Preparation and characterization of TiO₂-coated silk fibroin filters for photocatalytic oxidation of formaldehyde using waste silk cocoons

Authors Info

J. Triped¹, W. Sanongraj^{2*} and W. Khamwichee³

¹International Postgraduate Programmes in Environmental Management, Graduate School, Centre for Excellence on Hazardous Substance Management, Chulalongkorn University, Bangkok-10330, Thailand

²Research Excellence on Hazardous Substance Management, Department of Chemical Engineering, Faculty of Engineering, Ubonratchathani University-34190, Thailand

³School of Engineering and resources, Walailak University, Nakhonsithammarat-80160, Thailand

*Corresponding Author Email : wipadadechpanya@yahoo.com

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Abstract

Aim: The possibility of producing valued devices from low cost natural resources is a subject of broad interest. The present study explored the preparation and characterization of pure silk fibroin (SF) filters and TiO₂-coated SF filters for indoor air purification using waste silk cocoons generated from silk textile processing.

Methodology: Silk fibroin (SF) filter samples were characterized mainly by scanning electron microscopy, energy dispersive spectroscopy, Fourier transform infrared spectroscopy and mechanical analyses.

Results: The SEM results indicated that TiO₂ particles adhered well onto the silk fibroin filters. Compared to pure SF filters, the mechanical and thermal properties of TiO₂ SF filters were improved due to the conformational transition of silk fibroin to silk II structure. The percentage of catalyst (TiO₂) doses varied from 1.0, 2.5, 5.0, and 7.5 % (wt.cat.⁻¹ vol.sol.). The results derived from the kinetic model revealed that the photocatalytic rate followed the first order reaction. The highest removal efficiency of 68.21% was obtained at initial formaldehyde concentration of about 5.00 ppm and TiO₂-coated SF filters of 5.0 % TiO₂ wt.vol.⁻¹.sol.. The successful preparation of TiO₂-coated SF filters from waste silk cocoons provide a promising opportunity to widen potential applications of SF in the biomaterial field.

Interpretation: The successful preparation of TiO₂-coated SF filters from waste silk cocoons not only provides a promising opportunity to widen potential application of SF in indoor air purification but also enhances a waste minimization from silk textile processing.

Introduction

Formaldehyde (HCHO) is one of major indoor volatile organic compounds (VOCs). At ambient temperature, formaldehyde (CAS reg. no.50-00-0; 1 ppm = 1.2 mg m⁻³) is a flammable, colourless, reactive, and readily polymerized gas. Formaldehyde is irritating to the eyes and respiratory tract already at low concentrations (Lang *et al.* 2008). Its carcinogenic potential at a certain extent leads to development of air clean technologies. The application of traditional method for VOCs treatment by using photocatalytic oxidation (PCO) has gained attention as a possible alternative method for indoor air removal because it promises to clean air more efficiently and effectively. Photocatalysis is an emerging and promising technology for trace contaminant degradation (Zhong *et al.* 2010). PCO commonly uses nano-semiconductor catalysts and ultraviolet (UV) light to convert organic compounds in indoor air into benign and odorless constituents water vapor (H₂O) and carbon dioxide (CO₂) (Zhong *et al.* 2010). In the PCO reactions, pure or doped metal oxide semiconductors such as TiO₂, ZnO, CdS, and Fe (III)-doped TiO₂ are commonly used as photocatalysts. A lot of work has been done by many researches on the characterization of new photocatalytic textile materials for the removal of formaldehyde from indoor air by coating the textile materials with TiO₂. Recently, formaldehyde removal using PCO has drawn researchers' attention because of their high performance thus formaldehyde could be efficiently removed through the PCO process (Pierre-Alexandre *et al.* 2012). Moreover, titanium dioxide (TiO₂) is most extensively studied over the past decade because it is cheap, non toxic, and photostable (Rajh *et al.*, 1999).

Recently, in the development of new materials starting with SF, high purity SF can be readily obtained by degumming silk cocoons with 0.5 wt% Na₂CO₃ solution and washing them with de-ionized water to remove sericin (Jingxin *et al.*, 2008). SF fibre can be utilized to remove indoor air particulates (Triped *et al.*, 2010). Thailand has a sericulture industry consisting of approximately 148,754 families over an area of nearly 161,430 ha, with about 80% of the farmers residing in northeast Thailand. Thai production of raw silk fibres is approximately to the tune of 1,400 MT. Thai silk production has been a focus area in the textile industry and generates waste during the silk fibre processing which can be used as raw material for the study and development of silk materials. Thai silk is produced by caterpillars raised on mulberry leaves and are generated by weavers in Thailand (ARDA, 2014). Silk is a natural biopolymer produced by silkworms during formation of their cocoons. *Bombyx mori* silk is a well described natural fibre produced by silkworms. Natural silk fibre is one of the strongest natural materials due to the dominance of well orientated β -sheet structures of protein chains (Wang *et al.*, 2006).

Silk is composed of two proteins called fibroin and sericin. Silk fibroin (SF) is a natural protein produced by the domestic silkworm *B. mori*, which is composed of a heavy-chain (H-chain, 350 kDa) light-chain (L-chain, 25 kDa), and an

accessory protein (30 kDa) Fibroin is not soluble in water due to its high concentration of hydrophobic amino acids residues, such as alanine, on its surface and in its bulk Yongpei *et al.* (2012). Over the past few decades, *B. mori* has been explored to exploit the excellent characteristics of this protein for use as a textile fibre. SF has been used for centuries in other applications, such as biotechnology and biomedical materials, due to its desirable properties including biocompatibility, mechanical strength, high thermal stability, and microbial resistance Yongpei *et al.* (2012).

In light of the above, in the present study waste silk cocoons to prepare TiO₂-coated silk fibroin filters and characterize them with the aim of using them as biomaterial filters. Formaldehyde removal efficiency using synthesized SF filters via the photocatalytic oxidation process was also studied.

Materials and Methods

Preparation of TiO₂ B. mori silk fibroin filters : Silk cocoons were dried in sunlight and then cut into small pieces. They were de-gummed by boiling them with 2500 ml of 0.5% (w/w) in a sunlight soap solution at 90°C for 60 min and subsequently wash with distilled water. The SF fibres were uniformly reformed into rectangular-shaped filters and dried at 80°C for 3 hr in a vacuum oven. TiO₂ powder was dissolved in commercial grade polyvinyl acetate (PVA) (100 % v/v) and Tween 80 (100% v/v) solution. Finally, TiO₂ coating process was performed as follows: Firstly, TiO₂ was dissolved in 132 ml polyvinyl acetate solution to obtain the following concentrations of 1.0, 2.5, 5.0, and 7.5 % w/v PVA. Then, 1.125 ml of Tween 80 was added to the solution to enhance dissolution of TiO₂ in PVA solution and adhesion of TiO₂ onto the surface of SF filters, and left them until air dried. Finally, 56.25 ml of PVA solution was coated onto the filters using paint brush technique to minimize loss of TiO₂ from the filters (Makvilay *et al.*, 2014).

Scanning electron microscope analyses : The microstructures of pure SF filters and TiO₂-coated SF filters were examined using a scanning electron microscope (SEM, Model Jx-840, JEOL, Japan) at an acceleration voltage of 5kV. The TiO₂-coated SF filters were cryogenically fractured in liquid nitrogen, mounted onto aluminium specimen stubs using double-sided adhesive tape and sputter-coated with a thin layer of gold under rarefied Argon atmosphere. Suwannahong *et al.* (2012). The sputter rate and time were set to 10 nm min⁻¹ and 3 min, respectively. The thickness of gold film was approximately 30 nm.

Fourier transformed infrared (FT-IR) spectra : The secondary structure of samples were investigated using Fourier Transformed Infrared Spectroscopy (FT-IR) with a Perkin Elmer System 2000. Spectra were recorded in transmittance mode using KBr pellets in the range of 2000-550 cm⁻¹. Feng *et al.* (2007) The samples were dried and pressed against the crystal (by the sample holder) during measurements to ensure the highest

Fig. 1: Schematic diagram of the closed modeling room with the dimensions of 40 cm × 45 cm × 50 cm and the PCO reactor for studying removal efficiency of the TiO₂-coated SF filters

Table 1: Mechanical properties of silk fibroin filters

Samples (%TiO ₂ wt./ vol.sol.)	Maximum load (N)	Elastic value (stress, σ) (N/mm ²)	Strain (ϵ)
0 (pure SF)	3.020±0.094	0.088±0.002	0.184±0.039
1.0	6.093±1.106	0.140±0.022	0.085±0.185
2.5	9.155±4.138	0.206±0.080	0.029±0.089
5.0	9.673±0.046	0.245±0.001	0.021±0.075
7.5	17.314±3.401	0.440±0.080	0.028±0.073

contact surface area between the optical element and the sample.

Mechanical analyses : Mechanical properties including tensile stress and strain of synthesized SF fibres were measured. Static uni-axial tension tests were carried out at room temperature using a universal material test machine LR5K (Lloyd instruments, USA) with pneumatic clamps. The samples were analysed and prepared following the Dumbbell method ASTM D638. The load cell was set at 50 N. The cross-head speed was 10 mm min⁻¹ and the gauge length was 50 mm. (Triped *et al.*, 2010) The strain was calculated as the ratio of elongation to the gauge length of the test specimen, *i.e.*, the change in length per unit of original length. In each case, five specimens were tested to obtain an average value. Force-displacement curves were displayed and then used to determine the stress-strains of SF filters.

Photocatalytic oxidation reactor : Removal efficiency of TiO₂-coated SF filters was tested in a closed modelling room with the

flowing dimension 40cm × 45cm × 50cm as shown in Fig. 1. The temperature and relative humidity were continuously monitored by the Humidity and temperature data logger (HT 10). For all sets of experiment, temperature and relative humidity ranged from 25-30 °C and 65-70%, respectively. The TiO₂-coated SF filter was incorporated with the commercial air purifier equipped with two UV-C lamps. The modified air purifier was then placed inside the modelling room. Formaldehyde source was placed in the middle of the modelling room and allowed to reach equilibrium. A mixing electrical fan was installed in the room to ensure adequate mixing of formaldehyde in the room. Gaseous formaldehyde in the room was sucked through air purifier at an air flow rate of 5 l min⁻¹. Formaldehyde concentration was continuously measured every 5 min for 3 hrs with a HCHO meter (HAL-HFX205).

Results and Discussion

SEM images of TiO₂-coated SF filters at different TiO₂ dosages are

Fig. 2 : SEM micrographs at 2,000X of silk fibroin filters coated with (a) 1.0%, (b) 2.5%, (c) 5.0%, and (d) 7.5% TiO_2 wt./vol.sol. SEM micrographs reveal the fibrous morphology of the SF fibres

shown in Fig.2. The magnification used to obtain SEM images was obtained at 2,000X. SEM micrographs revealed the fibrous morphology of SF fibres. As seen in Fig. 2 TiO_2 was well dispersed onto the surface of SF filters at different dosages. However, a few clumps of TiO_2 particles were seen on the surface of SF filters at high TiO_2 dosages.

An EDS scanning electron microscope was used to separate characteristic X-rays of different elements from an energy spectrum. EDS was used to analyse the chemical composition of SF TiO_2 -coated filters. Fig. 3 shows EDS micrographs of TiO_2 -coated SF filters at dosages of 1.0, 2.5, 5.0, and 7.5% wt. TiO_2 vol¹.sol. The results showed that in analyses of all test samples characteristics X-ray frequencies of carbon, oxygen, gold, and the

last two peaks of titanium were detected as distinct peaks, respectively. The stronger peak from Ti was observed on addition of higher amount of TiO_2 .

To investigate the conformational characteristics of SF and TiO_2 -coated SF filters, samples were examined by FTIR spectroscopy. The chemical structures of filters is shown in Fig. 4. The infrared spectra of filters showed fingerprints of the samples with absorption peaks corresponding to the following amide bands: amide I, amide II and amide III. Amide I vibrations represents CO stretching, while amide II vibrations represents the bending of NH bonds associated with CN stretching (Franks *et al.*, 1993). Amide III vibrations are associated with the combination of NH deformation and CN stretching vibrations Magnani *et al.*, (1991).

From the figure, the characteristic bands corresponding to the amide groups were found in the region between 1700 -

Fig. 3 : EDS micrographs of silk fibroin filters coated with (a) 1.0%, (b) 2.5%, (c) 5.0%, and (d) 7.5% TiO₂ wt./vol.sol. The last two peaks of titanium (Ti) were detected as distinct peaks. The stronger peak from Ti was observed upon the addition of higher amounts of TiO₂

Table 2 : Simplified Langmuir-Hinshelwood form, $\ln(C/C_0) = kKt = K't$, at different doses of TiO₂

Dosage of TiO ₂ (%TiO ₂ wt./ vol.sol.)	Simplified Langmuir-Hinshelwood form	K'(min ⁻¹)	R ²	R.E. (%)
1.0	y = -0.0052x	-0.0052	0.9690	57.37 ± 1.49
2.5	y = -0.0049x	-0.0049	0.9804	61.95 ± 1.68
5.0	y = -0.0065x	-0.0065	0.9861	68.21 ± 0.48
7.5	y = -0.0049x	-0.0049	0.9819	44.00 ± 2.20

1200 cm⁻¹ Feng *et al.* (2007). Narrow absorption bands at 1622 cm⁻¹ (amide I), 1513 cm⁻¹ (amide II), and 1225 cm⁻¹ (amide III) attributed to the amide groups were due to the crystalline structures of the filters. These results indicate that the band at 1700 cm⁻¹ shows antiparallel arrangement of fibroin chains in the Silk II β -sheet domains (Lu *et al.*, 2010). A wide absorption band between 550 and 750 cm⁻¹ is due to the envelope of Ti-O bands (Simi *et al.*, 2009). As seen in fig. 4, the smaller peaks were observed with higher amount of TiO₂ coated on SF filters. The smaller peaks observed in the study might be due to the covering of TiO₂ the filter surfaces, which reduced light transmittance.

The resistance of pure SF TiO₂-coated SF filters against mechanical compression was analysed Dumbbell method ASTM D638, Type V test with a universal tensile testing machine (UTM), as shown in Table 2. The maximum value of

average stress (0.440 ± 0.080 N mm²) and average strain (0.028 ± 0.073) were obtained for TiO₂-coated SF filter at 7.5% TiO₂ wt vol⁻¹.sol. The higher stress and strain levels of TiO₂-coated SF filters might be a result of TiO₂ filling into pores of the SF filters, enhancing their strength.

A set of experiments were conducted to investigate the effect of TiO₂-coated SF filter on the removal efficiencies. For HCHO photocatalytic degradation using TiO₂-coated SF filter, the doses of TiO₂ varied from 1.0, 2.5, 5.0, and 7.5 % (wt.vol⁻¹.sol.) (Fig. 5). Shown in Fig. 6, the photocatalytic degradation rate of TiO₂-coated SF filters at 5.0 % TiO₂ wt.vol⁻¹.sol. was faster as compared to other TiO₂ dosages. The highest removal efficiency of 68.21% was obtained (Table 3).

Fig. 4: FTIR transmittance spectra of pure SF and TiO_2 -coated SF filters. The infrared spectra of the filters show fingerprints of the samples with absorption peaks corresponding to the following amide bands: 1622 cm^{-1} (amide I), 1513 cm^{-1} (amide II), and 1225 cm^{-1} (amide III)

Fig. 5 : Photocatalytic oxidation of gaseous formaldehyde at different catalyst (TiO_2) dosages: 1.0, 2.5, 5.0, and 7.5 % TiO_2 wt./vol.sol. The slopes of fitted straight line using the least square method follow the first order kinetic

Fig. 6 : The photocatalytic degradation rate of the TiO_2 -coated SF filters. Correlation between $\ln(C/C_0)$ and time at different catalyst (TiO_2) dosages: 1.0, 2.5, 5.0, and 7.5 % TiO_2 wt./vol.sol

Fig.5 shows correlation between $\ln(C/C_0)$ at different dosages of TiO_2 -coated SF filter using the same initial concentration of HCHO and illumination time. The plots indicated that the slopes of fitted straight line using least square method followed the first order kinetic for 1.0, 2.5, 5.0, and 7.5 % TiO_2 (wt.vol⁻¹.sol.). The simplified Langmuir-Hinshelwood form, $\ln(C/C_0) = -kKt = -K't$, at different doses of TiO_2 is displayed in Table 3.

The use of waste silk cocoons is an alternative method for preparing silk filters. ASF filter can be synthesized from waste silk cocoons through a degumming and TiO_2 coating process. The filters are crystallized to the β -sheet conformation and were found suitable for adherence to TiO_2 on the surface of SF filter. The mechanical and thermal properties of TiO_2 -coated SF filters

were improved. Thus, the successful preparation of TiO₂-coated SF filters from waste silk cocoons provides a promising opportunity to widen the potential applications of SF in the biomaterial field.

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