Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 504–509

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Spectroscopic analyses of the photocatalytic behavior of nano titanium dioxide

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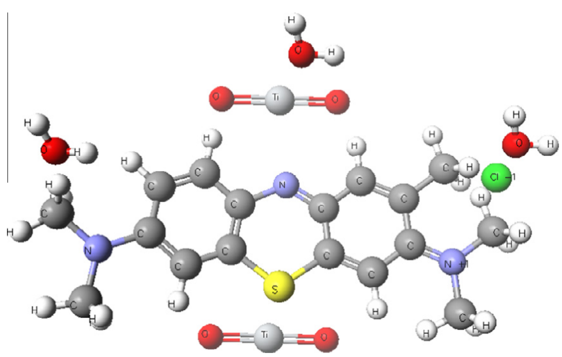
HIGHLIGHTS

- Anatase nano TiO_2 was synthesized with hydrolysis method.
- Molecular modeling was utilized to understand the effect of TiO_2 upon methylene blue.
- Maximum degradation efficiency (94.4%) after 120 min of UV irradiation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 August 2014
Received in revised form 11 September 2014
Accepted 18 September 2014
Available online 30 September 2014

Keywords:
Anatase TiO_2
FTIR
HRTEM
XRD
Photo-degradation
Molecular modeling

ABSTRACT

Nano titanium dioxide TiO_2 was synthesized using hydrolysis method then subjected to several characterizations. XRD revealed that the as-prepared sample is pure anatase phase and after calcinations at 500 °C for 3 h the crystallinity has increased. The crystallite size calculated by Debye–Scherrer's formula is 8 nm. The HRTEM image shows an average size of about 9 nm, which is close to the XRD calculation from Scherrer's formula. PM3 semiempirical quantum mechanical calculations were conducted to present the electronic as well as thermal properties for TiO_2. FTIR spectra between 800 and 400 cm^{-1} are the verification for the lattice vibrations of anatase TiO_2. The photo catalytic degradation of methylene blue (MB) was tested by the prepared nano TiO_2. Results indicate that, the maximum degradation efficiency reached 94.4% after 120 min of UV irradiation. This increase in the degradation efficiency of TiO_2 could be attributed to the reduction in particle size that enhanced the crystallinity as a result of heat treatment.

Introduction

Metal-oxide semiconductors such as titanium dioxide (TiO_2) are important materials for a variety of applications [1]. TiO_2 has excellent properties such as chemical stability, high refractive index, transparency in the visible range, high dielectric constant, low leakage current density and large band gap energy [2]. The photocatalytic reactions on semiconductor metal oxides irradiated with solar or artificial light are of great interest owing to their applications in the treatment of pollutants [3–6]. The visible light activate TiO_2 synthesized by different strategies were reviewed [7,8]. Wool

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http://dx.doi.org/10.1016/j.saa.2014.09.063
1386-1425/

fibers modified with solely TiO_2 nanoparticles and then with N-doped TiO_2 nanoparticles prepared by hydrothermal method where its photocatalytic effects was evaluated [9]. The photocatalytic performance of TiO_2, WO_3/TiO_2, Au/TiO_2, and $Au/WO_3/TiO_2$ and their corresponding nitrogen-doped metal oxide samples in the photo-oxidation of aqueous 2,4,6-trinitrotoluene (TNT) solution was investigated [10]. In order to study magnetic photocatalysts, a layer of magnetite Fe_3O_4 nanoparticles was loaded onto the surfaces of cenospheres using precipitation method, and then modified with saline coupling agent KH550. The modified Fe_3O_4 coated cenospheres were coated further with a film of anatase TiO_2 nanoparticles under hydrothermal conditions, and finally decorated with Ag nanoparticles by electroless deposition [11]. The photocatalytic activity of the as-prepared cenospheres for the methylene blue degradation was measured under both ultraviolet and visible light irradiation. As a result of the emerging applications of photocatalytic effects of TiO_2, many studies have been conducted for studying the coating of TiO_2 on different substrates like fly ash [12], silica [13], active carbon [14], and zeolite [15]. Adsorption and photocatalytic oxidation of acetaldehyde have been investigated on TiO_2 and sulphate-modified TiO_2 films by in situ FTIR spectroscopy and micro-kinetic modeling [16]. Cluster molecular modeling was utilized to the study of strong interaction for F-doped V_2O_5–WO_3/TiO_2 supported catalyst [17]. Molecular modeling with different methods and levels is a useful tool for studying the electronic, physical, chemical and biological properties for many systems and applications [18–23]. In the present work TiO_2 anatase nanoparticle was prepared with hydrolysis method then characterized with XRD, HRTEM and FTIR. Photocatalytic degradation studies were performed by mixing TiO_2 powder into methylene blue, then concentration of the degraded methylene blue was determined using UV–Vis technique.

Materials and methods

Chemicals

Titanium tetraisopropoxide $Ti(OC_3H_7)_4$ which is termed TTIP is purchased from Sigma Aldrich – Germany.

Ethyl alcohol (C_2H_5OH), Acetic acid (CH_3COOH) and Polyethylene glycol PEG (M.W 6000) were purchased from El-Nasr Pharmaceutical Company, Egypt.

Methylene blue was purchased from Oxford laboratory Reagent, Mumbai – India.

The purchased materials were used directly without further purification.

Synthesis of TiO_2 anatase nanoparticles

TTIP was dissolved in absolute ethanol in an ice bath then water was added to the solution during stirring at low speed. Acetic acid and PEG was added drop wise into the solution to restrain the hydrolysis process and consequently control the grain growth. During the addition of acetic acid the solution was stirred at high speed for 2 h and left over night to allow precipitation. After that, a two layer solution was formed, the upper layer being the organic byproduct of the hydrolysis, and the lower one was a precipitation of TiO_2. The precipitate was filtered, washed with distilled water several times and finally dried at 100 °C overnight. The obtained yellow block crystals were crushed and grounded into fine powder and calcinated at 500 °C for 3 h to get a pure anatase TiO_2 nanoparticle.

Photodegrdation experiment

Photocatalytic degradation experiment was performed by mixing 5 mg TiO_2 powder into methylene blue aqueous solution (5 mg/L) in a glass container at room temperature.

This container was then irradiated by UV light (12 watt) at wavelength 365 nm for 2 h.

Samples were collected every 10 min to follow up the changes in concentration of methylene blue.

The concentration of the degraded methylene blue was determined with UV–Vis spectrophotometer.

Characterization techniques

The final product was characterized by powder X-ray diffraction (XRD) with Philips PW3050/60 diffractometer (40 kV, 30 mA) using Cu Kα radiation. The crystallite size was calculated using Debye–Scherrer's formula:

$$D = K\lambda/(\beta \cos \theta) \quad (1)$$

where D is the crystal size; λ is the wavelength of the X-ray radiation (λ = 0.15406 nm) for Cu Kα, K is usually taken as 0.89, and β is the line width at half-maximum height [24].

Infrared transmission spectra were recorded by JASCO spectrophotometer model FT-IR 6100 type A.

The microstructures were examined with a high-resolution transmission electron microscope (HRTEM, FEI Philips Tecnai G2 S-Twin operated at 200 keV).

The concentration of the degraded methylene blue was determined using UV–Vis spectrophotometer model JASCO V-630.

2.4. Molecular modeling computational details

D-Gauss quantum mechanical calculations for TiO_2 were carried out using SCIGRESS program system at Spectroscopy Department, National Research Centre [25]. First the structure was optimized to locate the energy minimum then the vibrational frequencies for the studied structures were calculated at PM3 semiempirical quantum mechanical method. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the studied structures were calculated at the same level of theory. Some physical parameters as net atomic charges and charge distribution and some thermal parameters for the studied structures were calculated at the same level of theory.

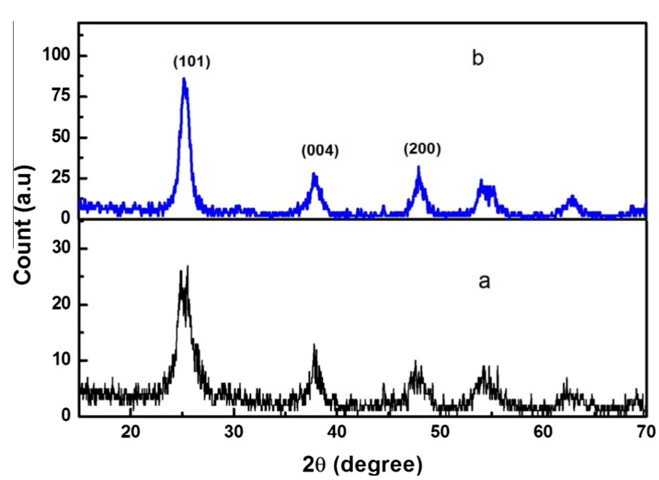

Fig. 1. XRD diffraction patterns for the studied samples whereas (a) as-prepared TiO_2 and (b) TiO_2 after calcinations at 500 °C for 3 h.