Journal of Luminescence 131 (2011) 570–576

Contents lists available at ScienceDirect

Journal of Luminescence

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

Enhanced photocatalytic degradation of Safranin-O by heterogeneous nanoparticles for environmental applications

Maged El-Kemary [a,*], Yasser Abdel-Moneam [b], Metwally Madkour [b], Ibrahim El-Mehasseb [a]

[a] *Chemistry Department, Faculty of Science, Kafrelsheikh University, 33516 Kafr ElSheikh, Egypt*
[b] *Chemistry Department, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt*

ARTICLE INFO

Article history:
Received 22 July 2010
Received in revised form
14 September 2010
Accepted 18 October 2010
Available online 11 November 2010

Keywords:
Ag–TiO_2
Safranin-O
Dye
Photodegradation
Photocatalytic activity

ABSTRACT

Nanostructure titanium dioxide (TiO_2) has been synthesized by hydrolysis of titanium tetrachloride in aqueous solution and Ag–TiO_2 nanoparticles were synthesized by photoreduction method. The resulting materials were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier-transform infrared (FT-IR) and UV–vis absorption spectroscopy. The experimental results showed that the sizes of the synthesized TiO_2 and Ag–TiO_2 particles are in the range of 1.9–3.2 nm and 2–10 nm, respectively. Moreover, Ag–TiO_2 nanoparticles exhibit enhanced photocatalytic activity on photodegradation of Safranin-O (SO) dye as compared to pure TiO_2. The positive effect of silver on the photocatalytic activity of TiO_2 may be explained by its ability to trap electrons. This process reduces the recombination of light generated electron–hole pairs at TiO_2 surface and therefore enhances the photocatalytic activity of the synthesized TiO_2 nanoparticles. The effects of initial dye and nanoparticle concentrations on the photocatalytic activity have been studied and the results demonstrate that the dye photodegradation follows pseudo-first-order kinetics. The observed maximum degradation efficiency of SO is about 60% for TiO_2 and 96% for Ag–TiO_2.

1. Introduction

Organic dyes are one of the major groups of pollutants in wastewaters produced from textile and other industrial processes [1–3], and over 15% of the textile dyes are lost in wastewater stream during dyeing operation. The textile industry produces large quantity of high colour effluents, which are generally toxic and resistant to destruction by biological treatment methods. A necessary criterion for the use of these dyes is that they must be highly stable in light and during washing. They must also be resistant to microbial attack. Therefore, they are not readily degradable and are typically not removed from water by conventional chemical wastewater treatment systems [4]. The superiority of photocatalytic degradation by semiconductors in wastewater treatment is due to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products and oxidation of pollutants. It is an effective and rapid technique for the removal of pollutants from wastewater [5,6].

The TiO_2 photocatalyst has attracted much interest in recent years for its highly active photocatalytic functions, such as the ability to decompose chemical compounds, as well as superhydrophilic and antibacterial properties [7–9]. The UV photon is able to activate the photocatalyst, which results in the excitation of an electron from the valence band (VB) to the conduction band (CB). However, one of the serious problems limiting the photocatalytic efficiency is recombination of photogenerated electrons and holes. The presence of a metal on the semiconductor markedly increases its efficiency [10,11]. TiO_2 semiconductor is most popular for heterogeneous photocatalysts among the semiconductors due to its excellent optical and electronic properties, low cost, non-toxicity and chemical and thermal stability [12]. The role of loaded metal is trapping and subsequent transfer of photoexcited electron onto photocatalyst surface and decreasing the recombination of hole–electron pairs [13]. Heterogeneous photocatalysis is a process in which the illumination of semiconductor materials absorbs light of energy more than or equal to its band-gap, thereby generating electrons and holes, which can further generate free-radicals in the system to oxidize the substrate. The resulting free-radicals are very efficient oxidizers of organic dyes [14,15].

Recently, we have studied fluorescence modulation and photodegradation characteristics of safranin-O dye in the presence of ZnS nanoparticles. The observed photodegradation efficiency was low (51%) [16]. Also, degradation efficiency of 48% was observed for ciprofloxacin drug under UV light irradiation in aqueous solution in the presence of ZnO nanoparticles [17].

In this study, we examined the Ag effect on the photocatalytic activity of TiO_2 nanoparticles by employing Safranin-O (SO) as model pollutants for environmental application. SO is a phenazine

---

[*] Corresponding author. Tel.: +20 47 3215176; fax: +20 47 3215175.
E-mail address: elkemary@yahoo.com (M. El-Kemary).

0022-2313/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2010.10.025

dye and has been widely used in the textile industry. The results showed that the photocatalytic activity of Ag–TiO_2 is much higher than that of pure TiO_2.

2. Experimental

2.1. Materials

3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride (SO, Scheme 1), silver nitrate (Merck, 98% pure), titanium tetrachloride ($TiCl_4$, 98%, Fluka) and ethanol (99.5%, Wako) were used without further purification. Double-distilled water was used throughout all experiments.

2.2. Equipments

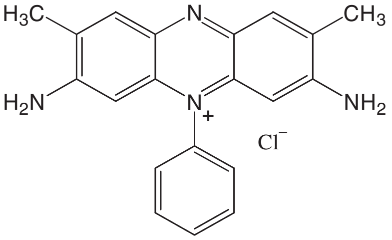
UV–vis absorption spectra were measured by a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded by a Shimadzu RF-5301PC spectrofluorometer. The Fourier-transform infrared (FT-IR) spectra were measured with a JASCO spectrometer 4100. The X-ray diffraction (XRD) measurements were conducted using an X'Pert PRO Panalytical diffractometer with copper target and nickel filter with CuK_α radiation (λ=0.154056 nm). The surface morphology of the nanoparticles was examined with a Transmission Electron Microscope JEOL JEM 1230 with a voltage of 120 kV. The average particle size was determined statistically by counting manually at least 30 particles.

2.3. Preparation of TiO_2 nanoparticles

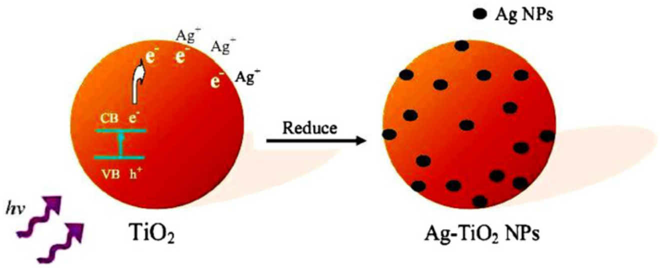
Recently, various nanostructured TiO_2 catalysts have been prepared by hydrolysis of titanium isopropoxide or titanium tetrachloride [18]. The nanostructured TiO_2 sample was prepared by hydrolysis of titanium tetrachloride $TiCl_4$. 4 ml $TiCl_4$ solution was dropped into 400 ml of a mixture of ethanol and distilled water (4:1). The mixture was heated at 80 °C under stirring, a white suspension of TiO_2 nanoparticles was formed in about 120 min of heating at 80 °C. The process was continued for 120 min after formation of the nanoparticles to eliminate most of the chloride ions as HCl gas. The nanoparticles were thrown down by centrifugation at 5300 rpm for 30 min. Then the precipitate was filtered and washed in water several times until the precipitate is free from impurities, dried in a drying oven at 50 °C and calcined at 400 °C for 4 h to obtain a white powder of TiO_2 nanoparticles.

2.4. Preparation of Ag–TiO_2 nanoparticles

Ag–TiO_2 nanoparticles were prepared via photoreduction process of Ag on the surface of TiO_2 (Scheme 2). 100 mg of the prepared TiO_2 was added to 50 ml solution of $AgNO_3$ (1×10^{-3} M) and irradiated under UV light for 4 min. The product was centrifuged, washed with distilled water and dried at 80 °C for 1 h. The colored product was designated as Ag–TiO_2. The colour of TiO_2 solution changed from white to yellow and finally colored in grayish brown due to deposition of silver on TiO_2.



Scheme 1. Safranin-O (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride).



Scheme 2. Photoreduction process of Ag on the surface of TiO_2.

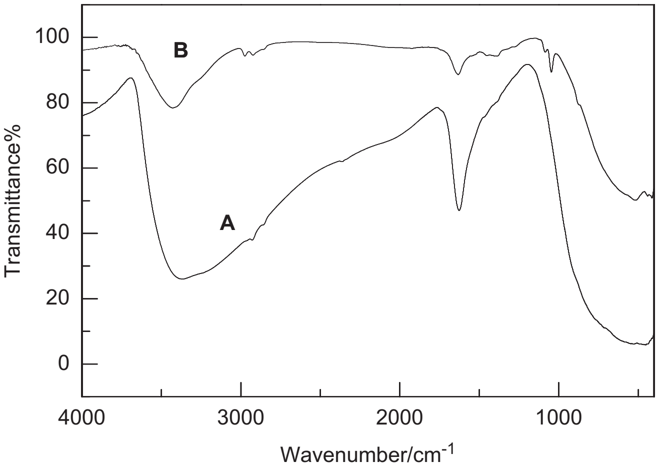


Fig. 1. FT-IR spectra of TiO_2 nanoparticles before (A) and after annealing (B) at 400 °C.

2.5. Photodegradation experiments

Experiments were carried out using a medium pressure Hg UV GL-58 lamp. The lamp emits predominantly at wavelength of 254 nm. To carry out the photocatalytic reactions, SO dye solution of concentration 1×10^{-5} M was taken in a 25 ml flask and an appropriate amount (120 mg L^{-1}) of solid TiO_2 was ultrasonicated for 10 min prior to irradiation to ensure that the suspension of the catalyst was uniform during the course of the reaction. The solution was irradiated with UV light. In a typical manner the photocatalytic degradation was performed using Ag–TiO_2 photocatalyst in the presence of UV light. The kinetics of the photocatalytic degradation of SO was studied by measuring the change in emission spectra at different time intervals. The data reported in this experiment were the average values obtained from the duplicate experiments and the acceptable error in this work was 3%.

3. Results and discussions

3.1. Characterization of TiO_2 and Ag–TiO_2 nanoparticles

Fig. 1 shows the FT-IR spectra of the prepared TiO_2 (a) and that after annealing at 400 °C (b). The FT-IR spectrum of TiO_2 had a large broad band at 3000–3500 cm^{-1} and rather narrow and week bands at 1640 and 1440 cm^{-1}, respectively. The broad band at 3000–3500 cm^{-1} could be assigned to ν_{OH} (stretching modes) while these at 1640 and 1440 cm^{-1} were assigned to δ_{OH} (bending modes) of hydroxyl (OH) group [19,20]. Peaks located at 515 and