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Photocatalytic Oxidation of Gaseous Formaldehyde Using the TiO_2 Coated SF Filter

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***Abstract*—**The research work covered in this study includes the morphological structure and optical properties of TiO_2-coated silk fibroin (SF) filters at 2.5% wt. TiO_2/vol. PVA solution. SEM micrographs revealed the fibrous morphology of the TiO_2-coated SF filters. An average diameter of the SF fiber was estimated to be approximately 10μm. Also, it was confirmed that TiO_2 can be adhered more on SF filter surface at higher TiO_2 dosages. The activity of semiconductor materials was studied by UV-VIS spectrophotometer method. The spectral data recorded shows the strong cut off at 390 nm. The calculated band-gap energy was about 3.19 eV. The photocatalytic activity of the filter was tested for gaseous formaldehyde removal in a modeling room with the total volume of 2.66 m^3. The highest removal efficiency (54.72 ± 1.75%) was obtained at the initial formaldehyde concentration of about 5.00 ± 0.50ppm.

***Keywords*—**Photocatalytic oxidation process, Formaldehyde (HCHO), Silk fibroin (SF), Titanium dioxide (TiO_2).

I. INTRODUCTION

INDOOR air pollution problem has been increasingly concerned in recent years. The studies on indoor air quality (IAQ) have been shifted gradually to indoor volatile organic compounds (VOCs). Formaldehyde (HCHO), one of indoor VOCs and as a major indoor air contaminant, is emitted extensively from modern building materials and household products [1]. Formaldehyde removal is vital for IAQ improvement and human's health due to its carcinogenic risk [2]. In particular, the removal of pollutants in indoor air is more important because they are strongly harmful to human health.

Photocatalytic oxidation (PCO) is remediation technology, which offers a number of advantages over conventional technologies. PCO is a promising air purification technology for trace contaminant degradation because it can degrade a broad range of VOCs to H_2O and CO_2 at room temperature and atmospheric pressure without significant energy input [3]-[5]. There are some reports on the photocatalytic degradation of formaldehyde [6], [7]. In the PCO reaction, pure or doped metal oxide semiconductors, such as TiO_2, ZnO, CdS, Fe (III)-doped TiO_2, are commonly used as the photocatalysts.

Pierre-Alexandre B. et al. 2010 [8] studied the characterization of new photocatalytic textile for formaldehyde removal from indoor air by coating the textile with TiO_2. The result proved that formaldehyde could be efficiently removed by using the PCO process.

Natural silk fiber is one of the strongest materials due to the dominance of well-orientated β-sheet structures of protein chains [9]. High purity silk fibroin (SF) can be obtained readily by degumming silk cocoon with 0.5 wt% Na_2CO_3 solution and washed with de-ionized water to remove the sericin [10]. SF fiber from silk cocoons such as *Bombyx mori* has been explored to exploit the excellent characteristics of this protein for over decades as a textile fiber in the production of bio-material, cosmetic cream, lotions, make-up, powder, bath preparations, and pharmaceuticals [11] due to its non-toxicity to cells, good mechanical properties, and slow degradation rate [12], [13]. In addition, Triped, J. et al. 2010 [14] reported that SF fiber can be applied for the removal of indoor air particulate.

In this study, cost-effective and simple preparation of photocatalytic SF filters was achieved by coating the surface of the SF filters with TiO_2. The synthesized filters were then incorporated with the commercial air purifier equipped with two UV-C lamps. The morphological structure and optical properties of the TiO_2-coated SF filters were analyzed. Also, the photocatalytic destruction of gaseous formaldehyde using the TiO_2-coated SF filters was conducted in the modeling room to examine the removal efficiency of the filters.

II. EXPERIMENTAL

A. Reagents and Materials

Sunlight soap, Ecoteric T80 or Tween80 (analytical grade from Ajax Finechem Pty led, Austria), Polyvinyl acetate (PVA) solution (commercial grade), Titanium dioxide (TiO_2) (Brand Tipaque code A-220 (Anatase), Formaldehyde solution (analytical grade from Ajax Finechem Pty led, Austria), and Cocoons of the *B. mori* silkworm collected from a local farm in Ubon Ratchathani province, Thailand, were used in this research.

B. Preparation of TiO_2-Bombyx mori Silk Fibroin

Silk cocoons were dried in sunlight and then cut into small lengths. Then they were de-gummed by boiling in sunlight soap solution at 90^0C for 60mins and washed with distilled water. After that, SF fiber was uniformly reformed into rectangular-shaped filters and dried at 80^0C for 3hrs in a vacuum oven. Finally, the SF filters was coated with 2.50%

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(wt./vol.) TiO_2 dissolved in commercial grade polyvinyl acetate (PVA) and Tween 80 solution using the paint brushing technique.

C. Silk Fibroin Fiber Characterization

Scanning Electron Microscope (SEM) Analysis

SEM characterization was performed using the JEOL, Model JxA840, Japan microscope at an acceleration voltage of 5kV. The TiO_2-coated SF filters was cryogenically fractured in liquid nitrogen and then mounted onto aluminum specimen stubs by means of double-sided adhesive tape and sputter-coated with a thin gold layer under rarefied Argon atmosphere. The sputter rate time was set for 10 nm/min and3 min, respectively. The gold film thickness was approximately 30 nm [15].

Optical Properties of TiO_2-Coated SF Filters

The ultraviolet-visible spectrum of the photocatalysts was recorded by a UV/VIS/NIR spectrophotometer (Lambda 1050, Perkin Elmer instrument, USA) along with 150mm sphere. TiO_2-coated SF filter sample was clamped on the external port of the integrating sphere. The scan wavelength ranges from 250 to 800nm. All spectra was monitored in the absorbance mode and acquired under ambient conditions. The optical absorbance spectra, the adsorption coefficient, and the band gap of the SF filters will be evaluated. The band gap engergy can be caculated using the following eqution; Band Gap Energy $(E) = h * c / \lambda$; where h = Planks constant = 6.626 x 10^{-34} (J.s), c = Speed of light = 3.0 x 10^8 (m/s), λ = Cut off walength (m), and 1eV = 1.6 x10^{-19} J [16].

D. The Modeling Room

Removal efficiency of the TiO_2-coated SF filters was tested in a closed modeling room with the dimensions of 1.20m × 1.20m × 1.85m 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 25-30ºC and 65-70%, respectively. The TiO_2-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 modeling room (Fig. 1). Formaldehyde source was placed in the middle of the modeling 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 the air purifier at an air flow rate of 84.40 ft^3/min. Formaldehyde concentration was continuously measured every 5 min. for 8 hrs .

E. Effect of Initial Formaldehyde Concentration on Removal Efficiency of the TiO_2-Coated SF Filters

Set of experiments was conducted to investigate the effect of initial formaldehyde concentrations on removal efficiency of the filters. There were two replications for each experiment. Experimental conditions were set as follows: the air flow rate of 84.40 ft^3/min and the catalyst dosage of 2.50 % (wt./vol.). While, the initial formaldehyde concentration was varied as 5.00 ± 0.50 ppm, 7.50 ± 0.50 ppm, and 10.00 ± 0.50 ppm. The Gaseous formaldehyde concentrations in the room were measure using the Hand-held Formaldehyde Meter (HAL-HFX205) until a steady state is reached. The steady state of formaldehyde concentration was reported as the initial concentration. Then the modified air purifier was turned on and the formaldehyde concentrations were continuously measured every 5 minutes until a steady state is reached.

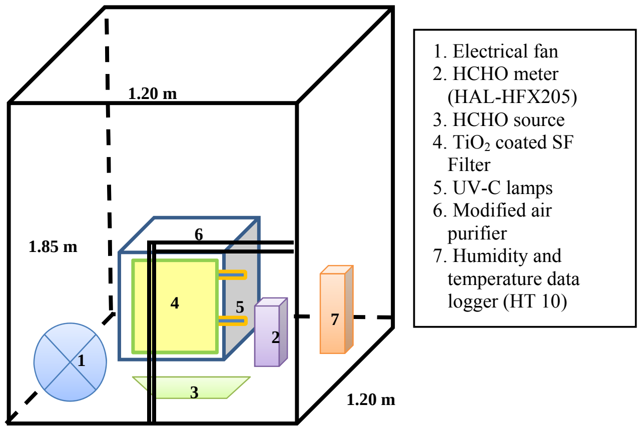

Fig. 1 Schematic diagram of the modeling room

III. Results and Discussions

A. Fiber Morphology and Optical Property

The SF fiber from the *Bombyx mori* silkworm was reformed into a rectangle shape (25cm x 36cm) having a yellowish color and thin sheet as shown in Fig. 2 (a). Then they were coated with 2.5% TiO_2 (wt./vol.). The TiO_2 coated SF filters have a light green color as shown in Fig. 2 (b). SEM micrographs of the TiO_2-coated SF filters at different TiO_2 dosages are shown in Figs. 3 (a)-(d). In which, Figs. 3 (a)-(d) are the images of the filters examined under four different magnifications as 50X, 100X, 500X, and 2000X, respectively. SEM micrographs revealed the fibrous morphology of the SF fiber. An average diameter of the SF fiber was estimated to be approximately 10 µm. As seen from the figure, it was confirmed that TiO_2 can be adhered more on SF filter surface at higher TiO_2 dosages.

The ultraviolet-visible spectrum of the photocatalysts was recorded by a UV-VIS spectrophotometer. The resulting spectrum was obtained for TiO_2. The spectral data recorded showed the strong cut off at 390 nm. Therefore, the band gap engergy can be caculated to be 3.185576 eV. This result agrees with other results [17].

B. Photocatalytic Degradation of Formaldehyde

Set of experiments was conducted to investigate the effect of initial formaldehyde concentration on the removal efficiencies of the filters. As seen from Fig. 4, the photocatalytic degradation rate of formaldehyde at the initial concentration of about 7.50 ppm was faster as compared to those of formaldehyde at other concentrations. While the highest removal efficiency (54.72 ± 1.75 %) was obtained at the initial concentration of about 5.00 ppm as displayed in Table I.

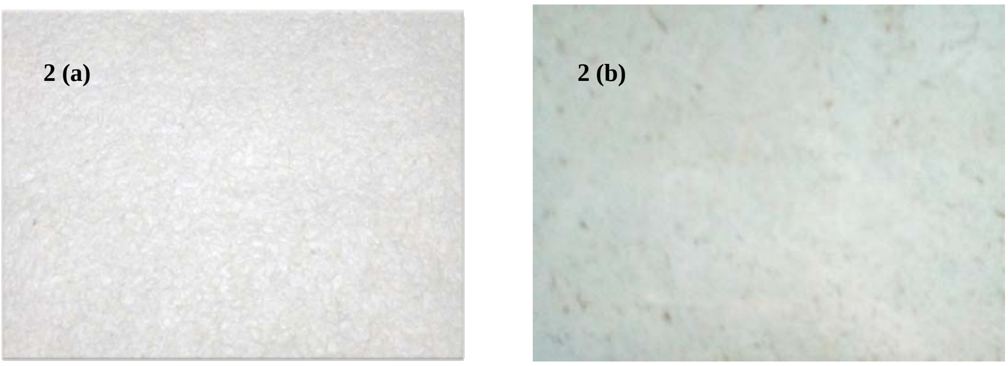

Fig. 2 The TiO_2-coated SF filter (a) before coating with TiO_2 and (b) after coating with TiO_2

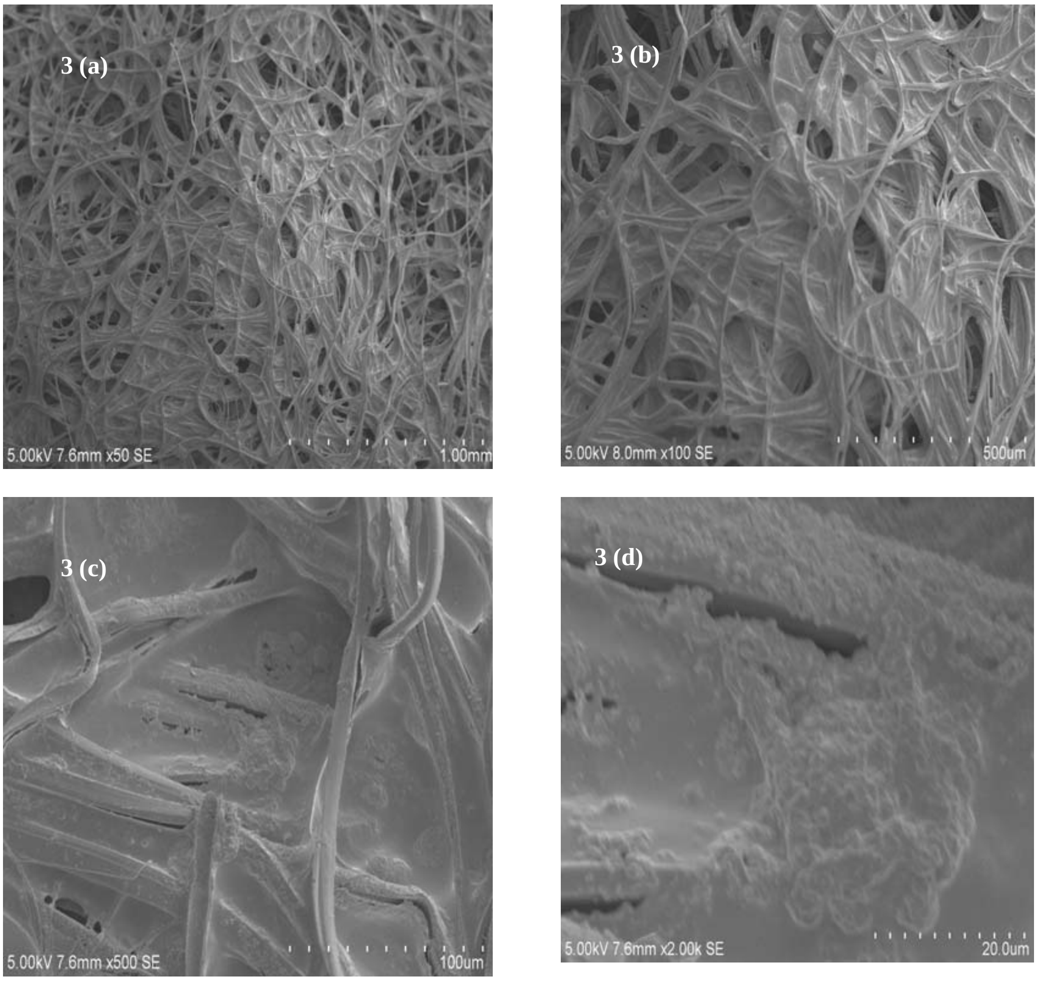

Fig. 3 SEM micrographs of the TiO_2-coated SF filters at different TiO_2 dosages

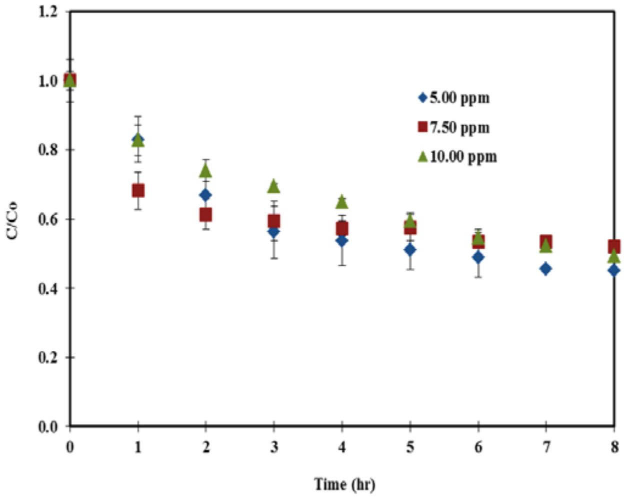

Fig. 4 Photocatalytic oxidation of gaseous formaldehyde at different initial concentrations

This may be due to the higher the initial concentrations, the more mass of formaldehyde pumped through the filter. Consequently, there are not enough reactive sites for such a relatively high formaldehyde concentration to be adsorbed onto them and reacted with hydroxyl radicals at this low catalyst dosage.

TABLE I
FORMALDEHYDE REMOVAL EFFICIENCIES

	Initial Concentrations of Formaldehyde (ppm)		
	5.00 ± 0.50	7.50 ± 0.50	10.00 ± 0.50
Percent formaldehyde removal efficiency	54.72 ± 1.75	47.09 ± 2.23	46.56 ±1.51

IV. CONCLUSION

The TiO_2-coated SF filters was readily synthesized using the sunlight soap solution. The results reported herein are the morphological structure and optical properties of the TiO_2-coated SF filters. SEM micrographs revealed the fibrous morphology of the SF fiber. TiO_2 can be adhered on silk fibroin filter. The band-gap energy of TiO_2 coated on the filters was calculated to be 3.185576 eV. The highest removal efficiency of the TiO_2 coated SF filters was approximately 54.72±1.75% at the initial concentrations of 5.00±0.50 ppm.

This new integrating material has demonstrated the potential use of the TiO_2 coated SF filters as an alternative and economic indoor air purifier.

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