Contents lists available at ScienceDirect



Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



# Effect of operational parameters on photodegradation of Direct Blue 53 by silver loaded-titania under ultraviolet and solar illumination



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#### ARTICLE INFO

Keywords: Ag-TiO<sub>2</sub> Photocatalysis UV light Direct Blue 53 Solar light

# ABSTRACT

Photocatalytic degradation of Direct Blue 53 (DB 53) by Ag loaded  $TiO_2$  has been investigated under UV and solar light. Photodeposition of 2.0% Ag on the surface of  $TiO_2$  enhanced its photoactivity in DB 53 degradation. Optimal experimental conditions on catalyst amount, pH and dye concentration have been investigated. Addition of some inorganic oxidizing species such as  $H_2O_2$ ,  $(NH_4)S_2O_8$  and  $KBrO_3$  up to a certain concentration enhanced the rate of degradation. The increased photoactivity of Ag– $TiO_2$  than bare  $TiO_2$  under UV and solar light illumination can be ascribed to the effect of silver deposits acting as electron traps on Ag– $TiO_2$  surface. The degradation efficiency of Ag– $TiO_2$  under solar radiation is higher than its efficiency in UV light.

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# 1. Introduction

Nowadays environmental challenges comprise an overall reduction of human disclosure to chemical pollutants and minimization of human impact on sensitive eco-systems and biodiversity. Heterogeneous photocatalysis involving TiO<sub>2</sub> has been systematically reviewed at fundamental and applied levels [1–3]. TiO<sub>2</sub> based photocatalysis has emerged as an exceedingly promising advanced oxidation technology that can successfully address the society for clean water based on the utilization of solar energy [4]. The ample verification of the effectiveness of TiO<sub>2</sub> to generate highly reactive hydroxyl radicals upon UV light irradiation, along with its environmentally benevolent properties and relatively low cost, has rendered TiO<sub>2</sub> a key material for the complete devastation of recalcitrant organic contaminants in water resources [5]. Furthermore TiO<sub>2</sub> is a universally used photocatalyst due to its easy availability, low cost, non-toxic and chemical stability.

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http://dx.doi.org/10.1016/j.mssp.2015.03.037 1369-8001/© 2015 Elsevier Ltd. All rights reserved. The major drawback of  $TiO_2$  is its large band gap (3.2 eV) which absorbs only 4% of UV light in solar spectrum [6,7]. Consecutively to overcome these drawbacks, researchers have adopted many approaches such as phase and morphological control, coupling of photocatalysts, metal halide loading and doping [8–14].

Modification of the TiO<sub>2</sub> surface with metals such as Pt, Pd, Au and Ag was reported to enhance the catalytic activity of TiO<sub>2</sub> material and increase the quantum yield [15–17]. Selvam et al. [18,19] reported that an easy onestep photocatalytic synthesis of 1-aryl-2-alkylbenzimidazoles by Pt loaded TiO<sub>2</sub> nanoparticles under UV and solar light and cost effective one-pot photocatalytic synthesis of quinaldines from nitroarenes by Ag loaded TiO<sub>2</sub>. It enables efficient quinaldine assembly from nitrobenzenes under photoirradiation conditions. This process has significant advantages when compared with other methods because of its very cheap and stable reactant, and also the reaction proceeds under mild ambient conditions. In particular, Ag nanoparticles deposited on TiO<sub>2</sub> surface  $(Ag/TiO_2)$  have been promising, thanks to the nontoxicity of Ag with catalytic and antibacterial activity [20,21]. In our previous paper we reported the synthesis, characterization and catalytic activity of Ag loaded TiO<sub>2</sub> [14]. For practical application of dye wastewater treatment by Ag-TiO<sub>2</sub>, there is a need to determine the optimal conditions of experimental parameters for economic and efficient removal of the dye. Hence the present study was carried out to evaluate the optimal experimental parameters on the degradation of azo dye Direct Blue 53 (DB 53) by Ag-TiO<sub>2</sub> under UV and solar light.

#### 2. Experimental

## 2.1. Materials

The Direct Blue 53 (DB 53) from CDH Chemicals Company was used as such. Titanium dioxide (anatase) with a BET surface area of 21.53 m<sup>2</sup> g<sup>-1</sup> and perchloric acid were obtained from Qualigens. Silver nitrate (analytical grade) from Merck was used as silver source for the preparation of Ag loaded TiO<sub>2</sub> photocatalysts. Preparation and characterization of Ag loaded TiO<sub>2</sub> were discussed in our earlier article [14]. The double distilled water was used to prepare experimental solution. The pH of the aqueous DB 53 dye solution before irradiation was adjusted using NaOH or H<sub>2</sub>SO<sub>4</sub>.

#### 2.2. Irradiation procedure

#### 2.2.1. UV light

For the degradation by UV-A light (365 nm), a Heber Multilamp-photoreactor HML MP 88 was used [22]. This model consists of 8 W medium pressure mercury vapor lamps set in parallel and emitting 365 nm wavelength. It has a reaction chamber with specially designed reflector made of highly polished aluminum and built in cooling fan. It is provided with a magnetic stirrer and 50 mL capacity reaction glass tubes. The light exposure length is 330 mm. The irradiation was carried out using four parallel 8 W medium pressure mercury lamps. The solution with Ag–TiO<sub>2</sub> and dye was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution.

## 2.2.2. Solar light

Solar light intensity was measured for each 30 min and the average light intensity over the duration of each experiment was determined. The sensor was always set in the position of utmost intensity. The intensity of solar light was précised using LT Lutron LX-10/A Digital Lux meter and the intensity was  $(1250 \times 100) \pm 100$  lx. The intensity was almost constant during the experiments.

#### 2.2.3. Photocatalytic studies

50 mL of DB 53  $(3 \times 10^{-4} \text{ M})$  with the appropriate amount of catalyst was stirred for 30 min in the dark prior to illumination consecutively to achieve highest adsorption of DB 53 onto the photocatalyst surface. During the illumination time no volatility of the solvent was noted. At specific time intervals 2–3 mL of sample was withdrawn and catalyst was detached by centrifugation. The changes in the concentration of DB 53 were monitored from their characteristic absorption at 315 nm and 603 nm using UVvisible spectrophotometer. The absorbance at 603 nm is used to monitor the decolorization of DB 53. The absorbance at 315 nm represents the aromatic part of DB 53 and its decrease indicates the degradation of aromatic part of dye molecule.

#### 3. Results and discussion

#### 3.1. Characteristics of catalyst

Ag-TiO<sub>2</sub> photocatalyst used in this study had been characterized by various surface analytical techniques [14]. Results of DRS spectra reveal that the loading of silver ions causes important changes to the absorption spectrum of TiO<sub>2</sub> ensuing in high absorbance from 400 nm to entire visible region. The XRD patterns of silver loaded TiO<sub>2</sub> samples almost overlap with that of bare TiO<sub>2</sub> showing no other diffraction peaks. This suggests that silver particles are well dispersed on the surface of the TiO<sub>2</sub> matrix. TiO<sub>2</sub> anatase type structure is kept almost same in all silver loaded catalysts. Analysis of SEM images exhibits that the allocation of silver on the surface of the TiO<sub>2</sub> is not uniform and that Ag-loaded TiO<sub>2</sub> catalyst contains irregular shaped particles, which are the aggregates of minute crystals. The EDX diagrams of 2% Ag-TiO<sub>2</sub> at two different regions give 2.09 and 6.88 atomic weight percentages of Ag. This clearly reveals that the deposition of silver on  $TiO_2$ is non-uniform. Increase in the silver content in the Ag-TiO<sub>2</sub> photocatalyst decreases the BET surface area catalyst.

# 3.2. Comparison of photocatalytic activities of $TiO_2$ and Ag loaded $TiO_2$ catalysts under UV and solar light

The UV–vis spectra of DB 53  $(3 \times 10^{-4} \text{ M})$  solution at different UV irradiation times are shown in Fig. 1. There is a small shift at 603 nm but there is no change in the lower wavelength maximum at 315 nm during irradiation but the intensity at 315 and 603 nm decreases gradually during the degradation.



**Fig. 1.** UV-visible spectra of DB 53 on irradiation in the presence of Ag-TiO<sub>2</sub> under UV light: Ag-TiO<sub>2</sub>=3 g/L, [DB 53]= $3 \times 10^{-4}$  mol/L, pH=5.0 ± 0.1,  $I_{UV}$ =1.381 × 10<sup>-6</sup> einstein L<sup>-1</sup> s<sup>-1</sup>.

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