Industrial Crops & Products 113 (2018) 210–216

Contents lists available at ScienceDirect

Industrial Crops & Products

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

Photocatalytic activity of nanostructured tubular TiO_2 synthesized using kenaf fibers as a sacrificial template

Edynoor bin Osman[a,b,c], Toshihiro Moriga[a,b,*], Kei-ichiro Murai[a], Mohd Warikh bin Abd Rashid[b,c], Mohd Edeerozey Abd Manaf[c], Toshihide Horikawa[a]

[a] Department of Chemical Science and Technology, Graduate School of Advanced Technology and Science, Tokushima University, 2-1 Minami-Josanjima, 770-8506 Tokushima, Japan

[b] Tokushima-UTeM Academic Center, Tokushima University, 2-1 Minami-Josanjima, 770-8506 Tokushima, Japan

[c] Department of Materials Engineering, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100, Durian Tunggal, Melaka, Malaysia

ARTICLE INFO

Keywords:
TiO_2
Kenaf fiber
Dip coating
Calcination temperature
Photocatalytic activity
Morphology

ABSTRACT

The photocatalytic oxidation of various organic pollutants under UV irradiation can be enhanced by using titanium dioxide (TiO_2) photocatalyst. In this study, tubular TiO_2 nanostructures were synthesized in a single step by depositing titanium (IV) isopropoxide precursor on kenaf fibers used as a sacrificial template. In the calcination temperature range of 500–700 °C, the produced tubular TiO_2 predominantly contained the anatase phase. X-ray diffraction studies were performed to examine the crystallinity and crystallite size of the produced tubular TiO_2, while its photocatalytic activity was determined by monitoring the degradation of methylene blue under ultraviolet irradiation. The obtained results showed that tubular TiO_2 formed at 500 °C exhibited the smallest crystallite size of 9.27 nm and fastest photocatalytic oxidation rate.

1. Introduction

Titanium dioxide (TiO_2) is a well-known material that has been extensively studied in the last few decades due to its potential applications in various fields. One of such applications involves using TiO_2 as a photocatalytically active material, whose properties can be triggered by light irradiation. Photocatalysis can be defined as the acceleration of a photoreaction by the presence of a catalyst (Ohama and Van Gemert, 2011). Due to its low cost, non-toxicity, and high stability, TiO_2 has many advantages over other photocatalytic materials (Chen and Mao, 2007).

It has been recently found that the materials with sizes in the nanometer range (1–100 nm) exhibit different properties as compared to those of their bulk counterparts. Thus, nano-sized TiO_2 can be potentially used as a photocatalytic material for the oxidation of organic pollutants, whose activity (and, therefore, the rate of chemical reaction) can be increased by increasing its surface area (Binas et al., 2017).

According to the results of previous studies (Macwan et al., 2011; Behnajady et al., 2011; Bagheri et al., 2013), the sol–gel method represents the most commonly used technique for the preparation of TiO_2 photocatalyst since it facilitates the synthesis of nanometer-sized crystallized TiO_2 powder with high purity at relatively low temperatures. In addition, during the last two decades, considerable efforts have been spent on the development of suitable synthetic strategies for nanomaterials with controlled shapes, sizes, compositions, and latitudinal arrangements. Template-assisted synthesis represents one of the most effective techniques for achieving a relatively high degree of control over the reaction parameters, which has many advantages over the synthesis conducted without a template. Various studies have been performed to identify available, environmentally friendly, and cost-effective templates for the efficient synthesis of nanomaterials (Liu et al., 2013).

In the past few years, kenaf plants have been extensively used (as compared to other natural resources) due to their ability to rapidly grow under various climatic conditions and low cost (Aziz and Ansell, 2004; Ramesh, 2016). Possible applications of kenaf fibers and their composites include insulated panels, ropes, automotive interior lining, and animal bedding materials as well as bio-engineering and biomedical devices (Ramesh, 2016; Namvar et al., 2014). In this study, a non-woven kenaf mat was used as a template for the deposition of titanium (IV) isopropoxide (TTIP) precursor, which was performed to synthesize TiO_2 in a tubular form. The obtained material was

* Corresponding author at: Department of Chemical Science and Technology, Graduate School of Advanced Technology and Science, Tokushima University, 2-1 Minami-Josanjima, 770-8506 Tokushima, Japan.
E-mail address: moriga@tokushima-u.ac.jp (T. Moriga).

https://doi.org/10.1016/j.indcrop.2018.01.027
Received 7 September 2017; Received in revised form 8 December 2017; Accepted 10 January 2018

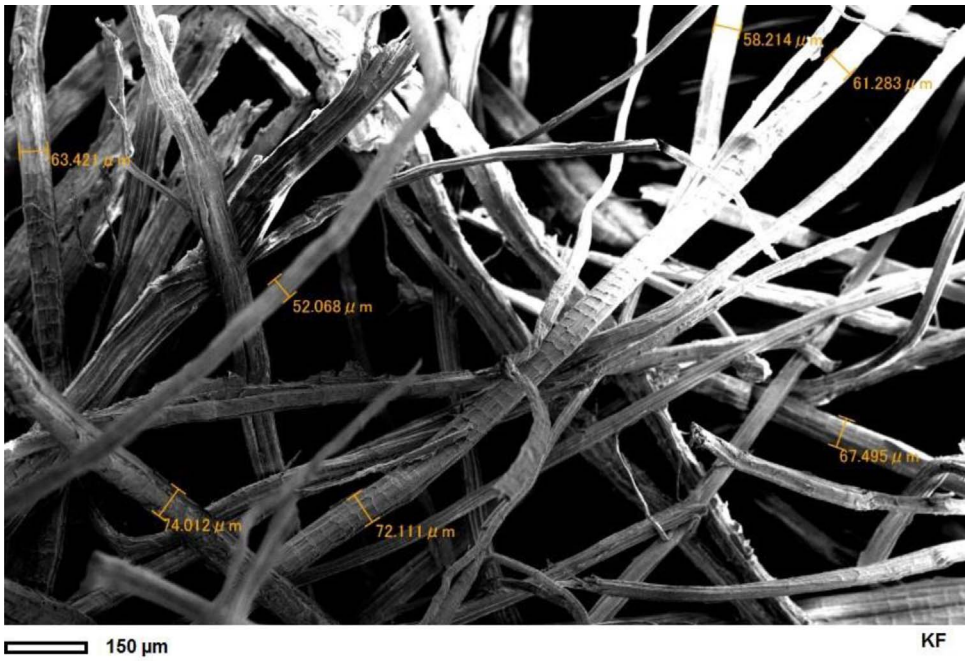

Fig. 1. SEM images of the as-received KFs (obtained at a magnification of 60×).

characterized by various techniques, and its photocatalytic activity was evaluated.

2. Experimental

Kenaf bast fibers (KFs) used in this study were purchased from Innovative Pultrusion Sdn. Bhd, Malaysia (they were received in the form of the non-woven mats with a surface density of 800 g/m^2; see Fig. 1). Initially, the as-received KF mats were treated with 5 wt.% of sodium hydroxide (NaOH) solution to remove impurities from the fiber surface. The utilized precursor solution was a mixture of 10 mL TTIP (97% purity, supplied by Aldrich Chemical) with 10 mL of acetic acid (≥99.8% purity, supplied by Aldrich Chemical). In addition, 100 mL of distilled water was added to the reaction mixture to accelerate the hydrolysis reaction. The desired pH range of the solution (4–6) was achieved by adding 1 mL of nitric acid (HNO_3), and the resulting mixture was stirred with a magnetic stirrer for about 16 h at 60 °C until a whitish blue colloidal suspension with high viscosity was produced.

To perform TiO_2 coating, a KF mat with a mass of about 0.5 g and dimensions of 2.5 × 2.5 cm was dipped in the precursor solution for 1 min and then pressed at an applied force of 2.5 kg/cm^2 (36 psi) for 30 s to squeeze the excess of TiO_2 precursor out of the mat. After that, the treated KF mat was dried at 90 °C for 3 h followed by the stepwise heating to 500, 600, 700, and 1000 °C for 4 h at each temperature to burn and completely remove any remaining KF species.

The resultant TiO_2 coatings were further examined and analyzed using thermogravimetric analysis (TGA), scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDX), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) analysis techniques. The BET technique is the most commonly used method for determining the surface area of powders and porous materials, which involves nitrogen adsorption measurements (here the Dollimore-Heal method was used to obtain the pore size distributions of tubular TiO_2 after heating to 500, 600, and 700 °C). Nitrogen gas (N_2) is generally utilized as a probe molecule, which is adsorbed on the surface of the studied solid under cryogenic conditions (corresponding to a temperature of 77 K in this work). The surface area of the solid is estimated from the measured monolayer capacity and cross-sectional area of the probe molecule (which is equal to 16.2 Å^2 in the case of nitrogen). The solution of methylene blue (MB) in water with a mass ratio of 1:500 was used to evaluate its photocatalytic degradation in the presence of TiO_2 (the mass ratio between TiO_2 and the MB solution was 1:300). The two materials were mixed thoroughly for 15 min using a magnetic stirrer to allow the absorption and desorption processes to proceed until completion (this procedure was performed under dark conditions to prevent any unwanted photocatalytic processes). After 15 min of stirring, the MB solution was exposed to the UV irritation with a wavelength of 365 nm. During the first 2 h, the solution was periodically (every 30 min) examined with an ultraviolet (UV) spectrophotometer (JASCO, model V-670) to monitor possible changes in the transmission of MB. Finally, the MB solution was exposed to UV irradiation for 24 h to complete the cycle and determine the photocatalytic activity of tubular TiO_2.

3. Results and discussion

3.1. TGA analysis

TGA analysis was performed on the raw and TiO_2-coated KFs to examine the thermal decomposition and degradation of these materials. Four stages of the thermal degradation of natural fibers were observed

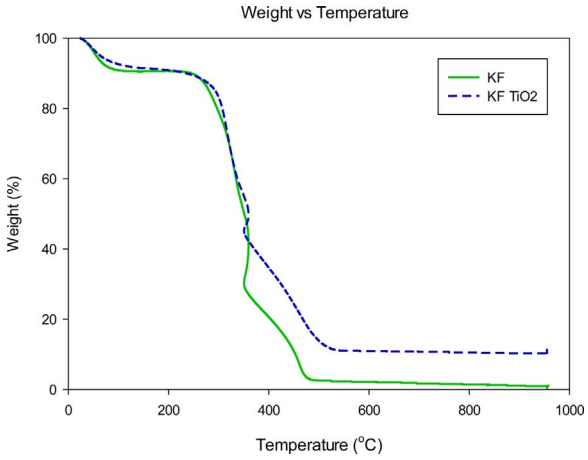

Fig. 2. TGA spectra recorded for TiO_2-coated KF and KF fibers.