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USE OF N, S-CODOPED NANO TITANIA AS PHOTOCATALYST FOR DEGRADATION OF BRILLIANT GREEN

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Abstract: In the present work the effect of doping of N and S on TiO_2 has been investigated using brilliant green as a model system. The rate of photocatalytic degradation of the dye was monitored spectrophotometrically. The effect of variation of different parameters like pH, concentration of brilliant green, amount of photocatalyst, dopant percentage and light intensity on the rate of photocatalytic degradation was also observed. On the basis of the observation, a tentative mechanism for the photocatalytic degradation of brilliant green has also been proposed. Environmental pollution in its various facets is a burning problem all over the world, out of which water pollution is a major problem. The present work contributes in the solution of waste water treatment by degrading organic pollutant in harmless products.
Keywords: Brilliant green, N, S-codoped titania, Photocatalyst.
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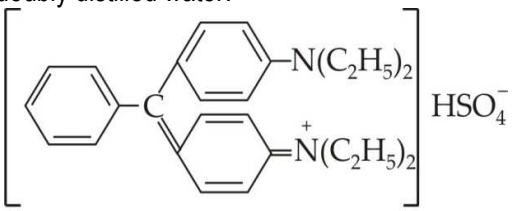
INTRODUCTION

The efficient utilization of solar energy is one of the major goals of modern science and engineering that will have a great impact on technological applications (Khan and Akikusa,1999).TiO_2 is one of the promising materials as photocatalyst because of its high efficiency, low cost, chemical inertness, and photostability (Schiavello and Dordrecht,1985). However, the wide spread technological use of TiO_2 is impaired by its wide band gap (3.2eV), which requires ultraviolet irradiation for photocatalytic activation. Because UV light accounts for only a small fraction (5%) of the Sun's energy compared to visible light (45%), any shift in the optical response of TiO_2 from the UV to the visible spectral range will have a profound positive effect on the photocatalytic efficiency of this material. An initial approach for shifting the optical response of TiO_2 from the UV to the visible spectral range was the doping of TiO_2 with transition metal elements (Chiou and Juang, 2007). Aluminium (III)-modified TiO_2 was prepared by sol-gel process and the degradation of dye pollutants under visible irradiation was examined by Zhao *et al.* (2008). The photocatalytic degradation of organic dyes methyl violet, cibacron blue FMR, maxilon red by TiO_2 and Ag-loaded TiO_2 has been reported by Sokmen *et al.*, (2000) However, metal doping has several drawbacks. The doped materials have been shown to suffer from thermal instability, and the metal centers act as electron traps, which reduces the photocatalytic efficiency. Furthermore, the preparation of transition metal doped TiO_2 requires more expensive ion implantation (Yamashita *et al.*, 1998). Later, it was shown that the desired band gap narrowing of TiO_2 can be better achieved by using anionic dopant species rather than metals ions. There are numerous recent reports on non metal doped TiO_2 systems, for example, carbon (Palanivelu *et al.*, 2007; park *et al.*, 2009), nitrogen (Prokes *et al.*, 2005; Sakthivel *et al.*, 2004; Torres *et al.*, 2004), boron (Grabowska *et al.*, 2009; Shahina

et al., 2008), sulfur (Tachikawa *et al.*, 2004; Umebayashi *et al.*, 2002) and fluorine (Huang *et al.*, 2006) doped photocatalysts. Li *et al.*, (2005) synthesized N, F-codoped TiO_2 photocatalysts by spray pyrolysis using $TiCl_3$ and NH_4F precursors and observed an enhanced photoreactivity of the TiO_2 in visible light. Codoping strategies have revealed the development of visible active photocatalysts in case of TiO_2 (Yang *et al.*, 2006). Guotian *et al.*, (2011) have prepared codoped TiO_2. It was observed that the photocurrent of this titania nanotube array films was greatly enhanced compared to that of undoped samples under visible light irradiation and the photocatalytic activities of the samples were evaluated on the removal of methylene blue under visible light irradiation. Looking to the importance of non-metal doping of semiconductor, in the present work, an attempt has been made to synthesize nanoparticles of N, S-codoped titania and its photocatalytic activity has been compared with pure titania.

EXPERIMENTAL

The commercial dye brilliant green (BG) was obtained from sd-fine Chem and was used as such without purification (λ_{max} = 630 nm). The dye solutions with different concentrations were further prepared using doubly distilled water.



Structure of Brilliant Green

A 200 W tungsten lamp (Phillips) was used for irradiating the solution in the visible range. A UV-Visible spectrophotometer (Systronics Model 106) was used for measuring optical density at different time intervals. The pH of the solution was adjusted with previously standardized H_2SO_4 and NaOH solutions. Other materials such as $Ti(OiPr)_4$ and Thiourea were purchased from Spectrochem and Himedia, respectively.

Synthesis of pure TiO_2: In a typical procedure, 50 mL of isopropyl alcohol and 100 mL of doubly distilled water was added into 10 mL of $Ti(OiPr)_4$ with vigorous stirring and the solution was kept overnight at room temperature. Then the solution was dried in an oven at 80ºC for 2 hrs and calcined at 400ºC for 3 hrs. Pure titania was obtained in the form of white powder.

Sythesis of N, S-codoped TiO_2: In a typical procedure, 50 mL of isopropyl alcohol and 0.5, 1, 1.5, 2.0 and 2.5 g of thiourea in 100 mL of doubly distilled water was added into 10 mL of $Ti(OiPr)_4$ in five different beakers, respectively with vigorous stirring and the solution was stand overnight at room temperature. Then the solution was dried in oven at 80ºC for 2 hrs and calcined at 400ºC for 3 hrs to get N, S-codoped titania as pale yellow powder. Here, the codoped titania samples have been synthesized with different amount of thiourea as dopant source *i.e.* 0.5, 1.0, 1.5, 2.0 and 2.5%.

A stock solution of brilliant green of concentration 1.00×10^{-3} M was prepared in doubly distilled water. This stock solution was further diluted as and when required. The optical density of brilliant green solution was determined with the help of a spectrophotometer at λ_{max} = 630 nm. The solution of brilliant green with concentration 2.50×10^{-5} M was prepared in doubly distilled water and 0.12 g of 1.5 % N, S-doped TiO_2 was added to it. The pH of reaction mixture was adjusted to 8.5 and this solution was exposed to a 200 W tungsten lamp. A decrease in absorbance of dye solution was observed with increasing time of exposure. The rate constant for this reaction was determined with the help of the following rate equation:

Rate constant (k) = 2.303 × Slope

The typical run for the photocatalytic degradation of brilliant green in the presence of pure TiO_2 and N, S-doped TiO_2 has graphically represented in Figure 1. Optimum rate

conditions and rate constants for pure TiO_2 and N, S-doped TiO2 have also been given below.
pH = 8.5
Brilliant Green (BG) = 2.50×10^{-5} M
N, S-TiO_2 = 0.12 g (1.5%)
Light Intensity (LI) = 50.0 $mWcm^{-2}$
Rate constant for N, S-TiO_2; k = 1.61×10^{-4} sec^{-1}
Rate constant for Pure TiO_2; k = 1.28×10^{-4} sec^{-1}

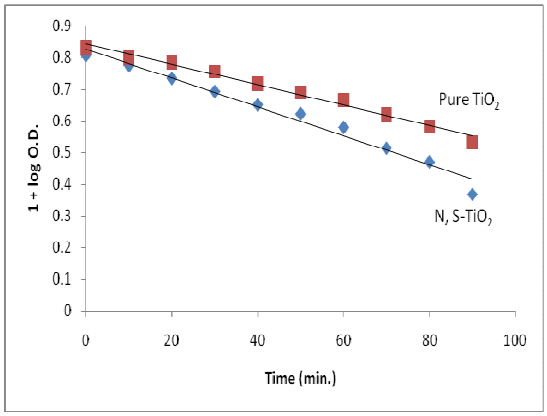


Figure 1. A Typical Run

The photocatalytic degradation of the dye is influenced by some factors and therefore, these were varied to find out the optimum conditions for the degradation of the dye.

Effect of pH: The pH of the solution is likely to affect the degradation of brilliant green dye. The effect of pH on the rate of degradation of the dye was investigated in the pH range 5.0-10.0. The results are reported in Table 1.

Table 1. Effect of pH

BG = 2.50×10^{-5} M N, S-TiO_2 = 0.12 g
LI = 50.0 $mWcm^{-2}$ % of Dopant = 1.5

pH	k × 10^4 (sec^{-1})
5.0	1.30
5.5	1.35
6.0	1.40
6.5	1.43
7.0	1.48
7.5	1.54
8.0	1.58
8.5	1.61
9.0	1.56
9.5	1.50
10.0	1.46

It has been observed that the rate of photocatalytic degradation of brilliant green was increased as pH was increased from 5.0 to 8.5 and it got an optimum value at pH 8.5. On further increasing the pH, the rate of the reaction was decreased. This behavior may be explained on the basis that the rate of photocatalytic degradation of dye increases when pH was increased from 5.0 to 8.5 as the availability of reducing species $O_2^{-\bullet}$ will increase. Thus, the rate of photocatalytic degradation of the dye increases. Above pH 8.5, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of brilliant green converts in its neutral form, which faces no attraction towards the negatively charged semiconductor surface and $O_2^{-\bullet}$. Hence, the rate is retarded.

Effect of Dye Concentration: The effect of dye concentration was studied by taking different concentrations of brilliant green. The results are tabulated in Table 2.

Table 2. Effect of dye Concentration

pH = 8.5 N, S-TiO_2 = 0.12 g
LI = 50.0 $mWcm^{-2}$ % of dopant = 1.5

Brilliant Green × 10^5 M	k × 10^4 (sec^{-1})
2.00	1.43
2.10	1.47
2.20	1.51
2.30	1.53
2.40	1.56
2.50	1.61
2.60	1.57
2.70	1.53
2.80	1.48
2.90	1.45
3.00	1.42

The rate of photocatalytic degradation of the dye was found to increase on increasing the concentration upto 2.50×10^{-5} M. It may be due to the fact that as the concentration of the dye was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of degradation of the dye was observed. The rate of photocatalytic degradation was found to decrease with increase in the concentration of the dye further as the dye itself will start acting as a filter for the incident irradiation. It will not permit the desired light intensity to reach the

semiconductor particles and as a result, the degradation rate decreases.

Effect of Amount of Semiconductor: The effect of amount of semiconductor was observed by taking different amount of semiconductor. The results are reported in Table 3.

Table 3. Effect of Amount of Semiconductor

pH = 8.5 BG = 2.50 × 10^{-5} M
LI = 50.0 mWcm^{-2} % of dopant = 1.5

Amount of N, S-TiO_2 (g)	k × 10^4 (sec^{-1})
0.04	1.45
0.06	1.49
0.08	1.53
0.10	1.57
0.12	1.61
0.14	1.60
0.16	1.60

It was observed that the rate of reaction was increased with increase in the amount of semiconductor N, S-doped TiO_2. The rate of degradation was optimum at 0.12 g of the photocatalyst. Beyond 0.12 g, the rates of reaction become virtually constant. This behavior may be explained on the basis that as the amount of semiconductor was increased, the exposed surface area of the semiconductor surface also increases. However, after this limiting value (0.12 g), an increase in the amount of semiconductor only increases the thickness of the semiconductor layer and not the exposed surface area. This was also confirmed by using reaction vessels of different dimensions. It was observed that the point of saturation is shifted to a higher value for vessels of larger capacities while it is shifted to lower value for vessels of smaller capacities.

Effect of % Variation of Dopant: The effect of % variation of dopant was observed by taking different % of dopant *i.e.* Thiourea. The results are reported in Table 4.

Table 4. Effect of % Variation of Dopant

pH = 8.5 N, S-TiO_2 = 0.12 g
LI = 50.0 mWcm^{-2} BG =2.50 × 10^{-5} M

% of Dopant	k × 10^4 (sec^{-1})
0.5	1.52
1.0	1.56
1.5	1.61
2.0	1.55
2.5	1.50

It was observed that as the % of dopant was increased, the rate constant was also increased. At 1.5 % of dopant, the rate of reaction was optimum but after that rate of reaction decreases. It is may be due to the reason that freely active site of titania decreases beyond 1.5% of dopant and accordingly, the rate of reaction starts decreasing.

Effect of Light Intensity: To investigate the effect of light intensity on the photocatalytic degradation of brilliant green, the distance between the light source and the exposed surface area was varied. The results are summarized in Table 5.

Table 5. Effect of Light Intensity

pH = 8.5 BG = 2.50 × 10^{-5} M
N, S-TiO_2 = 0.12 g % of Dopant =1.5

Intensity of light (mWcm^{-2})	k × 10^4 (sec^{-1})
30.0	1.55
40.0	1.57
50.0	1.61
60.0	1.58
70.0	1.53

The results indicate that photocatalytic degradation of brilliant green was accelerated as the intensity of light was increased from 30.0 to 50.0 mWcm^{-2}, because an increase in the light intensity will increase the number of photons striking per unit area of semiconductor surface per unit time. On further increasing the intensity of light above 50.0 mWcm^{-2}, there was a decrease in the rate of reaction. This may be due to some side reactions or thermal effect.

Mechanism: On the basis of the above observations, a tentative mechanism for photocatalytic degradation of brilliant green is proposed as:

$$^1BG_0 \xrightarrow{h\nu} {}^1BG_1 \quad \text{..... (i)}$$

$$^1BG_1 \xrightarrow{ISC} {}^3BG_1 \quad \text{..... (ii)}$$

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB) \quad \text{... (iii)}$$

$$e^- + O_2 \longrightarrow O_2^{\bullet-} \quad \text{..... (iv)}$$

$$O_2^{-\bullet} + {}^3BG_1 \longrightarrow \text{Leuco BG} \quad \text{.... (v)}$$

$$\text{Leuco BG} \longrightarrow \text{Products} \quad \text{..... (vi)}$$

Brilliant green dye (BG) absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting N, S-TiO_2 (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will reduce the dye brilliant green to its leuco form, which may ultimately degrade to harmless products. It was also confirmed that this degradation proceeds through reduction by using hydroxyl radical scavenger (2-propanol), where the rate of degradation was not affected appreciably.

CONCLUSION

Pure TiO_2 and N, S-TiO_2 semiconductors have been prepared by sol-gel method. The observations of photocatalytc degradation of brilliant green dye revealed that N, S-TiO_2 extended the absorption of TiO_2 into the visible light range, which was confirmed by higher photocatalytic activity of N, S-TiO_2 than the pure TiO_2 under visible light irradiation. These improved properties can be attributed to the increased visible light absorption, the improved photogenerated electrons–hole separation and the surface defects produced by N and S co-doping. Doping of semiconductors by metals or non-metals reduces its band gap and as a result the activity of semiconductor is increased. In benign nature of non-metal makes its use more fruitful in compare to metals. The present work contributes in the enhancement of titania performance by doping it with nitrogen and sulphur.

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