Preparation and Characterization of N-doped TiO_2 with Enhanced Photocatalytic Activity

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***Abstract* – TiO_2 is the most frequently employed photocatalyst in realising complete mineralization of organic pollutants in water treatment. Its large bandgap energy necessitates though UV excitation to induce charge separation within the particle. Nitrogen doped into substitutional sites of TiO_2 has shown bandgap narrowing and photocatalytic activity in the visible light. N-doped and non-doped mesoporous titania were synthesized using hydrothermal and ultrasound methods. Titanium-tetraisopropoxide was used as Ti precursor. UV-VIS and N_2 adsorbtion-desorbtion techniques were used to investigate the structure, morphology and optical properties of these photocatalysts. The photocatalytic activity of mesoporous titania was studied by different dyes photoreactions.**

I. INTRODUCTION

In the environmental technology sector, industrial wastewater treatment is gaining importance for the removal of organic pollutants [1]. Large amounts of organic pollutants consumed in the industries are being released into the eco-system over the past few decades and they constitute a serious threat to the environment [2]. As chemical and agricultural wastes, these contaminants are frequently carcinogenic and toxic to the aquatic system because of their aromatic ring structure, optical stability and resistance to biodegradation [3].

Catalytic technologies are gaining recognition in the field of environmental protection [4]. In past decades, the traditional physical techniques for the removal of organic pollutants from wastewaters have included adsorption, biological treatment, coagulation, ultrafiltration and ion exchange on synthetic resins. Those methods have not always been effective and they may not actually break down the pollutants in wastewater. For example, adsorption technology does not degrade the contaminants, but essentially transfers the contaminants from one medium to another, hence, contributing to secondary pollution [2].

Heterogeneous photocatalysis becomes an elegant alternative for dye degradation. Many photocatalysts have been used to degrade organic pollutants: ZnO, Nb_2O_5, TiO_2 [5-7].

Photocatalytic oxidation in the presence of semiconducting materials such as TiO2, of organic compounds with environmental concern (e.g. pesticides, dyes, etc.), have been studied extensively during the last 20 years [8]. TiO_2 is interesting due its range of applications: ability to split water into H_2 and O_2 [9] and use in dye sensitised solar cell (DSSC) or Graetzel cells [10] being very topical.

Anatase is a metastable low temperature form of TiO_2 and generally accepted as the most suitable for photochemical devices [11,12]. When processing TiO_2 precursors there is a limit to the upper processing temperature. This limit is process dependent e.g. direct oxidation or sol–gel, and varies from 500 to 1000 °C [13]. Low temperature processing is considered valuable, as it affords low energy operations, and an ability to use a wider variety of substrates.

The use of TiO_2 photocatalyst for the degradation of organic pollutant has been studied extensively. However the large band gap of TiO_2 requires higher energy artificial UV light for activation [14].

Doping of TiO_2 with either anion, cation or codoping with different dopants was found to be an effective method to achieve efficient photocatalysts in the visible-light range [10].

There is an increasing interest in the synthesis of N-doped TiO_2 photocatalysts and related areas as these narrow band gap semiconducting materials can be used for visible light photocatalysts [9]. Asahi et al. [15] reported that substitutional doping TiO_2 with nitrogen could narrow its band-gap by mixing of N 2p and O 2p states in the valence band and consequently induce the absorption edge red-shifted to lower energies (longer wavelengths, especially in the visible region), enhancing its visible-light responsive photocatalytic activity. Some studies [16,17] however proposed the appearance of intragap localized N 2p states, related to the photothreshold energy decrease, facilitating the formation of oxygen vacancies.

Many of the dyes used in industry are toxic and carcinogenic, and this poses a serious hazard to aquatic living organisms. The toxicity and impact of dyes released to the environment have therefore been extensively studied [18]. Furthermore, because of the increasingly strict restrictions on the organic composition of industrial effluents, it is essential to eliminate dyes from wastewater before they can be discharged into the environment [19].

Rose Bengal (Acid Red 94) is a tetraiodo-substituted dye of the xanthenes class of dyes. It exhibits unusual spectroscopic and photochemical properties including a large absorption coefficient in the visible region and a high tendency for intersystem crossing to produce a photochemically active triplet excited state. Despite the numerous applications of Rose Bengal dye in various areas, information on its photolytic decolorization is not available in the literature [20]. The molecular formula for this dye is $C_{20}H_4Cl_4I_4O_5$ and the molar mass is 973,67 g/mol.

II. MATERIALS AND METHODS

Mesoporous titania was synthesized using hydrothermal and ultrasound methods. Different blockcopolymers, such as Pluronic P123 and F127, and titanium-tetraisopropoxide as Ti source were used for the TiO2 synthesis. Different types of N-doped and non-doped mesoporous titania were synthesized by varying composition of the surfactant.

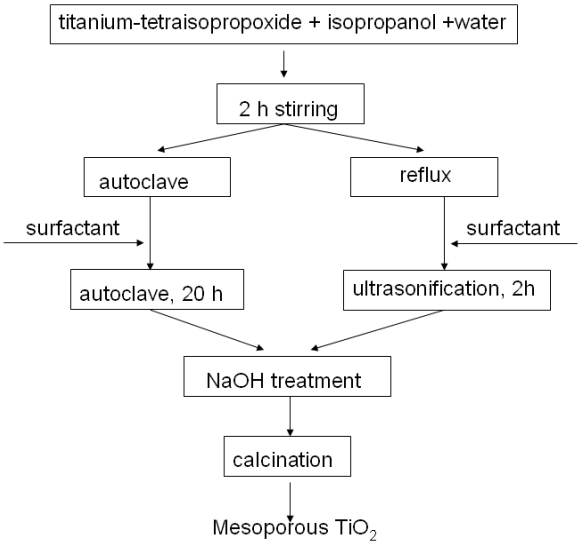

Fig.1. The synthesis procedure for the non-doped mesoprous TiO_2

The obtained mesoporous TiO_2 was used next in the doping step of the synthesis. This involved mixing calculated quantities of TiO_2 and urea such that the Ti: Urea ratio in the final solution was 1:2. This solution was then filtrated. The dry residue was transferred to calcination furnace and heated at 400°C for 4h to obtain the final sample.

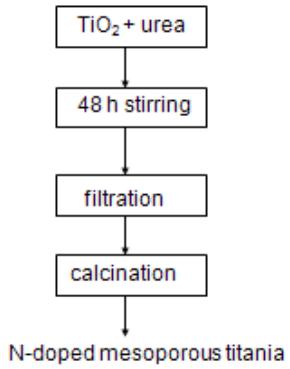

Fig. 2. The synthesis procedure for the N-doped mesoprous TiO_2

III. RESULTS

UV absorption spectrum and N_2 adsorbtion-desorbtion techniques have been used to investigate the structure, morphology and optical properties of these photocatalysts.

The UV–vis spectra of the samples are shown in Fig. 3. The TiO_2 7c sample shows single sharp edges with the band-gap absorption onset at 387 nm (characteristic for TiO_2) ,while the sample containing N exhibits a slight deviation, which indicates the absorption edge extending into the visible region.

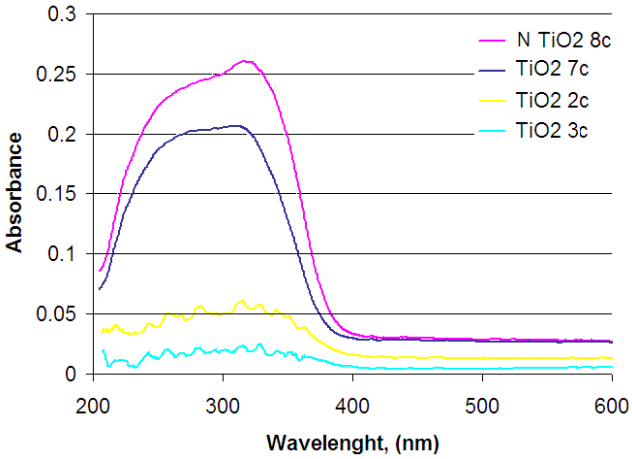

Fig. 3. UV-VIS spectra of some synthetised samples

TABLE 1. SAMPLES NOTATION

Sample	2c	3c	7c	8c
Method	A+A	A+US	REF+US	REF+US
Surfactant	P123	F127	P123	P123

A – autoclave
US – ultrasound
REF – reflux
P123 – Pluronic P123
F127 – Pluronic F 127

In Fig.4. the isotherms for samples 3c, 7c and 8c have been displaced with 50, 150 and 250 cc/g STP.

All the four isotherms can be considered as type IV, which is typical for mesoporous materials.

The large amount of pores of 3 – 7 nm in diameter and the BET surfaces values of 200 – 290 m^2/g demonstrate also the fact that the synthesized samples are mesoporous materials .

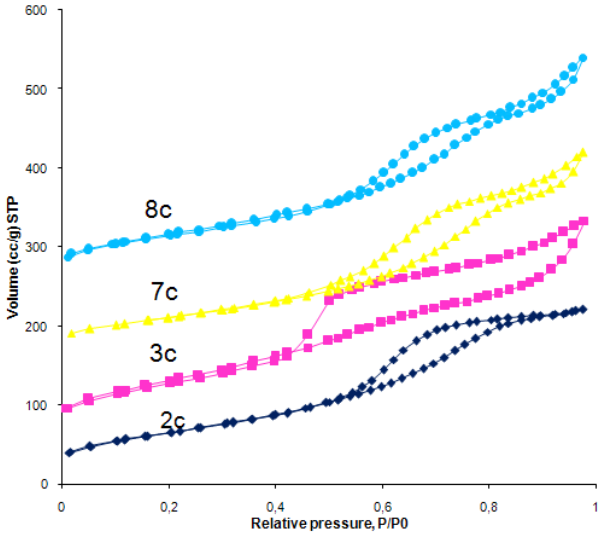

Fig.4. N2 adsorption - desorption isotherms

The photocatalytic activities of both mesoporous titania and N-doped mesoporous titania were studied for the photodegradation of the dye Rose Bengal.

The experiments were conducted using 300 mL dye solution prepared with pure water. The solutions were magnetically stirred in the dark for 30 minutes after adding

the catalyst to ensure the adsorption / desorption equilibrium. Samples consisting in three milliliters of the suspension were taken at specific time intervals and were immediately centrifuged at 2500 rpm for 5 min to completely remove the catalyst particles. Zero time reading was considered to be when the lamp was turned on.

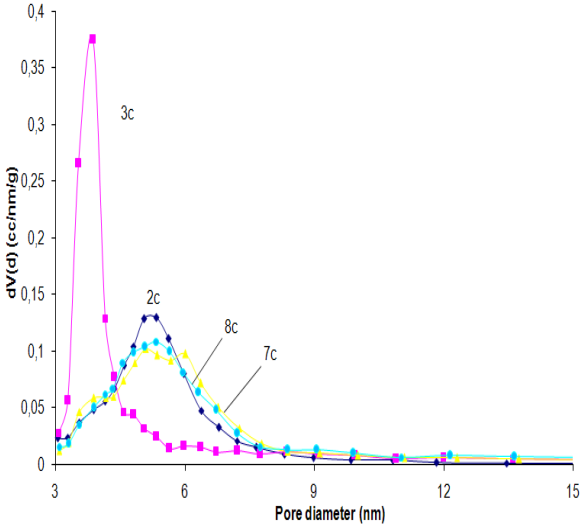

Fig. 5. Pore size distribution (BJH method)

TABLE 2. DIMENSIONAL PROPERTIES OF THE SYNTHESIZED MATERIALS

	2c	3c	7c	8c
BET Surface area (m^2/g)	229,6	290	211	243
Pore diameter (nm)	5,341	3,9	5,1	5,35
Pore volume (cm^3/g)	0,334	0,46	0,424	0,45

From the experimental results it was observed that the N-doped mesoporous titania obtained by ultrasound method has higher photocatalytic activity than the undoped mesoporous TiO_2 (Fig. 6). Moreover, the N-doped mesoporous titania also has photocatalytic activity under visible light, unlike the undoped mesoporous TiO_2 (Fig. 7).

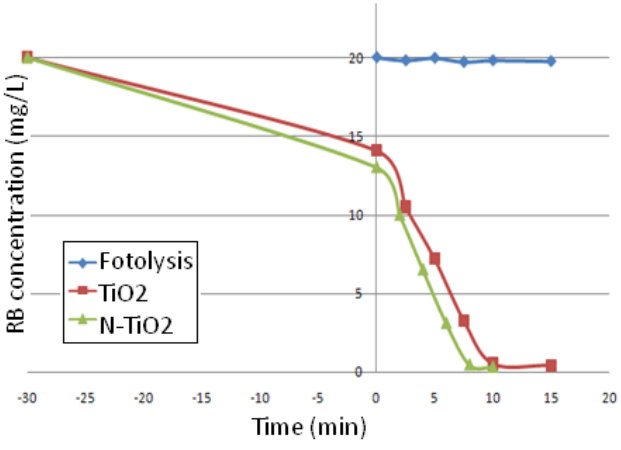

Fig. 6. Photocatalytic activity of N-doped and non-doped mesoporous titania under UV light

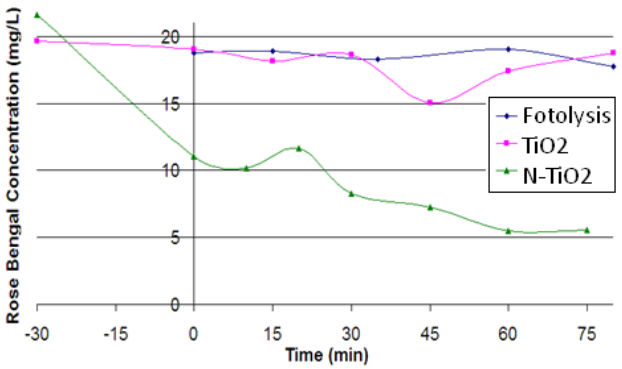

Fig. 7. Photocatalytic activity of N-doped and non-doped mesoporous titania under visible light

IV. CONCLUSIONS

We synthesized N-doped and non-doped mesoporous titania via hydrothermal and ultrasound methods using blockcopolymers (Pluronic P123 and F127) as surfactants and organic sources of Ti.

After the samples characterization it was concluded that all the obtained samples are mesoporous materials, having a large amount of pores of 3 – 8 nm in diameter and BET surfaces values of 200 – 290 m^2/g.

Synthetized mesoporous titania (N-doped and non-doped) were used as heterogeneous catalysts for the treatment of textile wastewater containing dyes. We found that N-doped anatase titania could be prepared by a simple method using titanium tetraisopropoxide and urea. It was observed that the N-doped mesoporous titania obtained by ultrasound method has proven to have photocatalytic activity in visible light, unlike the undoped mesoporous TiO_2.

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