

Photocatalytic performance of Sn-doped TiO₂ nanostructured mono and double layer thin films for Malachite Green dye degradation under UV and vis-lights

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Abstract

Nanostructure Sn⁴⁺-doped TiO₂ based mono and double layer thin films, contain 50% solid ratio of TiO₂ in coating have been prepared on glass surfaces by spin-coating technique. Their photocatalytic performances were tested for degradation of Malachite Green dye in solution under UV and vis irradiation. Sn⁴⁺-doped nano-TiO₂ particle a doping ratio of about 5[Sn⁴⁺/Ti(OBuⁿ)₄; mol/mol%] has been synthesized by hydrothermal process at 225 °C. The structure, surface and optical properties of the thin films and/or the particles have been investigated by XRD, BET and UV/vis/NIR techniques. The results showed that the double layer coated glass surfaces have a very high photocatalytic performance than the other one under UV and vis lights. The results also proved that the hydrothermally synthesized nano-TiO₂ particles are fully anatase crystalline form and are easily dispersed in water. The results also reveal that the coated surfaces have hydrophilic property.

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1. Introduction

Textile industry wastewater is heavily charged with unconsumed dyes, surfactants and sometimes traces of metals. These effluents cause a lot of damage to the environment. In most countries researchers are looking for appropriate treatments in order to remove pollutants, impurities and to obtain the decolourization of dyehouse effluents [1–3]. Usually, the conventional biological treatment processes do not readily remove dyes from textile wastewater, because of their resistance to biological degradation [4,5]. Various chemical, physical and biological processes are currently used such as flocculation, ultrafiltration, adsorption, ozonation and chlorination [6]. These processes are not efficient because they appear in solid wastes, thus creating other environmental problems requiring further treatment. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove hazardous dyes and organics

from industry effluents [4]. One of the effective methods of wastewater treatment containing dyes is their photocatalytic degradation in solutions illuminated with UV irradiation, which contains a suitable photocatalyst, mainly TiO₂ sold commercially as Degussa P25 and Hombicat UV100. These are recognized as excellent photocatalysts and have good prospects in water and air purification [7–9]. The photodegradation of the hazardous materials in colloidal and particulate TiO₂ catalyst suspensions has been well studied [10,11]. However, this application has not been successfully commercialized, in part because of the costs and difficulties in separating the TiO₂ nanoparticles from the suspension after degradation has occurred. To solve this problem, TiO₂ film photocatalysts have been widely researched in photodegradation [12–14]. In recent years, nano-TiO₂ based thin films with super-hydrophilic and photocatalytic characteristics have attracted a great deal of attention. They have many advanced functions and features, including self-cleaning, antifogging, deodorizing and sterilizing. When exposed to UV light, organic compounds can be break down with TiO₂ films and enable water to spread evenly on their super hydrophilic surface to easily realize surface self-cleaning. Many researchers

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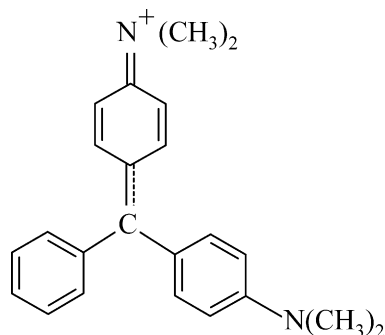
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have focused on this subject [15–18]. In order to synthesize of TiO_2 , different processes have been reported, such as sol–gel process [19], hydrolysis of inorganic salts [20], ultrasonic technique [21], microemulsion or reverse micelles and hydrothermal process [22–24]. A multitude of polar or non-polar solvents have been used in these processes. In these processes, high calcination temperature above 450°C is usually required to form regular crystal structure, except for the hydrothermal process. However, in the meantime, the high temperature treatment can decline the surface area and surface hydroxyl or alkoxide groups on the surface of TiO_2 , which provide easy dispersion, are lost. Thus, in this work, the hydrothermal process was selected to synthesize of Sn^{4+} -doped nanosized TiO_2 particles at low temperature, which seems to be really attractive to further improve the photocatalytic activity of TiO_2 . Compared with the other TiO_2 powders, these TiO_2 nanoparticles have several advantages, such as being in fully pure anatase crystalline form, having fine particle size with more uniform distribution and high-dispersion ability either in polar or non-polar solvents, stronger interfacial adsorption and easy coating on different supporting material. In this work, photocatalytic activity of hydrothermally synthesized nanostructure Sn-doped TiO_2 based mono and double layer thin films supported on glass surfaces were examined for degradation of Malachite Green (MG), which one of the hazardous dye, in aqueous solutions under UV and vis-lights and the results were compared.

2. Experimental

2.1. Chemicals and apparatus

The reagents employed were titanium (IV)-*iso*-propoxide, $[\text{Ti}(\text{OPr}^i)_4]$, 97%, Fluka], as TiO_2 source; tin (IV) chloride (Alpha, 98%) as dopant; deionized water as hydrolysis agent; tetraethylorthosilicate (TEOS, Aldrich, 98%) as a binder agent; hydrochloric acid (Merck, 37%) as catalyst; 2-butoxyethanol (2-BuOEtOH, Aldrich, 99%) and ethyl alcohol (EtOH, 96%) as solvents. The glass plate (5 cm \times 5 cm) as substrate. Malachite Green (MG), which was used as a model pollutant and purchased from a local textile factory was of analytical reagent grade; its chemical formula can be presented as:



Malachite Green

Nano- TiO_2 particle was synthesized by Berghoff model hydrothermal unit interfaced with a temperature (up to 240°C) and time controller unit. In order to determine the crystal phase,

Rigaku Geigerflex D Max/B model X-ray diffractometer (XRD) with Cu $\text{K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$) in the region $2\theta = 10\text{--}70^\circ$ with a step size of 0.04° was used. The average crystallite size of TiO_2 nanoparticles were estimated according to the following Scherrer's equation:

$$d_{hkl} = \frac{k\lambda}{\beta \cos(2\theta)}$$

where d_{hkl} is the average crystallite size (nm), λ the wavelength of the Cu $\text{K}\alpha$ radiation applied ($\lambda = 0.154056\text{ nm}$), θ the Bragg's angle of diffraction, β the full-width at half maximum intensity of the peak observed at $2\theta = 25.20$ (converted to radian) and k is a constant usually applied as ~ 0.9 . The BET surface area, average pore diameter and micropore volume of the nanosized- TiO_2 particle was calculated from the N_2 adsorption isotherm using ASAP 2000 model BET analyzer at liquid N_2 temperature. During the BET analysis, sample was degassed at 150°C for 4 h before N_2 adsorption. Pore size distribution of nano- TiO_2 was computed by DFT plus method. Contact angles of coatings with water were measured by using a goniometer (RAME HART 100-00 model). Film thickness on the coated glass surface was measured by Perthometer (MAHR-M1 Model).

Dye concentration in the aqueous solution after irradiation was measured by a Varian Carry 5000 model UV–vis–NIR spectrophotometer. Coated glass/dye solution was irradiated with Solar Box 1500 model (Erichsen, Germany) radiation unit with Xe-lamp (690 W/m^2) and a controller to change the irradiation time and power input from 390 to 1100 W/m^2 for different time without cut-off filter and with 400 nm cut-off filter without shaking.

2.2. TiO_2 powder synthesis

$\text{Ti}(\text{OPr}^i)_4$ was dissolved in *n*-propanol. After stirring for 5 min at ambient temperature, the HCl solution (0.1N) was added. After stirring a few minute, tin (IV) chloride was added. The last solution was stirred until it formed a clear and homogeneous solution at ambient temperature. Then, water was added within 10 min into the last solution dropwise by burette. HCl/ $\text{Ti}(\text{OPr}^i)_4$, $\text{Sn}^{4+}/\text{Ti}(\text{OPr}^i)_4$ and $\text{H}_2\text{O}/\text{Ti}(\text{OPr}^i)_4$ ratios (mol/mol) were 0.19, 0.05 and 2, respectively. The reaction was allowed for 2 h, then the homogeneous and transparent solution was obtained. Sol-solution was then transferred into a 250 ml Teflon crucible, then left in a pre-heated (220°C) stainless steel autoclave device. The reaction allowed at 220°C for 2 h. After this time, autoclave was removed from the hydrothermal unit and cooled to room temperature. The as-obtained powders were dried using rotary evaporator at 40°C for 5 h. Thus, nanosized and white colour TiO_2 crystallite was obtained.

2.3. The preparation of coating solutions

Before preparing the coating solutions, the TiO_2 sol was prepared. For this purpose, required amount of TiO_2 was dispersed ultrasonically in deionized water without using dispersant. For preparing coating solution, EtOH was added to TEOS and stirred for 10 min at room temperature. HCl was allowed to react with

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