Journal of Industrial and Engineering Chemistry 17 (2011) 603–607

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Preparation and characterization of the electrospun PCS/TiO_2 fiber mat by electron beam irradiation

Dong-Kwon Seo, Joon-Pyo Jeun, Phil-Hyun Kang *

Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, 1266 Sinjeong-dong, Jeongeup-si, Jeollabuk-do 580-185, Republic of Korea

ARTICLE INFO

Article history:
Received 20 May 2010
Accepted 24 October 2010
Available online 13 May 2011

Keywords:
TiO_2
Polycarbosilane
Photocatalyst
Electrospinning
Radiation processing

ABSTRACT

The PCS/TiO_2 fiber mat was fabricated from polycarbosilane (PCS) and titanium (IV) butoxide using an electrospinning technique. The fiber mat was irradiated with an electron beam to induce structural crosslinking. Subsequently, the crosslinked PCS/TiO_2 fiber mat was heat-treated at 1,300 °C in air. The PCS/TiO_2 fiber mat was characterized with FE-SEM, EDX, XPS, XRD, TGA, and a Raman spectrum analysis. The heat-treated PCS/TiO_2 fiber mat has an average diameter of 2 and a high specific surface area which was 22.35 m^2/g .The surface of PCS/TiO_2 fiber mat showed a newly interconnected worm-like substructure composed of TiO_2 nanoparticles. The PCS/TiO_2 fiber mat was evaluated for the photodecomposition of dye methylene blue under ultraviolet light. UV–vis result shows that about 90% of methylene blue was degraded after 2 h under UV light by PCS/TiO_2 fiber mat. On the other hand, about 55% dye was degraded by TiO_2 nanopowder.

1. Introduction

TiO_2 has been widely used in environmental applications, especially in the detoxification of water [1–3] and air [4,5], because of its high activity, chemical stability, robustness against photocorrosion, low toxicity and availability at low cost [6–9]. This photocatalyst can completely mineralize toxic and nonbiodegradable organics to CO_2, H_2O and inorganic constituents. The mechanism of the photocatalytic reaction in the presence of TiO_2 involves a free-radical reaction initiated by ultraviolet (UV) light. TiO_2 is usually used as powder in solution. However, disadvantages of powder form such as a catalyst include low efficiency of light use, difficulty of stirring during reaction and separation after reaction. In order to achieve rapid and efficient decomposition of organic pollutants and easy manipulation in a total catalytic process, it may be effective to prepare photocatalyst with high surface areas to concentrate the pollutants around the photocatalyst [10–16]. To solve this problem, a photocatalytic membrane reactor has been developed using various membrane techniques. For a membrane reactor, the development of filters and complex apparatus is required, and the process cost is relatively high. The immobilization of TiO_2 catalysts on various substrates has also been studied, but this process has significantly decreased removal efficiencies of organic pollutants due to the reduction of the active photocatalytic surface area. Therefore, it is very important to develop an immobilized form of TiO_2 with a high active surface area. Electrospinning is a simple and inexpensive technique for producing continuous submicron- to nano-sized polymeric fibers. The obtained fibers have very high continuous surface areas [17–22]. Curing is an essential step in the preparation of PCS/TiO_2 fiber mat which was to prevent the mat melting during the heat treatment process. The fiber mat was irradiated with an electron beam (e-beam) to induce structural crosslinking. E-beam irradiation technology has a many advantage such as a high effect, no waste, economically competitiveness.

In this study, we fabricated PCS/TiO_2 fiber mat with high efficiency and high active surface area by electrospinning technique. The electrospun PCS/TiO_2 fiber mat was cured by e-beam irradiation and then heat-treated in a tube furnace at atmospheric pressure under air at a temperature of 1,300 °C for 1 h. The microstructure of the PCS/TiO_2 fiber mat was observed with field emission scanning electron microscope (FE-SEM). The distribution and compositions of the PCS/TiO_2 fiber mat were analyzed using energy dispersive X-ray spectroscopy (EDX). Potential changes in polymer chemistry were characterized by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and X-ray diffractometer (XRD). And the photocatalytic activity of the PCS/TiO_2 fiber mat was analyzed with UV–vis spectrometer.

* Corresponding author. Tel.: +82 63 570 3061; fax: +82 63 570 3068.
E-mail address: phkang@kaeri.re.kr (P.-H. Kang).

1226-086X/$ – see front matter © 2011 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jiec.2011.05.003

2. Experimental

2.1. Materials

PCS (M.W. = 2,580 g/mol, NIPUS, Japan) and titanium (IV) butoxide (M.W. = 340.32 g/mol, Aldrich, USA) were used as the precursor for the PCS/TiO_2 fiber. Xylene was purchased from Aldrich, USA and used as a solvent without any further purification. Methylene blue (MB) was selected as model pollutant for photodegradation.

2.2. Preparation of PCS/TiO_2 fiber mats

A polymer solution was prepared by dissolving PCS in titanium (IV) butoxide (50/50 wt%). The solution was heated to 180 °C in a nitrogen atmosphere for 1 h with stirring, and then dried in a vacuum oven for 48 h.

A final solution was prepared by dissolving polymer in xylene (50/50 wt%). The solutions were obtained by heating at 80 °C for 4 h with stirring in order to obtain the homogenous solution. In the electrospinning process, a high electric potential was applied to a droplet of the polymer solution at the tip (ID 0.36 mm) of a syringe needle. The solution was then ejected through a syringe using a syringe flow pump at a feed rate of 0.003 ml/min while a voltage of 15 kV was applied with a tip-target distance of 120 mm.

The electrospun PCS/TiO_2 fibers were cured by e-beam irradiation under an argon atmosphere. The fibers were set on a water-cooled stainless-steel bed to prevent the temperature of the PCS/TiO_2 fibers from rising during irradiation in the argon-filled chamber. The e-beam was generated with a 1.14 MeV acceleration voltage, 4 mA of current, and a 10 MGy absorbed dose.

Finally the PCS/TiO_2 fiber mat was heat-treated in a tube furnace at a heating rate of 10 °C/min to 1,300 °C under an air for 1 h.

2.3. Photocatalytic experiment

The photocatalytic activity of the PCS/TiO_2 fiber mat was evaluated by the degradation of a standard solution of MB in a photochemical reactor. A 50 W lamp as the UV light source (365 nm) was exposed in a cylindrical glass vessel (diameter: 8 cm, height: 10 cm). Reaction was prepared by using known weight and size (0.1 g, 5 cm × 5 cm × 0.1 cm) of PCS/TiO_2 fiber mat and TiO_2 nanopowder (0.1 g, size: 25 nm) into the beaker containing 300 mL of 10 ppm MB solution. Approximately 3 mL in volume were collected with 10, 20, 30, 60 and 120 min after UV irradiation.

2.4. Characterization

The microstructures of the PCS/TiO_2 fiber mat were observed using FE-SEM (Sirion, FEI, Netherlands) equipped with EDX (ISIS, OXFORD, England). Raman spectra were recorded with a Jobin-Yvon Labram HR microanalytical spectrometer equipped with a motorized *xy* stage and autofocus. The spectra were generated with a 17 mW, 514.5 nm Ar-ion laser excitation and were dispersed with the 1,800 g/mm grating across the 0.8 m length of the spectrograph. The chemical state of the PCS/TiO_2 fibrous surface was investigated using XPS (MultiLab 2000, Thermo Electron Corporation, England) with Mg Kα radiation. The applied power was 14.5 keV and 20 mA, and the base pressure of the analysis chamber was less than 10^{-9} Torr. The crystal phase of the PCS/TiO_2 fiber mat was analyzed by XRD. The specific surface area of PCS/TiO_2 fiber mat was determined from the BET measurement (ASAP2020, Micromeritics, USA). The thermal stability of PCS/TiO_2 fiber mat was performed using a TA instrument equipped with a TGA (Q600). Runs were performed at a heating rate of 10 °C/min, under a nitrogen atmosphere at temperatures ranging from room temperature to 1,300 °C.

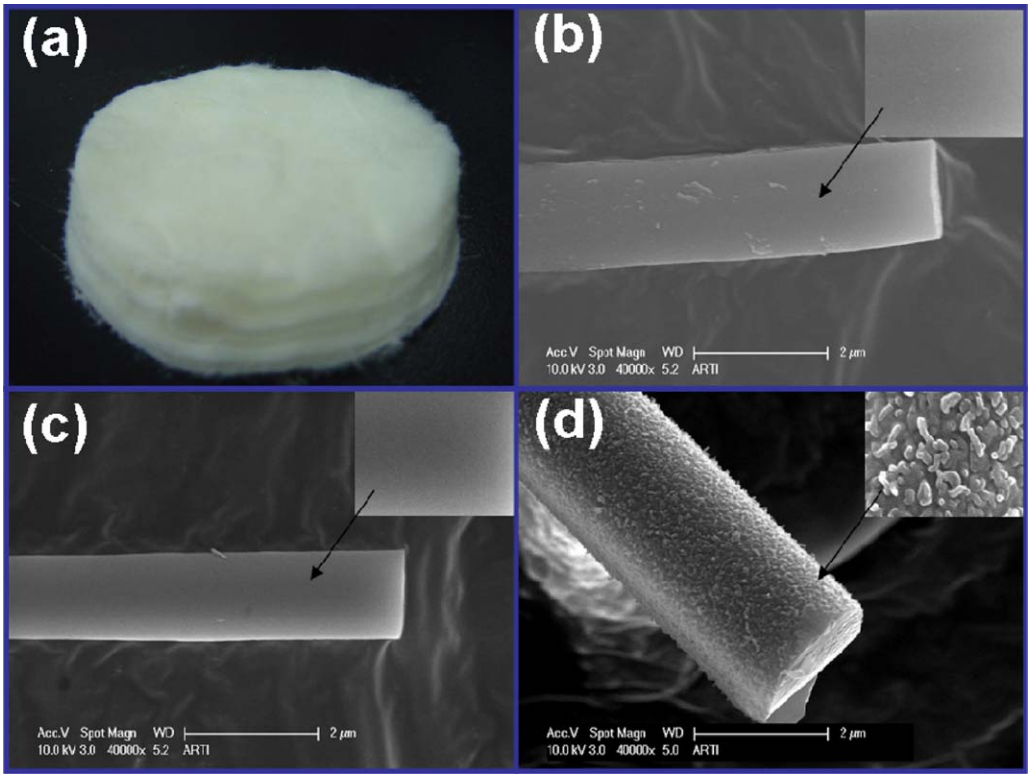

Fig. 1. (a) Photograph of PCS/TiO_2 fiber mat, SEM images of (b) the electrospun PCS/TiO_2 fiber mat, (c) e-beam cured PCS/TiO_2 fiber mat, and (d) heat-treated PCS/TiO_2 fiber mat.