Journal of Photochemistry and Photobiology A: Chemistry 348 (2017) 226–237

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Invited paper

SiO_2 encapsulated TiO_2 nanotubes and nanofibers for self-cleaning polyurethane coatings

Chao Chen, William Z. Xu, Paul A. Charpentier*

Department of Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario, Canada N6A 5B9

ARTICLE INFO

Article history:
Received 8 March 2017
Received in revised form 20 June 2017
Accepted 8 August 2017
Available online 16 August 2017

Keywords:
SiO_2
TiO_2
Nanofiber
Nanotube
Polyurethane

ABSTRACT

TiO_2 nanotubes and nanofibers are of great interest due to their defined dimensions, high specific surface areas, and enhanced photocatalytic activity. In the application of self-cleaning polymer coatings, the enhanced photocatalytic activity improves the self-cleaning ability but also facilitates photodegradation of the polymer matrix. In order to overcome the drawbacks of TiO_2 nanotubes and nanofibers, a thin layer of SiO_2 was coated onto the surface of TiO_2 nanotubes and nanofibers in this work. The effect of the SiO_2 shell on the photocatalytic activity of the TiO_2 core was investigated by UV–vis spectroscopy, photodegradation of methylene blue solution, and measurement of photo-generated hydroxyl radicals. In general, the photocatalytic activity of the SiO_2-coated TiO_2 nanostructures decreased with an increasing amount of SiO_2 coated onto the surface of TiO_2 nanostructures. By incorporating SiO_2-modified TiO_2 nanostructures into the polyurethane (PU) matrix, it was found that the hydrophobicity and mechanical strength of the resulting composites was enhanced while the photocatalytic activity increased with increasing loading of the photocatalyst. This approach of coating TiO_2 nanostructures with a thin layer of SiO_2 provides a new route towards the development of long-lasting self-cleaning coatings using 1D TiO_2.

1. Introduction

Nanotubes and nanofibers are one-dimensional (1D) nanostructures which provide high specific surface areas and high mechanical strength [1,2]. They have helped inspire the nanotechnology field and trigged many efforts in the fields of physics, chemistry, and materials science. Carbon is still the most common material in preparing 1D geometry nanomaterials [3,4]. However, other materials such as transition metal oxides have been synthesized in 1D geometry [5,6]. In recent years, 1D nanostructures based on TiO_2 have attracted much attention due to their often enhanced photocatalytic properties in specific crystal structures, i.e. anatase and rutile [7–9]. Shape-controlled synthesis is a method developed recently to enhance the catalytic effect of TiO_2 nanostructures [10]. Synthesizing TiO_2 nanotubes or nanofibers instead of TiO_2 nanoparticles is a promising method, similar to shape-control to alter the photocatalytic activity [2,11].

Generally, there are three common methods to synthesize TiO_2 nanotubes, i.e. template preparation [12,13], anodic oxidation [14], and chemical processing [15]. The template preparation method requires template removal, which can lead to poor structural integrity of the resulting nanostructure. Anodic oxidation is able to synthesize nanotubes with uniformity in size, although normally only larger diameter structures are possible, with smaller diameters being of higher scientific interest. Chemical processing such as hydrothermal is the classic method for preparing nanotubes with the smallest size, with the hydrothermal conditions controlling the mesoporous structure of the nanotubes [16].

TiO_2 nanofibers are commonly prepared via hydrothermal synthesis [17], electrospinning [18,19], and the sol-gel method [11,20]. Using supercritical CO_2 as an environmentally friendly and functional solvent, our group has demonstrated the synthesis of TiO_2 nanofibers [11,21]. Supercritical CO_2 has attracted considerable attention in recent years due to its lack of solvent residue, inexpensive and nontoxic, and negligible surface tension, which makes it ideal for nanomaterial synthesis [11,22,23].

Titania can be modified by doping with various elements including N, C, Fe [24–26], and depositing with other metal oxides [27–29]. However, there is a lack of investigation of SiO_2's effect on nanotubes and nanofibers. Due to their high photocatalytic activity under UV light, TiO_2 is ideal for preparing self-cleaning coatings with polymers such as polyurethane (PU) [30,31]. However, self-

* Corresponding author.
E-mail address: pcharpentier@eng.uwo.ca (P.A. Charpentier).

http://dx.doi.org/10.1016/j.jphotochem.2017.08.014
1010-6030/

cleaning coatings usually suffer from photodegradation caused by the nanofiller's photoactivity. From our previous study [32], it was found that coating of SiO_2 on the surface of TiO_2 nanoparticles influenced the photocatalytic activity of the formed PU composite films, resulting in reduced photodegradation. In this study, TiO_2 nanotubes and nanofibers were coated with a thin layer of SiO_2 via the Stöber process [33,34]. The SiO_2-coated TiO_2 nanotubes and nanofibers were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV–vis), and photoluminescence to examine the effect of SiO_2 on the 1D TiO_2 nanostructures. The SiO_2-coated TiO_2 nanostructures were then integrated into a PU matrix for the synthesis of self-cleaning coatings. It was expected that coating TiO_2 nanotubes and nanofibers with a thin layer of SiO_2 would help protect the PU coatings from photodegrading, extending the life span of the self-cleaning TiO_2-PU coatings. The physical, mechanical, and self-cleaning properties of the prepared nanostructures integrated PU coatings were studied to examine the effect of SiO_2 layers on these coatings.

2. Experimental

2.1. Materials

Alkyltrimethylammonium bromide (C16TAC) (≧95%), tetraethoxysilane (TEOS), anatase TiO_2 (<25 nm, 99.7%), and titanium isopropoxide (97%) were purchased from Sigma Aldrich, Canada. Methanol, 28% aqueous ammonia solution, acetic acid (99.7%), and methylene blue were purchased from Caledon, Canada. Sodium hydroxide (97%) was purchased from ACP Chemicals. Carbon dioxide (99.99%) was purchased from Praxair Inc., Canada. Poly aspartic ester, poly hexamethylene diisocyanate, and isophorondiamine – isobutyraldimine were obtained from Bayer MaterialScience. All the chemicals were used as received without further purification.

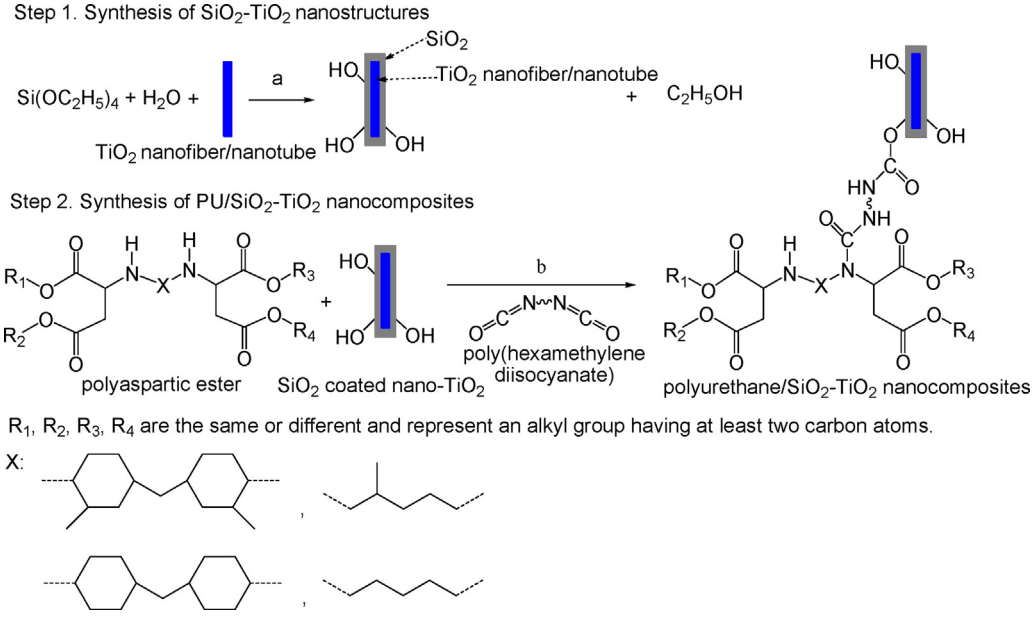
2.2. Synthesis procedure

TiO_2 nanotubes were synthesized by following the classic hydrothermal reaction [35]. Briefly, 10 g of anatase TiO_2 was dispersed in 100 mL of 10 M NaOH solution in a 250-mL round bottom flask by sonication. The dispersion was then stirred at 110 °C in an oil bath for 20 h. After that, the product was washed repeatedly with distilled water followed by neutralization to pH = 7 using 0.1 M HCl solution. The obtained product was then calcined at 200 °C for 2 h.

Synthesis of TiO_2 nanofibers were performed in supercritical CO_2 by following the previously reported method [11]. Briefly, 10.6 g of titanium isopropoxide (TIP) and 8.13 mL of acetic acid (molar ratio of TIP to acetic acid = 1:4.07) were added in a 25-mL autoclave reactor followed by pumping CO_2 to the reactor. The reaction was performed at 60 °C at 6000 psi with continuous stirring for 3 h. Then the product was aged for 3 days followed by 3 days of washing with CO_2 at a flowrate of 0.5 mL/min. The obtained product was then calcined at 400 °C for 1 h.

The syntheses of SiO_2 encapsulated TiO_2 nanostructures and PU/SiO_2-TiO_2 nanocomposites are illustrated in Scheme 1. SiO_2 encapsulated TiO_2 nanostructures were performed using the classic Stöber process [32,34]. Briefly, 0.1 g of TiO_2 nanotubes or nanofibers were dispersed in 5-mL of methanol and sonicated for 30 min to form solution A. 0.02 g of C16TAC surfactant, 1.8 g of deionized water, 0.7 g of 28% aqueous ammonia solution were added to 10 mL of methanol to form solution B. To solution B was added 20, 40, or 60 mg of TEOS, resulting in the feeding weight ratio of SiO_2 to TiO_2 being 5.40:100, 10.8:100, or 16.2:100 respectively. After preparation, solution A was poured into the above mixture of TEOS and solution B, followed by continuous stirring for 24 h. The product was isolated by centrifugation and then washed with methanol repeatedly, and dried in a vacuum oven at 50 °C for 48 h.

Polyurethane coatings were prepared with the weight ratio of SiO_2-TiO_2:polyol mixture (with weight ratio of poly aspartic ester: isophorondiamine – isobutyraldimine being equal to 4:1): poly hexamethylene diisocyanate being equal to 5:425:250. The SiO_2-



Scheme 1. Schematic diagram of the synthesis of SiO_2-coated TiO_2 nanostructures and the preparation of polyurethane/SiO_2-TiO_2 nanocomposites. (a) room temperature in methanol solution; (b) room temperature with catalyst isophorondiamine – isobutyraldimine.