Reactive Yellow 125 degradation using titanium dioxide doped with N

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ABSTRACT

The aim of this paper was the syntheses of titanium dioxide undoped and doped with nitrogen ion through sol-gel method in order to degrade *Reactive Yellow 125* dye from water. The obtained nanomaterials were characterized by XRD, DRUV-VIS and SEM/EDX. N-doped TiO_2 catalyst exhibited good electrocatalytic activity for RY125 discoloration and degradation under both UV and VIS irradiation, which gives a practical utility of this catalyst.

Keywords: titanium dioxide, nitrogen doped titania, water treatment

INTRODUCTION

As recalcitrant organic pollutants continue to increase in air and wastewater streams, environmental laws and regulations become more stringent [1, 2]. Wastewaters from various industries, factories, laboratories, etc. are serious problems to the environment. Several of these chemicals such as azo dyes, herbicides, and pesticides are actually present in rivers and lakes, and are in part suspected of being endocrine-disrupting chemicals (EDCs) [3, 4]. Degradation of dyes in industrial wastewaters has therefore received increasing attention and some methods of remediation have been preferred. Traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants [5, 6]. These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. This will require a further treatment of solid-wastes and regeneration of the adsorbent which will add more cost to the process. Microbiological or enzymatic decomposition, biodegradation, ozonation, and advanced oxidation processes such as Fenton and photo-Fenton catalytic reactions, H_2O_2/UV processes have also been used for dyes removal from wastewaters. Recent studies have been devoted to the use of photocatalysis in the removal of dyes from wastewaters, particularly, because of the ability of this method to completely mineralize the target pollutants. Titania photocatalysis also referred to as the "Honda–Fujishima effect" was first unfolded by the pioneering research of Fujishima and Honda [7]. Consequently, the application of titania photocatalysis extended to environmental frontiers [8]. Titanium dioxide (TiO_2) or titania is a very well-known and well researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. The interests in TiO_2-based photocatalysts have also led to the development of several methods of preparing the catalysts for varied usages. Various methods are available for the preparation of TiO_2-based photocatalysts, such as electrochemical, precipitation, hydrothermal and solvothermal, sol–gel, etc [9].

2. MATERIALS AND METHODS

2.1. N-doped TiO_2 synthesis

The materials used for the synthesis were: titanium isopropoxide (TTIP, Fluka), ethanol, distilled water, urea ($(NH_2)_2CO_2$, Merk).

Sol-gel (SG) method presumes the mixing of 30 mL of ethanol with 5 mL of TTIP (the precursor for Ti) added by drop wise. After a few minutes of stirring, distilled water was added also in drops. The doping precursors, $(NH_2)_2CO_2$ for N-doped TiO_2 synthesis, were added after the pH adjustment. The solution was continuous stirred for one hour and the obtained materials were filtered, washed and dried at 60°C. The thermal treatment was achieved for 2 hours at 500°C and 600°C temperatures.

2.2. Materials characterization

Phase characterization of undoped and N-doped TiO_2 nanocrystals was carried out by X-ray diffraction (XRD) using a PANalytical X'PertPRO MPD Difractometer, Cu tube. The particles size and morphology of the materials were determined using Scanning Electron Microscopy (SEM) using an Inspect S PANalytical model coupled with EDX device for elemental identification. The light absorption properties of the prepared materials crystallized in pure anatase phase were studied by DRUV-VIS performed under ambient conditions in the wavelength range of 300-550 nm.

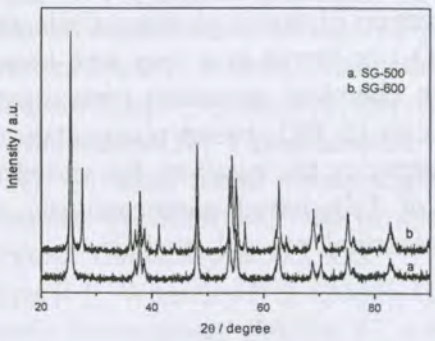
2.3. Photocatalytic measurements

The photocatalytic activities of the prepared materials were assessed through degradation of 50 mg L^{-1} *Reactive Yellow 125* in an RS-1 photocatalytic reactor (Heraeus, Germany). The volume of the reaction solution was 200 ml, into which 0.2 g of photocatalyst was added. UV and VIS irradiation was provided by a medium-pressure Hg lamp (300 W). After irradiation time of 2 hours, the suspension was sampled and filtered through a 0.2 μm membrane filter. The concentration of RY125 was measured in terms of absorbance at 225 nm and 388 nm characteristics to aromatic ring degradation and respective, discoloration with a Carry 100 Varian spectrophotometer.

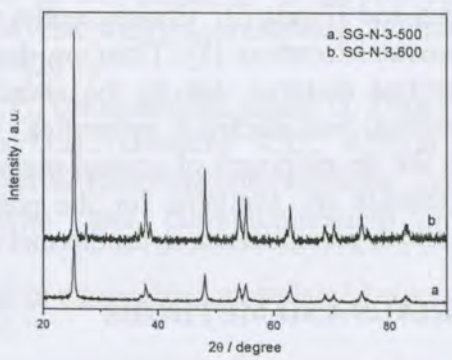
3. RESULTS AND DISCUSSIONS

3.1. N-doped TiO_2 nanocrystals characterization

From the XRD spectra it can be seen that the sample SG-500 (spectra a, Fig.1i.) crystallized in anatase form, and for sample SG-600 (spectra b, Fig.1i.) it appeared phase transition, anatase-rutile. The specific peaks of anatase TiO_2 corresponding to $2\theta \sim 25.2°$, 37.87°, 48.01°, 53.81°, 62.67°, 75.07 [10] and for rutile the $2\ \theta$ values are 27.5°, 30.8°, 36.4°[12]. The XRD patterns for N-doped TiO_2 (Fig. 1ii) shows that the anatase phase is predominant at 500°C, and when the temperature is increased at 600°C rutile phase occurred.



i)



ii)

Fig.1. XRD patterns for i) undoped TiO_2 and ii) N-doped TiO_2

Figure 2 presents the *DRUV-VIS* spectra recorded for SG-500 and SG-N-500 (Fig. 2). Spectra analysis shows that undoped TiO_2 synthesized by sol-gel route adsorbs only in UV domain at the wavelength around 390 nm. The literature data presented that the anatase form of undoped TiO_2 has band-gap energy about 3.2eV, which means that for electrons excitation the semiconductor needs to be expose to a radiation with the wavelength smaller or equal with 385 nm, namely in UV domain [13]. The nitrogen presence slightly shifts the spectra to VIS domain.

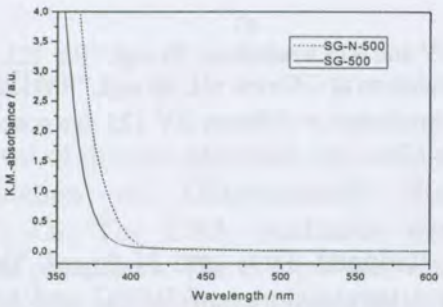


Fig. 2. DRUV-VIS spectra of synthesized materials

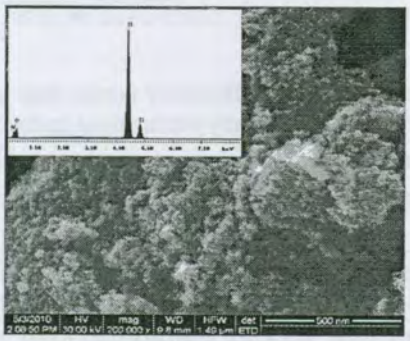
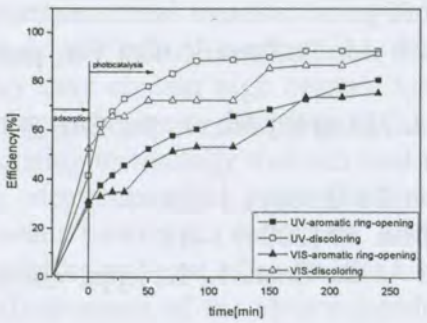


Fig. 3. SEM image of N-doped TiO_2; Inset: EDX spectra

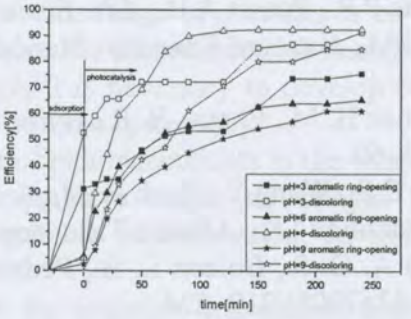
The SEM morphology of N-doped TiO_2 is shown in Fig. 3. Particles shape of doped TiO_2 obtained by sol-gel method present nano-spherical morphology, highly agglomerated. EDX patterns confirm the nitrogen doping ions presence in titanium dioxide structure (Inset Fig. 3).

3.2. Photocatalytic application of N-doped TiO_2 catalyst

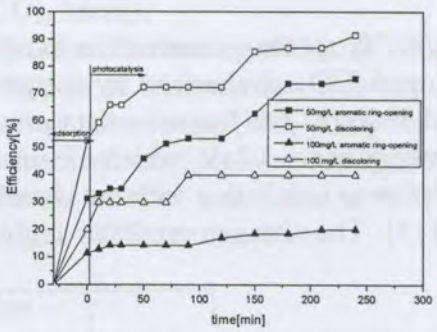
Figure 4 a-c show the results of photocatalytic application for RY125 degradation and discoloration. This exhibited a good electrocatalytic activity under both UV and VIS irradiation and as we expected the discoloration efficiency was better in comparison with aromatic ring opening (Fig. 4 a), which informed that intermediates occurred during the photocatalytic process. The aromatic ring opening is favored by acidic pH (see Fig. 4 b). Also, it is noticed that RY125 concentration increasing led to process efficiency decreasing.



a)



b)



c)

Fig.4. a)Photocatalytic process efficiency versus time under UV and VIS irradiation; 50 mgL^{-1}RY 125, pH=3; b) Photocatalytic process efficiency versus time under VIS irradiation at different pH; 50 mgL^{-1}RY 125 c). Photocatalytic process efficiency versus time under VIS irradiation at different RY 125 dye concentrations; pH=3

CONCLUSIONS

In this study two types of materials, i.e., undoped TiO_2 and N-doped TiO_2 were synthesized through sol-gel method at two different temperatures of 500°C and 600°C for degradation of RY 125 from water. XRD spectra revealed that at 500°C it was obtained pure crystalline phase of anatase, and at 600°C phase transition occurred from anatase in rutile. Undoped/doped TiO_2 particles synthesized by sol-gel method presented nano-spherical morphology, highly agglomerated. N-doped TiO_2 catalyst exhibited good electrocatalytic activity for RY125 discoloration and degradation under both UV and VIS irradiation. The best degradation performance was achieved and acidic conditions, and higher dye concentration decreased the photocatalytic performance of this catalyst.

ACKNOWLEDGEMENTS

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