



Enhancement of formaldehyde degradation by amine functionalized silica/titania films

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Received 08 January 2009; revised 13 March 2009; accepted 26 May 2009

Abstract

Doping amine functional groups into $\text{SiO}_2/\text{TiO}_2$ films for enhancing the decomposition of formaldehyde has been investigated using the modified sol-gel method to prepare organic-inorganic hybrid photocatalysts via the co-condensation reaction of methyltrimethoxysilane (MTMOS) and amine functional groups. *n*-(2-Aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPTMS) and 3-aminopropyl-trimethoxysilane (APTMS) were selected to study the effect of amine functional groups on the enhancement of formaldehyde adsorption and degradation under a UV irradiation process. Physicochemical properties of prepared photocatalysts were characterized with nitrogen adsorption-desorption isotherms measurement, X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The results indicated that the APTMS/ $\text{SiO}_2/\text{TiO}_2$ film demonstrated a degradation efficiency of 79% superior to those of $\text{SiO}_2/\text{TiO}_2$ and AEAPTMS/ $\text{SiO}_2/\text{TiO}_2$ films due to the synergetic effect of adsorption and photocatalytic properties. The APTMS/ $\text{SiO}_2/\text{TiO}_2$ film can be recycled with about 7% decreasing of degradation efficiency after seven cycles.

Key words: photocatalysis; titania; functional groups; formaldehyde

DOI: 10.1016/S1001-0742(08)62482-1

Introduction

Formaldehyde is an important chemical used by industry to manufacture numerous household products. The emission of this gas from building and furnishing materials is an important health risk as it is a major cause of “sick building syndrome”. This condition is characterized by nausea, irritation of the eyes and respiratory tract, chest tightness, skin rashes, and allergic reactions (Noguchi *et al.*, 1998). The removal of gaseous formaldehyde by titania (TiO_2) photocatalysts has received much attention during the last decade. Many studies have modified TiO_2 with porous materials to improve the photocatalytic activity. Among these materials, silica (Zhang *et al.*, 2001), zeolite (Panpa *et al.*, 2008), clay (Daniel *et al.*, 2007), and activated carbon (Shi *et al.*, 2008), are the most commonly used. It has been found that the porous materials can enhance the photocatalytic activity due to a higher specific surface area and more effective adsorption sites. Furthermore, many publications have reported the doping of adsorbent species into the photocatalysts to improve the removal efficiency by specific substrates adsorption, such as lanthanide oxide-doped TiO_2 for enhancing the degradation of *p*-chlorophenoxyacetic acid (Jin *et al.*, 2008), sepiolite-supported TiO_2 for β -naphthol removal (Okte and Sayinsoz, 2008), and H β zeolite-supported TiO_2

for removing aqueous propoxur solution (Mahalakshmi *et al.*, 2009). However, the incorporation of TiO_2 photocatalyst with a formaldehyde-adsorbent species has not yet been explored. Recently, Sae-ung and Boonamnuayvitaya (2008) found that amine functional groups ($-\text{NH}_2$) in the amine-functionalized SiO_2 adsorbents have specific affinities for formaldehyde molecules, resulting in the high capacitive adsorption of gaseous formaldehyde. Therefore, the enhancement of formaldehyde degradation by doping amine functional groups into the $\text{SiO}_2/\text{TiO}_2$ photocatalyst could be expected.

In the present study, the objective was to synthesize amine functionalized $\text{SiO}_2/\text{TiO}_2$ film for improving gaseous formaldehyde degradation. The synergetic effect of formaldehyde adsorption and photocatalytic decomposition during the degradation process was investigated. The roles of amine functional groups as adsorption sites for formaldehyde at the catalyst surface were clarified. The efficiency of formaldehyde degradation by the TiO_2 photocatalytic reaction with or without doping amine functional groups was compared. The repetitive use of the film for degrading formaldehyde was also tested.

1 Materials and methods

1.1 Materials

Amorphous TiO_2 powder (BET surface area of 50 m^2/g , average primary particle size of 21 nm) used for

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preparing the photocatalyst was commercial P-25 (TiO₂, analytical grade, Degussa, Germany). Methyltrimethoxysilane (CH₃Si(OCH₃)₃, MTMOS, synthesis grade, Merck, Germany) was used as the SiO₂ precursor. The amine functional groups were generated from 3-aminopropyl-trimethoxysilane (NH₂(CH₂)₃-Si(OCH₃)₃, APTMS, synthesis grade, Merck, Germany) and *n*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (NH₂(CH₂)₂NH(CH₂)₃-Si(OCH₃)₃, AEAPTMS, synthesis grade, Merck, Germany). The other chemicals used in the synthetic procedures were hydrochloric acid (HCl, analytical grade, J.T. Baker, USA), ammonium hydroxide (NH₄OH, analytical grade, Mallinckrodt, France) and deionized water. Formaldehyde gas used in this study was generated by heating paraformaldehyde powder (95%, synthesis grade, Merck, Germany) at 200°C for 35 min.

1.2 Synthesis of the photocatalytic films

In a typical preparation of APTMS/SiO₂/TiO₂ thin films, the total molar ratio of MTMOS : APTMS : methanol : H₂O : NH₄OH was 0.975 : 0.025 : 19.1 : 5.31 : 0.08. The sol was prepared by two separated hydrolysis procedures; (1) APTMS (0.025 mol) was added into the mixture of methanol (6.37 mol), H₂O (2.67 mol) and 0.055 mol/L HCl aqueous solution and stirred by a magnetic stirrer at 50°C for 1 h; (2) MTMOS (0.975 mol) was separately hydrolyzed with the above mentioned procedure (1).

After that, both hydrolyzed solutions were mixed together. Then, amorphous TiO₂ powder (5 wt.%), previously calcined at the determined temperature, was simultaneously added with the mixture of NH₄OH (0.08 mol) and methanol (6.37 mol) into the hydrolyzed solution and stirred at room temperature. The calcination temperature of amorphous TiO₂ powder was varied from 200 to 600°C.

The sol was coated on glass sticks (8 mm in diameter, 60 mm in length) by laboratory-constructed dip-coating instrument with a withdrawal rate of 25 cm/min and air-dried at room temperature. The glass sticks were washed with deionized water twice and acetone twice, and then dried in desiccators before use. The other photocatalysts of AEAPTMS/SiO₂/TiO₂ and SiO₂/TiO₂ were prepared by the same procedures, but substituting APTMS with AEAPTMS and excluding amine functional groups.

1.3 Characterization

The crystallographic structure of photocatalysts was identified by X-ray diffraction analysis, XRD (D8Discover, Bruker, Germany). The XRD patterns were carried out at room temperature using Cu K_α radiation ($\lambda = 0.1542$ nm), performed over angular ranges of $2\theta = 20\text{--}80^\circ$, scanned at a speed of 0.4°/s in steps of 0.02°. The equipment was operated at 40 kV and 40 mA. The average crystallite size of the anatase phase TiO₂ was calculated by Scherrer's equation (Eq. (1)).

$$\text{Average crystallite size} = K \times \lambda / \beta \times \cos\theta \quad (1)$$

where, λ (Å) is the radiation wave length, β is the integral width of the peak at $2\theta = 25.3^\circ$, θ is Bragg's angle in the (101) plane, and K is Scherrer's value (0.94).

Functional identification of the photocatalysts before and after formaldehyde adsorption was demonstrated by using Fourier transform infrared (FT-IR) spectroscopy. The transmission spectra of the samples were recorded using the KBr pellet containing 0.1% of sample. The pellets (12.7 mm in diameter and 1 mm thick) were prepared by a hydraulic press at 10 tons and dried overnight at 100°C before recording spectra. The spectra were measured from 4000 to 450 cm⁻¹ and recorded on a Perkin-Elmer 1760X spectrometer (USA).

Specific surface area, pore size and pore volume of the photocatalysts were determined using nitrogen adsorption-desorption isotherms by surface area and pore size analyzer (Autosorb-1, Quantachrome Corp., USA). Prior to measurement, all photocatalysts were degassed at 110°C under nitrogen flow for 3 h. The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature (77 K). The specific surface area was calculated using multipoint Brunauer-Emmett-Teller (BET) analysis.

1.4 Degradation efficiency of the photocatalysts

The photocatalytic procedure of prepared films for the formaldehyde decomposition was examined by a laboratory-constructed "irradiation box" with a dimensions of 400 mm × 360 mm × 130 mm. Two 8-W UV lamps ($\lambda = 254$ nm) were co-axially installed inside the box. Figure 1 shows the scheme of the irradiation box. All experiments were conducted in a dark room, and temperature was controlled at 28°C.

The evaluation of the degradation efficiency of the coated film on glass sticks was conducted by putting a coated glass stick in a vial, enclosing it with rubber cork and sealing with an aluminous cap. A series of six 60 mL vials was placed between two parallel UV lamps. A 2.5-mL quantity of air inside the vials was substituted by a determined concentration of formaldehyde gas to obtain the initial formaldehyde concentration around 7000 ppmv. The initial formaldehyde concentration in the vial was determined by gas chromatography (GC 6890, Perkin-Elmer, USA) equipped with DB-WAX column. After that, the cover of the irradiation box was closed for 60 min to allow the films to adsorb the formaldehyde, then the UV lamps were turned on for 60 min to perform the

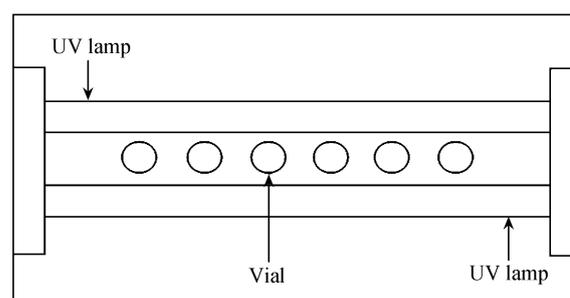


Fig. 1 Schematic diagram of "irradiation box".

photocatalytic reaction.

At a fixed time intervals, the 0.6 mL samples of gas in the vials were collected and injected into gas chromatography to determine the concentration of formaldehyde remaining in the vials. Adsorption, photocatalytic and overall degradation efficiencies of photocatalysts were calculated by the following Eq. (2):

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

where, η is degradation efficiency, C_0 and C_t are formaldehyde concentration at initial and time t (min), respectively. Note that: $C_0 = C_t = 0$, $C_0 = C_t = 60$ for calculating the adsorption efficiency, $C_0 = C_t = 60$, $C_0 = C_t = 120$ for calculating the photocatalytic efficiency and $C_0 = C_t = 0$, $C_0 = C_t = 120$ for calculating the overall efficiency.

2 Results and discussion

2.1 Characteristics of photocatalysts

It is well-known that calcination improves the crystallinity of TiO_2 . The amorphous TiO_2 changes to the anatase phase or rutile phase with increasing calcination temperature. Figure 2 shows the XRD patterns of APTMS/ SiO_2 / TiO_2 photocatalyst calcined at different temperatures from 200 to 600°C. The XRD result indicates that the sample calcined at 200°C is still amorphous. The anatase peaks (JCPDS 21-1272) appearing at 300°C resulted from a phase transition from amorphous to anatase. The anatase peak intensity increased with increasing temperature from 300 to 500°C. The average crystallite size of anatase phase calculated from Scherrer's equation (Eq. (1)) is 17.2 nm for 500°C. The rutile phase of TiO_2 (JCPDS 89-0552) was observed when calcined above 400°C. It is remarkable that around 600°C, the peak intensity of rutile phase still increases, while those of anatase phase decreases drastically. We confirmed that TiO_2 crystallite shifts from the anatase to the rutile phase.

Many studies have confirmed that the anatase phase of TiO_2 is a superior photocatalyst than its rutile phase. It has more beneficial characteristics for photocatalytic activity,

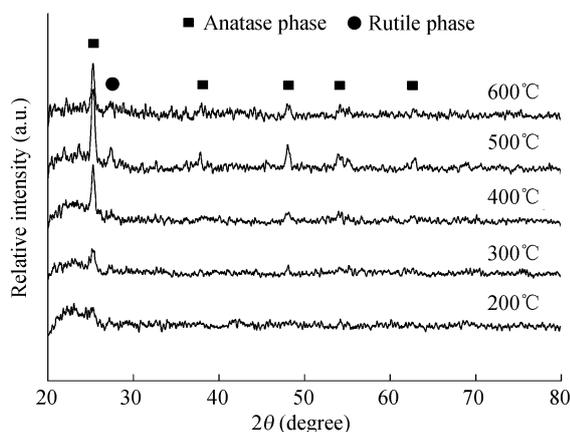


Fig. 2 XRD patterns of APTMS/ SiO_2 / TiO_2 photocatalyst with different calcined temperatures.

such as higher surface area, porosity, hydroxyl groups and band-gap energy (Tayade *et al.*, 2007). Since the anatase phase is believed to have more photocatalytic activity than that of rutile phase, the calcination temperature of TiO_2 at 500°C, which yields the highest peak intensity of anatase TiO_2 , was used throughout this study.

Figure 3a shows the FT-IR spectra of intact SiO_2 / TiO_2 , APTMS/ SiO_2 / TiO_2 and AEAPTMS/ SiO_2 / TiO_2 . Based on the research of literature (Wang *et al.*, 2006; Sae-ung and Boonamnuayvitaya, 2008; Zhou *et al.*, 2006), peaks corresponding to the Si–O–Si bond stretching of the silanol group near 1127 and 1030 cm^{-1} , the O–Ti–O lattice near 680 and 557 cm^{-1} , and the N–H stretching near 1416 cm^{-1} were observed. We can confirm that SiO_2 , TiO_2 and amine groups were successfully immobilized in the photocatalysts.

The surface textural properties of the prepared photocatalysts were characterized by nitrogen adsorption-desorption analysis, and the results are summarized in Table 1.

Table 1 Surface textural properties of the prepared photocatalysts

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
$\text{SiO}_2/\text{TiO}_2$	26.33	3.307	6.37
APTMS/ SiO_2 / TiO_2	402.40	0.485	4.82
AEAPTMS/ SiO_2 / TiO_2	6.96	0.019	10.74

Compared with the SiO_2 / TiO_2 photocatalyst, the BET surface area was improved after doping APTMS into the SiO_2 / TiO_2 . However, the BET surface area of the photocatalyst was decreased significantly when doping AEAPTMS into the SiO_2 / TiO_2 . This result was also observed by Sae-ung and Boonamnuayvitaya (2008), that applying short amine chains into SiO_2 network can produce a higher specific surface area than that of long chains. The average pore diameters in Table 1 show exactly the same trend as BET surface area. The total pore volume of SiO_2 / TiO_2 was higher than that both of APTMS/ SiO_2 / TiO_2 and AEAPTMS/ SiO_2 / TiO_2 .

2.2 Formaldehyde degradation

2.2.1 Control experiments

Prior to the evaluation of degradation efficiency of the prepared photocatalysts in detail, some control experiments were designed and repeated for three times. The results are shown in Fig. 4.

First, the degradation of formaldehyde in the absence of photocatalytic films was tested for 20 min and a negligible loss of formaldehyde was found in both dark and UV-exposed condition. Then, the adsorption of formaldehyde was checked with SiO_2 / TiO_2 , APTMS/ SiO_2 / TiO_2 , and AEAPTMS/ SiO_2 / TiO_2 films. A better adsorption characteristic was found in the presence of APTMS/ SiO_2 / TiO_2 film. After that, the same set of these photocatalysts was exposed to the UV light to decompose formaldehyde by photocatalytic reaction. Formaldehyde remaining in the vials for all films was significantly loss and the lowest

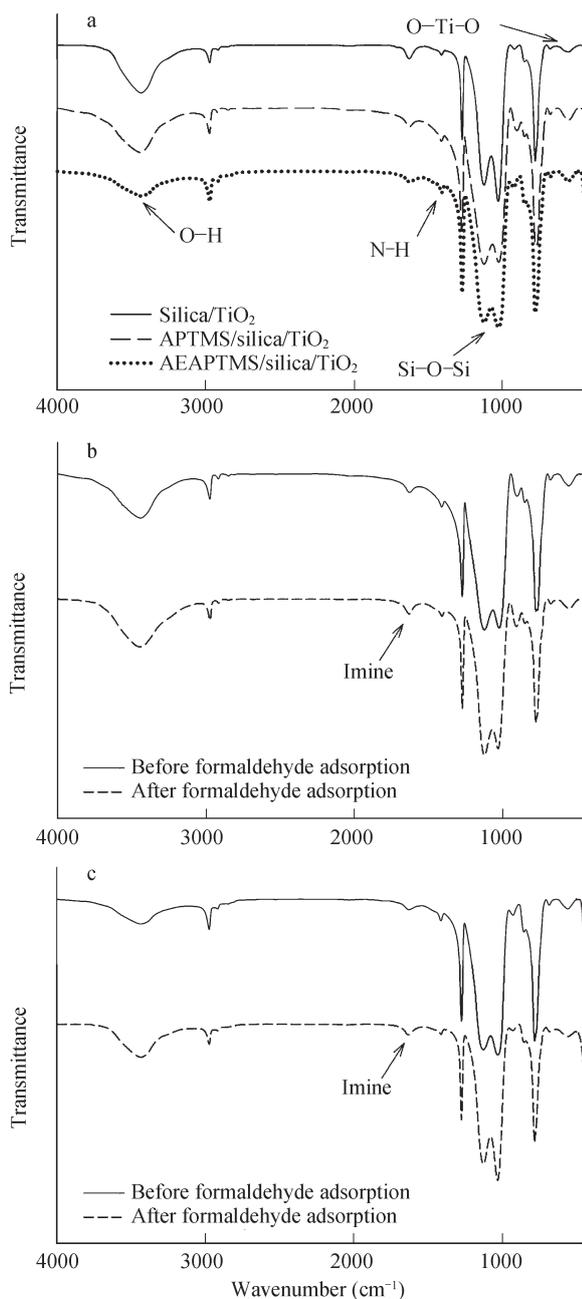


Fig. 3 FT-IR spectra of intact photocatalysts (a), APTMS/SiO₂/TiO₂ (b) and AEAPTMS/SiO₂/TiO₂ (c).

formaldehyde concentration was achieved again in the presence of APTMS/SiO₂/TiO₂ film. It was also noted that bare SiO₂ never involved in the photocatalytic degradation of formaldehyde (data not shown).

2.2.2 Adsorption and photocatalytic degradation efficiency of photocatalysts

Figure 5 shows the profiles of formaldehyde concentrations before and after UV irradiation for SiO₂/TiO₂, APTMS/SiO₂/TiO₂, and AEAPTMS/SiO₂/TiO₂ films. Formaldehyde adsorbed onto the films rapidly to around 20%–30% of the initial formaldehyde concentration within 10 min and reached equilibrium in 60 min. After starting the photocatalytic reaction, the formaldehyde concentration decreased drastically within 20 min. The adsorption,

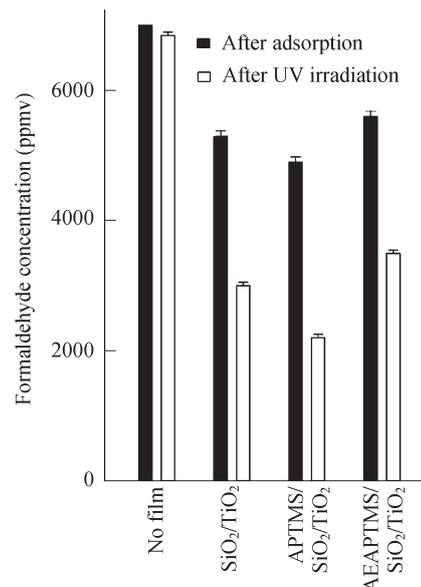


Fig. 4 Formaldehyde degradation by photocatalyst film.

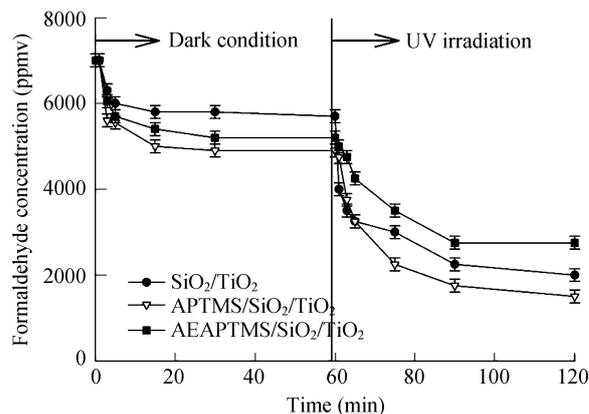


Fig. 5 Changes in formaldehyde concentrations depending on the treatment time before and after UV irradiation for SiO₂/TiO₂ (a), APTMS/SiO₂/TiO₂ (b), and AEAPTMS/SiO₂/TiO₂ (c).

the photocatalytic and the overall efficiencies of the photocatalysts are shown in Fig. 6.

The important factor for the adsorbent and photocatalyst is the specific surface area, which is dependent on the preparation methods (Huang and Saka, 2003). Compared with bare SiO₂/TiO₂ film, doping APTMS into SiO₂/TiO₂ increased both formaldehyde adsorption and photocatalytic efficiencies. This can be explained by the higher specific surface area of APTMS/SiO₂/TiO₂. The large surface area of the photocatalyst favors the formaldehyde adsorption on amine sites. From the FT-IR results, formaldehyde can be adsorbed on the surface of APTMS/SiO₂/TiO₂ films by interacting with amine sites to form imine groups, which was proved by the slight increase of the peak around 1670 cm⁻¹ in the FT-IR spectra (Fig. 3b). In addition, a great loss of formaldehyde in the presence of UV light was clearly observed in Fig. 5, indicating that the APTMS/SiO₂/TiO₂ film is involved in the photocatalytic activity. Thus, the overall degradation efficiency of the APTMS/SiO₂/TiO₂ was enhanced by approximately 8%. Considering the total pore volume and average pore size diameter, it is noticed

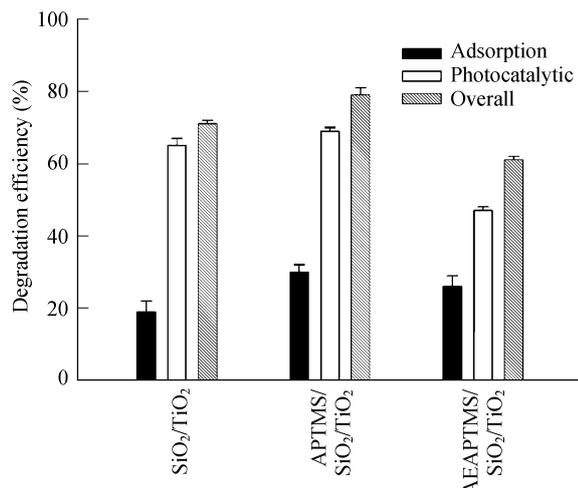


Fig. 6 Formaldehyde adsorption, photocatalytic and overall degradation efficiencies of the photocatalysts.

that the decreasing of these parameters has no influence on the degradation efficiency. From the above discussion, we concluded that the enhancement of formaldehyde degradation efficiency was resulted from the synergetic effect of adsorption and subsequent photocatalytic decomposition.

On the other hand, a synergetic effect of adsorption and subsequent photocatalytic decomposition did not take place when the AEAPTMS was applied into the SiO₂/TiO₂ film. Although the AEAPTMS/SiO₂/TiO₂ film can adsorb formaldehyde on amine sites (Fig. 3c) and enhance adsorption efficiency, it demonstrates the lowest photocatalytic and overall efficiency among the prepared films. This result can be ascribed to the remarkable diminishing of specific surface area and total pore volume.

2.2.3 Repetitive use of the photocatalytic film

The results of repetitive use of the APTMS/SiO₂/TiO₂ film to degrade formaldehyde are shown in Fig. 7. The sample was used repeatedly for seven cycles. The formaldehyde adsorption efficiency of the film over seven uses gave the value of about 16%, slightly down compared to that of the first use (19%). However, the overall degradation efficiency of the film was still as high as the first cycle. It can be seen from this figure that the overall degradation

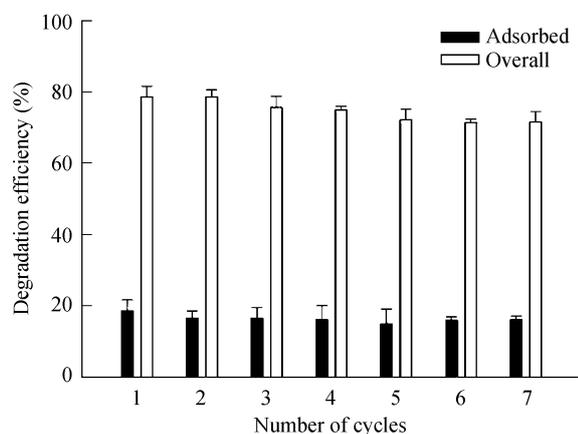


Fig. 7 Effect of repetitive use of the APTMS/SiO₂/TiO₂ film.

efficiency was still higher than 70% after the film was used for seven cycles. It may be suitable for the practical use of ambient air purification.

Moreover, the existence of the amine functional groups after seven times of UV irradiation was verified by FT-IR measurement (data not shown). Some degradation of the amine groups may take place after photocatalytic reaction, resulting in the decreasing of formaldehyde degradation efficiency. However, the degradation of the amine groups may occur at high temperature since the melting point of the amine groups is around 240°C (Sae-ung and Boonamunayvitaya, 2008).

3 Conclusions

Amine-functionalized SiO₂/TiO₂ thin film photocatalysts were prepared using the modified sol-gel method. The calcination temperature of 500°C was considered the most appropriate condition, yielding the highest intensity of anatase peak as shown in the XRD patterns. The average crystallite of the anatase phase was 17.2 nm calcined at 500°C. The FT-IR spectra indicate that the obtained films consisted of the amine groups, TiO₂, and SiO₂. The enhancement of formaldehyde degradation by doping amine functional groups was clarified by the adsorption and the photocatalytic reaction tests. Among the SiO₂/TiO₂, the APTMS/SiO₂/TiO₂ and the AEAPTMS/SiO₂/TiO₂ films, the APTMS/SiO₂/TiO₂ film shows the highest adsorption and photocatalytic efficiencies, and overall degradation. It was found that the APTMS/SiO₂/TiO₂ film with a higher specific surface area (402.4 m²/g) achieves 79% overall degradation efficiency, whereas the AEAPTMS/SiO₂/TiO₂ film with a low specific surface area shows the lowest formaldehyde adsorption, photocatalytic, and overall efficiencies. A higher specific surface area indicates an increased surface adsorption of formaldehyde on an amine adsorption site and higher photocatalytic efficiency. The enhancement of the overall degradation efficiency of the APTMS/SiO₂/TiO₂ film can be attributed to the synergetic effect of adsorption and subsequent photocatalytic decomposition. The formaldehyde degradation efficiency was still higher than 70% after the film was used for seven times.

Acknowledgments

This work was supported by the Royal Golden Jubilee of Thailand Research Fund and the Department of Chemical Engineering at King Mongkut's University of Technology Thonburi.

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