemical conversion and storage of solar energy. Kluwer Academic, The Netherlands, pp. 251–276

Blake DM (1999) Bibliography of work on the photocatalytic removal of hazardous compounds from water and air. Nat Renew Energy Lab 1617:35–98

Boye B, Dieng MM, Brillas E (2002) Degradation of herbicide 4-chloraphenoxy acetic acid by advanced electrochemical oxidation methods. Environ Sci Technol 36:3030–3035

Buechler KJ, Noble RD, Koval CA, Jacoby A (1999) Investigation of the effect of controlled periodic illumination on the oxidation of gaseous trichloroethylene using a TiO_2 thin film. Ind Eng Chem Res 38:892–896

Chen CC, Chaudhary AJ, Grimes SM (2005) Photodegradation of acid blue −29 and ethyl violet in the presence of NaOH and aluminium ions. J Hazard Mater 117:171–178

Denizil A, Say R, Arica Y (2000) Removal of heavy metal ions from aquatic solutions by embrane chromatography. Sep Purif Technol 21:181–190

Fijushima A, Rao TN, Tryk DA (2000) Titanium dioxide photocatalysis. J Photochem Photobiol C Photochem Rev 1:1–21

Ghorai TK, Dhak D, Biswas SK, Dalai S, Pramanik P (2007) Photocatalytic oxidation of organic dyes by nano-sized metal-molybdate incorporated titanium dioxide (MxMoxTi1 − xO6) (M = Ni, Cu, Zn) photocatalysts. J Mol Catal A Chem 273:224–229

Hermann JM (1999) Heterogenous photocatalysis: fundamentals and application to the removal of various types of aqueous pollutants. Catal Today 53:115–129

Hoffmann MR, Martin ST, Choi W, Bahanmann DW (1995) Environmental application of semiconductor photocatalysis. Chem Rev 95:69–96

Kansal SK, Singh M, Sud D (2007) Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. J Hazard Mater 141(3):581–590

Konstantinou IK, Sakellarides TM, Sakkas VA, Albanis TA (2001) Photocatalytic degradation of selected s-triazine herbicides and organophosphorus insecticides over aqueous TiO_2 suspensions. Environ Sci Technol 35:398–405

Linsebigler AL, Lu G, Yates JT (1995) Photocatalysis on TiO_2 Surfaces: principles, mechanisms, and selected results. Chem Rev 95(3):735–758

Mills A, Hunte SL (1997) An overview of semiconductor photocatalysis. J Photochem Photobiol A 108:1–35

Zhang X, Zhou M, Lei L (2005) Preparation of anatase TiO_2 supported on alumina by different metal organic chemical vapor deposition methods. Appl Catal A Gen 282:285–293