Applied Surface Science 275 (2013) 36–42

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Visible-light self-cleaning cotton by metalloporphyrin-sensitized photocatalysis

Shabana Afzal [a], Walid A. Daoud [b,*], Steven J. Langford [c]

[a] School of Applied Sciences and Engineering, Monash University, Churchill 3842, Australia
[b] School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
[c] School of Chemistry, Monash University, Clayton 3800, Australia

ARTICLE INFO

Article history:
Available online 26 January 2013

Keywords:
Visible-light photocatalysis
Porphyrin
Titanium dioxide
Self-cleaning

ABSTRACT

Thin films of *meso*-tetra(4-carboxyphenyl)porphyrin with different metal centres (MTCPP, M = Fe, Co and Zn) in combination with anatase TiO_2 have been formed on cotton fabric. Their self-cleaning properties have been evaluated by conducting the photocatalytic degradation of methylene blue under visible-light irradiation. All MTCPP/TiO_2-coated cotton fabrics showed superior self-cleaning performance as compared to the bare TiO_2-coated cotton. Among the three metal porphyrins, FeTCPP showed the highest photocatalytic activity with complete degradation of methylene blue in 180 min. The fabrics were characterized by FESEM, XRD, UV–vis and fluorescence spectroscopy.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of the photocatalytic property of TiO_2 by Honda and Fujishma [1], the potential use of titanium dioxide in various environmental applications has been well explored. With the growing interest in photo-induced self-purification materials, self-cleaning surfaces have been developed using TiO_2 coatings on various substrates. Fujishima et al. have developed the first self-cleaning ceramic in 1990 [2]. Later on, the concept of TiO_2 photocatalysis was extended to the development of self-cleaning glasses, tents, window blinds and lamp covers [3]. Nanocrystalline TiO_2 particles immobilized on activated carbon, glass, polymeric materials and silica have been achieved [4,5], however most of these techniques required high temperature processing [6,7], thus limiting their application to substrates of low thermal resistance such as textiles. Therefore, the past decade has been witnessing extensive research to grow TiO_2 nanocrystals on organic fibres.

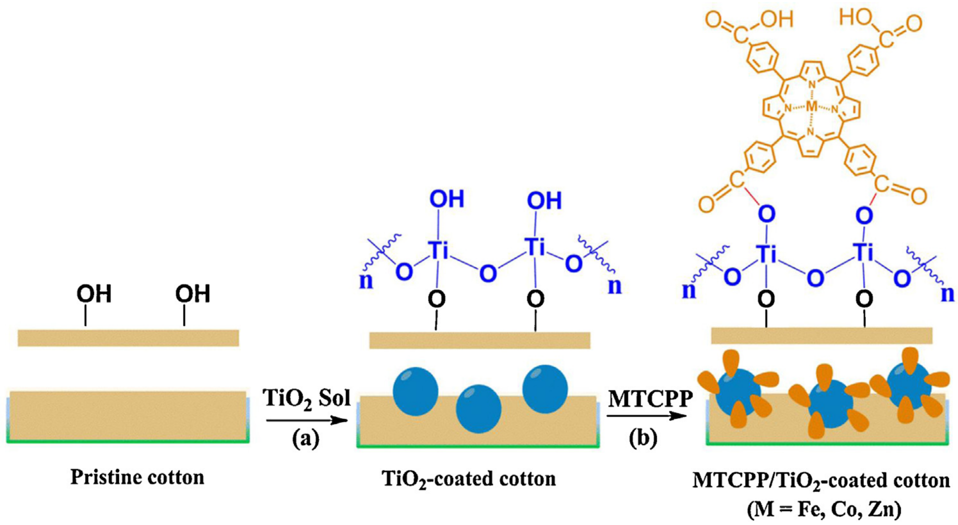
By using a nanotechnological approach in combination with a low-temperature sol-gel process, Daoud et al. have successfully developed an anatase TiO_2-based self-cleaning cotton that showed efficient photocatalytic properties under UV light [8–10]. A number of other UV-active textiles such as wool and polyester using various techniques of surface modification have also been developed [11,12]. TiO_2 has a wide band gap of 3.2 eV, due to which it can only be excited effectively under UV irradiation. Ultraviolet radiation reaching the earth is only 4–6% of the total solar irradiance, whereas 45% consists of visible-light [13]. For efficient utilization of solar light, many methods have been reported in literature to extend the light absorption of TiO_2 in the visible region; such as metal doping [14–16], non-metal doping [17], ion-implantation [18] and photosensitization [19]. Following some of these methods, very few visible-light driven self-cleaning textiles have been developed using metals [20] and non- metals [21].

Photosensitization using dyes allows efficient sensitization of TiO_2 in the visible region as compared to the other methods [22]. In photosensitization method, a photo-induced electrons transfer process takes place from excited dye to the conduction band of TiO_2 [23]. These electrons can then react with atmospheric O_2 to form superoxide radical anions ($O_2^{\bullet-}$), which can cause oxidation of organic impurities present on the surface of catalyst [24,25]. Porphyrins are considered as efficient sensitizers to harvest light when adsorbed on the surface of TiO_2 [23]. Due to an extensive system of delocalized π electrons, porphyrins have very strong absorption in the visible region [26–28]. According to electrochemical measurements, electron injection from the excited state of porphyrins to the conduction band of TiO_2 is thermodynamically favoured [29]. Furthermore, the photophysical properties of porphyrins can be easily tuned by modifying the peripheral substituents and/or through metal complexation [30,31].

Recently, we have successfully developed self-cleaning cotton based on *meso*-tetra(4-carboxyphenyl)porphyrin (TCPP)-sensitized TiO_2 that showed significant photoactivity under visible-light as compared to bare TiO_2 [32]. In this manuscript, films of *meso*-tetra(4-carboxyphenyl)porphyrin with different metal centres (MTCPP, M = Fe, Co and Zn) have been formed on TiO_2-coated cotton fabric. The self-cleaning properties of fabrics have been investigated by studying the photocatalytic degradation of methylene blue (MB) under visible-light irradiation. Using a

* Corresponding author at: School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong. Tel.: +852 3442 4499; fax: +852 3442 0688.
E-mail address: wdaoud@cityu.edu.hk (W.A. Daoud).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.01.141



Scheme 1. Formation of thin films of MTCPP on TiO_2-coated cotton. (a) Treatment of pristine cotton with TiO_2 colloid to form TiO_2 coating on cotton. (b) Treatment of TiO_2-coated cotton with MTCPP solution in DMF to form MTCPP/TiO_2-coated cotton.

simple post-adsorption method, self-assembled monolayers of MTCPP have been formed on TiO_2-coated cotton, as shown in Scheme 1.

2. Experimental

2.1. Synthesis of MTCPP/TiO_2-coated cotton

2.1.1. Synthesis of TiO_2 colloid

Colloidal TiO_2 anatase was prepared by adding a solution of titanium tetraisopropoxide and acetic acid drop wise to acidified water using 1.4% HNO_3. The mixture was stirred at 60 °C for 16 h.

2.1.2. Preparation of TiO_2-coated cotton

The TiO_2 colloid was applied to scoured cotton fabric through a dip-pad-dry-cure process. In order to remove impurities from cotton, it was scoured by the non-ionic detergent (Kieralon ® F-OLB Conc.) before application of TiO_2 colloid. The scouring was carried out at 80 °C for 30 min. The scoured cotton pieces were dipped in the colloid for 1 min and then pressed in automatic horizontal press at 7.5 rpm with a nip pressure of 2.75 kg cm^{-2}. The pressed samples were then exposed to ammonia fumes until the surface pH 7 was reached. The neutralized samples were dried at 80 °C in a drying oven and cured at 120 °C for 3 min.

2.1.3. Synthesis of MTCPP

Fe(III), Co(II) and Zn(II) complexes of *meso*-tetra(4-carboxyphenyl)porphyrin were synthesized according to a method reported in literature [33]. Metal porphyrins (MTCPP) were synthesized by refluxing 0.33 mmol of TCPP with 1.82 mmol of $FeCl_3.6H_2O$, $Zn(Ac)_2$ and $CoCl_3.6H_2O$ in DMF for 2 h. MTCPPs were precipitated by adding in excess water. DMF and water were removed from the precipitates by repeated centrifugation. Solid dry precipitates of each metal complex were obtained by freeze drying.

2.1.4. Preparation of MTCPP/TiO_2-coated cotton

For MTCPP deposition, TiO_2-coated cotton samples were dipped in the corresponding MTCPP solution in DMF and heated at 100 °C for 5 h. The samples were then repeatedly washed with DMF to remove unreacted MTCPP molecules.

2.2. Characterization

The surface morphology of the samples was studied using field emission electron microscopy (JEOL 7001F FEGSEM). The crystallinity of TiO_2 films on cotton was determined by low angle X-ray diffraction (XRD, Philip 1140 diffractometer). The diffraction patterns of anatase TiO_2 were compared with reference to ICDD (2006) database. The UV–vis absorption spectra of MTCPP in DMF and MTCPP adsorbed on TiO_2-coated cotton were recorded on Cary 5000 spectrophotometer. The steady-state fluorescence quenching experiments were performed on Cary Eclipse fluorescence spectrophotometer.

2.3. Photocatalytic degradation

For the evaluation of self-cleaning properties, photocatalytic degradation of methylene blue (MB) was evaluated quantitatively. MTCPP/TiO_2-coated cotton pieces (0.5 g, 1.5 × 1.5 cm) were immersed in petri dish containing acidified MB (10 ml, 15.6 μM, pH = 1). The petri dishes were placed in a light-box and irradiated by visible-light for 3 h, using fluorescent lamp (30 W, 5.02 $mWcm^{-2}$ irradiance). During irradiation, the petri dishes were vigorously shaken using a bench top shaker. Prior to irradiation, the petri dishes were kept in dark for half an hour in order to attain adsorption-desorption equilibrium. The change in the concentration of MB was monitored by recording UV–vis spectra at different time intervals, during the course of photocatalytic reaction.

2.4. Stability of coating

The stability of MTCPP/TiO_2-coated cotton samples was tested against detergent, petroleum ether and water, using a modified AATCC Test Method 190-2003. The samples were washed with each solvent for 45 min at room temperature at constant stirring of 200 rpm, followed by rinsing with water and the air drying. To determine the amount of porphyrin retained on the cotton samples, UV–vis spectra of the samples were recorded before and after washing.

Download English Version:

https://daneshyari.com/en/article/5360254

Download Persian Version:

https://daneshyari.com/article/5360254

Daneshyari.com