Preparation and characterization of TiO$_2$-coated silk fibroin filters for photocatalytic oxidation of formaldehyde using waste silk cocoons

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 TiO$_2$-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 TiO$_2$ particles adhered well onto the silk fibroin filters. Compared to pure SF filters, the mechanical and thermal properties of TiO$_2$ SF filters were improved due to the conformational transition of silk fibroin to silk II structure. The percentage of catalyst (TiO$_2$) doses varied from 1.0, 2.5, 5.0, and 7.5 % (wt.cat. / 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 TiO$_2$-coated SF filters of 5.0 % TiO$_2$ (wt./vol.sol.). The successful preparation of TiO$_2$-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 TiO$_2$-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.

Keywords
Biomaterials, Photocatalytic oxidation, Silk cocoons, Silk fibroin, Titanium dioxide
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 nanosemiconductor 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 w% 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. Thailand production has been a focus area in the textile industry and silk fibres is approximately to the tune of 1,400 MT. Thai silk production 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 polynvinyl 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 polynvinyl 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 polynvinyl 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 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 JxA-840, JEOL, Japan) at an acceleration voltage of 5kVA. 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. To record the spectra, the samples were dried and pressed against the crystal (by the sample holder) during measurements to ensure the highest spectroscopic.
**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 following dimension 40 cm × 45 cm × 50 cm 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
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 sheen in TiO was well dispersed onto the surface of SF filters at different dosages. However, a few clumps of TiO particles were seen on the surface of SF filters at high TiO 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-coated filters. Fig. 3 shows EDS micrographs of TiO-coated SF filters at dosages of 1.0, 2.5, 5.0, and 7.5% wt. TiO vol. 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 -
Characterization of TiO$_2$ coated silk fibroin using silk cocoons

Table 2: Simplified Langmuir-Hinshelwood form, ln(C/C$_0$) = kkt = K', at different doses of TiO$_2$.

<table>
<thead>
<tr>
<th>Dosage of TiO$_2$ (%TiO$_2$ wt./vol.sol.)</th>
<th>Simplified Langmuir-Hinshelwood form</th>
<th>K' (min$^{-1}$)</th>
<th>R$^2$</th>
<th>R.E. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>y = -0.0052x</td>
<td>-0.0052</td>
<td>0.9690</td>
<td>57.37 ± 1.49</td>
</tr>
<tr>
<td>2.5</td>
<td>y = -0.0049x</td>
<td>-0.0049</td>
<td>0.9804</td>
<td>61.95 ± 1.68</td>
</tr>
<tr>
<td>5.0</td>
<td>y = -0.0065x</td>
<td>-0.0065</td>
<td>0.9861</td>
<td>68.21 ± 0.48</td>
</tr>
<tr>
<td>7.5</td>
<td>y = -0.0049x</td>
<td>-0.0049</td>
<td>0.9819</td>
<td>44.00 ± 2.20</td>
</tr>
</tbody>
</table>

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 TiO$_2$ coated on SF filters. The smaller peaks observed in the study might be due to the covering of TiO$_2$ the filter surfaces, which reduced light transmittance.

A set of experiments were conducted to investigate the effect of TiO$_2$-coated SF filter on the removal efficiencies. For HCHO photocatalytic degradation using TiO$_2$-coated SF filter, the doses of TiO$_2$ 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 TiO$_2$-coated SF filters at 5.0 % TiO$_2$ wt. vol.$^{-1}$ sol. was faster as compared to other TiO$_2$ dosages. The highest removal efficiency of 68.21% was obtained (Table 3).

The resistance of pure SF TiO$_2$-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 mm$^{-2}$) and average strain (0.028±0.073) were obtained for TiO$_2$-coated SF filter at 7.5% TiO$_2$ wt. vol.$^{-1}$ sol. The higher stress and strain levels of TiO$_2$-coated SF filters might be a result of TiO$_2$ filling into pores of the SF filters, enhancing their strength.
The use of waste silk cocoons is an alternative method for preparing silk filters. A SF filter can be synthesized from waste silk cocoons through a degumming and TiO₂ coating process. The filters are crystallized to the β-sheet conformation and were found suitable for adherence to TiO₂ on the surface of SF filter. The mechanical and thermal properties of TiO₂-coated SF filters

Fig. 5: Photocatalytic oxidation of gaseous formaldehyde at different catalyst (TiO₂) dosages: 1.0, 2.5, 5.0, and 7.5 % TiO₂ 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 TiO₂-coated SF filters. Correlation between ln(C/C₀) and time at different catalyst (TiO₂) dosages: 1.0, 2.5, 5.0, and 7.5 % TiO₂ wt./vol.sol.

The FTIR transmittance spectra of pure SF and TiO₂-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).

The use of waste silk cocoons is an alternative method for preparing silk filters. A SF filter can be synthesized from waste silk cocoons through a degumming and TiO₂ coating process. The filters are crystallized to the β-sheet conformation and were found suitable for adherence to TiO₂ on the surface of SF filter. The mechanical and thermal properties of TiO₂-coated SF filters
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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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