

Preparation of Visible-Light-Responsive TiO₂ Doped Ag Thin Film on PET Plastic for BTEX Treatment

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Abstract: This study aims to develop a visible-light responsive thin film for treatment of gaseous pollutants such as Benzene, Toluene, Ethylbenzene and Xylene (BTEX). Silver (Ag) doped titanium dioxide (Ag/TiO₂) thin films were synthesized via sol-gel method with different Ag contents. The thin film was formed by dip coating on polyethylene terephthalate (PET) substrate before activating with UV lamp. The X-ray diffractograms demonstrated the heterogeneous phase between anatase crystal of TiO₂ and nanosilver. The shift of the wavelength absorption edge to visible light was observed on the composite film due to a decrease of band gap energy. The photocatalytic activity of the thin films was evaluated by the decolorization of 10⁻⁵ M methylene blue (MB) dye and the degradation of 25 mg/l gaseous BTEX. The thin film containing Ag/Ti molar ratio as 0.1 exhibited 80% decolorization of methylene blue and 79, 82, 86, 88% degradation of BTEX under visible light, respectively. Thus, the Ag/TiO₂ thin film coated on PET substrate can be applied for dye treatment as well as indoor air treatment.

Keywords: BTEX, photocatalysis, silver, titanium dioxide, thin film, visible light.

1. Introduction

Nowadays, Thailand is facing serious air pollution problems, especially in urban areas, resulting from rapid industrialization, urbanization and transportation development. At present, the Thai government considers the emission and toxicity of volatile organic compounds (VOCs) as an important environmental issue. VOCs are identified as toxic air pollutants which affect health, such as carcinogenic, mutagenic risks as well as global warming and ozone depletion [1-5]. Volatile aromatic hydrocarbons, especially benzene, toluene, ethylbenzene and xylene (BTEX) are classified as hazard air pollutants accounted in US EPA hazardous air pollutant list [6]. American Conference of Governmental Industrial Hygienists (ACGIH) and World Health Organization (WHO) recommended 5 ppm as the standard maximum level of BTEX. Although the effects of the exposure to VOCs are widely known, there are only a few reports focusing on the appropriate abatement technologies for VOCs control.

Photocatalysis is a technology for completely removing or decomposing many toxic organic pollutants. Among photocatalysts, TiO₂ emerges as an effective substance with relatively low prices, chemical stability and no toxicity [7-9]. However, TiO₂ photocatalyst generates electron and hole pair (e⁻/h⁺) upon irradiation under UV-light ($\lambda < 388$ nm) due to its wide band gap of 3.2 eV [10-13]. In general, UV light has low intensity as compared to other spectrums of solar light. This is a drawback of using TiO₂ for indoor air treatment which is commonly applied under visible light. Thus, there are many studies focusing on production of visible light responsive TiO₂. Some studies reported that decorating TiO₂ with silver nanoparticles (Ag) can enhance the photocatalytic activity of TiO₂ significantly due to increasing the lifetime of e⁻/h⁺ pairs and reducing energy band gap from UV to visible-light region [14-17]. In practice, TiO₂ can be immobilized as a thin film to avoid recovery of TiO₂ after use. The TiO₂ thin film can be coated on various solid substrates such as glass, ceramic tile, and plastics. TiO₂ thin film coated on plastic substrates has many benefits such as simple use, flexibility, light weight and low cost and can be made into a wide range of shapes. Nevertheless, there are few

studies on TiO₂ thin films coated on plastic substrates due to the limitation of their relatively low thermal stability.

This study aims to develop the visible light responsive photocatalyst by doping silver on TiO₂ and then coating on polyethylene terephthalate (PET) as a thin film. The characteristics of the prepared thin films were investigated by various instruments. The photocatalytic reactivity of the thin films was determined by the decolorization of methylene blue dye (MB) and degradation of gaseous BTEX under visible light. The reaction kinetic of those photocatalytic reactions was then proposed.

2. Experimental

2.1 Preparation of TiO₂ and Ag/TiO₂ Sol-gel

Titanium (IV) n-butoxide and silver nitrate (AgNO₃) were used as titanium and silver sources for preparation of TiO₂ and Ag/TiO₂ photocatalysts. The precursory titanium solution was prepared with the molar ratios of Ti(C₄H₉O)₄: 18 C₂H₅OH: 0.5C₅H₈O₂: 2H₂O: 0.2HNO₃ [12] under vigorous stirring for 1 h at room temperature. The silver nitrate solution was prepared by dissolving AgNO₃ with ethanol. The molar ratios of Ag/Ti were varied from 0.01 to 0.2. After that, the mixture was stirred at room temperature for 1 h until completely dissolved. Then, the solution was refluxed at 80°C for 8 h providing as-synthesized TiO₂ and Ag/TiO₂ gel which was ready for coating on plastic substrate.

2.2 Preparation of TiO₂ and Ag/TiO₂ Thin Film

Polyethylene terephthalate (PET) with the dimensions of 1 mm × 20 mm × 30 mm was used as a plastic substrate. PET sheets were cleaned with the mixture of ethanol and deionized water and dried before dipped into TiO₂ and Ag/TiO₂ sol-gel with the automatic dip coater. The constant withdrawing speed was controlled at 10 cm min⁻¹. Afterward, the as-prepared TiO₂ and Ag/TiO₂ thin films were cured with 125 W UV lamp for 20 min to activate the active phase of TiO₂ and improve the adherence between the film and the substrate. The prepared thin film was ready for sample characterizations.

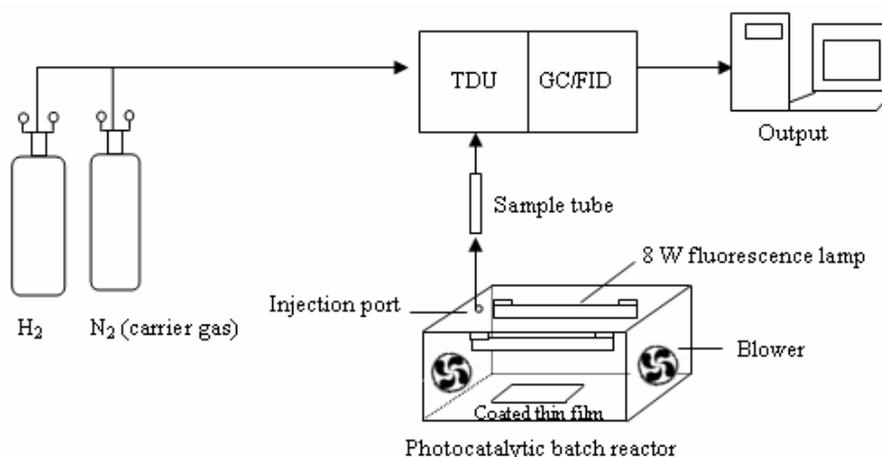


Figure 1. Schematic diagram of experimental procedure.

2.3 Characterizations

The crystallinity of TiO₂ and Ag/TiO₂ thin films deposited on the PET substrates was studied by X-ray diffraction spectrometer (XRD) with the model D8 Advance with Eulerian Cradle Bruker using Cu K α radiation. The accelerating voltage and the emission current were 40kV and 40 mA, respectively. The UV-vis spectra of thin films obtained by UV-vis NIR spectrophotometer (Hitachi U-4100) was used to measure the wavelength absorption of TiO₂ and Ag/TiO₂ thin films in a range of 300-800 nm. The surface morphology of the thin films was examined by using JEOL scanning microscope model JSM-5410. The hydrophilic property of thin film was determined by water contact angle measurement (ASTM F22-02) [18].

2.4 Photodecolorization of MB and its reaction kinetic

The photocatalytic reactivity of TiO₂ and Ag/TiO₂ thin films was determined from the decolorization of 15 ml methylene blue solution (10⁻⁵ M) under fluorescence irradiation using 18 W fluorescence lamp, Philip. The 5 ml of methylene blue solution was sampled every 60 min and analyzed by UV/vis spectrophotometer (Genesys 10-S, Thermo Electron Corporation). After that the analyzed sample was taken back into the methylene blue solution for continuous testing. The reduction of maximum wavelength absorption intensity (λ_{max}) at 664 nm was observed using UV-Vis spectrophotometer. The photodecolorization rate was calculated by plotting $\ln C_0/C$ versus times based on first order reaction according to Eq. (1).

$$\ln \frac{C_0}{C} = kt \quad (1)$$

2.5 Photodegradation of BTEX and its reaction kinetic

The selected TiO₂ and Ag/TiO₂ thin films deposited on PET substrates were used as photocatalysts for treatment of gaseous BTEX (25 ppm). The experiment was tested in a closed chamber reactor (23×32×13 cm). Two 8 watts fluorescence lamp were used as a visible light source. The 0.5 ml of BTEX gas was sampled every 30 min and analyzed by gas chromatography/flame-ionization detector (GC/FID, Shimadzu GC-14B) with injection temperature of 100°C, column temperature of 100°C and detection temperature of 150°C. The schematic diagram of this process is shown in Fig. 1.

3. Results and Discussion

3.1 Characterizations

The XRD diffractograms of TiO₂ and Ag/TiO₂ are presented in Fig. 2. All thin films exhibited the relevant peaks of TiO₂ anatase phase at 2θ equal to 25° (1 0 1), 37° (1 1 0), 48°

(2 0 0), 54° (2 1 1), and 62° (2 0 4). No TiO₂ appeared as rutile phase was observed in all samples. The samples containing Ag showed the characteristic peak of crystal state of Ag⁰ at 2θ equal to 38° (1 1 1), 44° (2 0 0) and 64° (2 2 0). It was seen that the peak intensity of anatase phase of pure TiO₂ was obviously stronger than that of Ag/TiO₂, which may have been due to the formation of TiO₂ crystal having been disturbed by Ag doping. However, the optimal Ag constituent is expected to boost up the photocatalytic reactivity of TiO₂ under visible light. Unlike other studies of calcining titania thin film at high temperature [12,14,19], this study applied UV curing for activating reactive crystals of titania. The XRD results confirmed that high temperature calcinations can be replaced by UV curing which does not cause thermal deformation of plastic substrate.

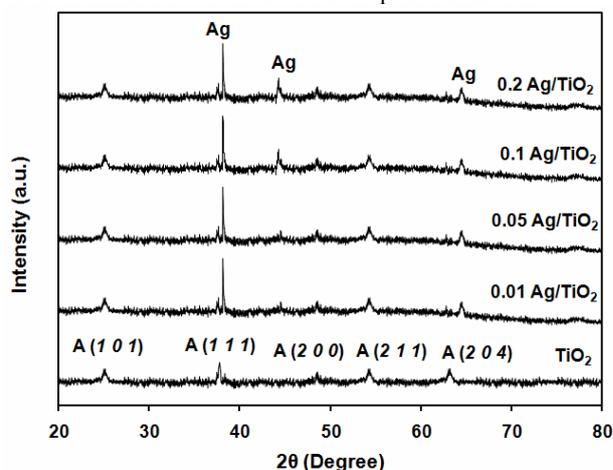


Figure 2. XRD patterns of TiO₂ and Ag/TiO₂ thin films coated on PET.

The optical absorbance spectra of the TiO₂ and Ag/TiO₂ thin films were measured in the region of 300–800 nm by using UV-VIS-NIR spectrometer, as shown in Fig. 3. It is clear that the absorption edge was shifted to visible region due to Ag doping. In other words, Ag doping causes decreasing in band gap energy, which is the minimum energy to promote the excited electron from valence band to conduction band. The more Ag content, the higher wavelength absorption. A similar trend was also observed in Lan Sun et al. (2009) and He et al. (2002). Both studies concluded that the absorption edge shift possibly linked to the interaction of silver and TiO₂ [20-21]. To confirm this result, the band gap energy was calculated by Eq. (2):

$$E = \frac{hc}{\lambda} \quad (2)$$

Where, E = band gap energy, J
 h = Planks constant = 6.626×10^{-34} Js,
 C = Speed of light = 3.0×10^8 m/s,
 λ = Cut-off wavelength, m

The cut-off wavelength was determined by linear extrapolation from the inflection point of the curve to the baseline.

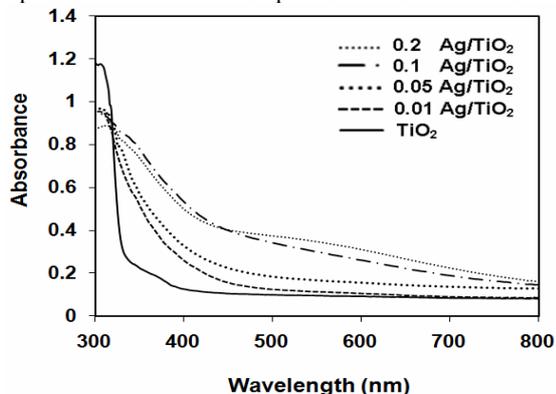


Figure 3. Absorption spectra of TiO_2 and Ag/TiO_2 thin films coated on PET analyzed by UV/VIS/NIR spectrophotometer.

Table 1 shows the calculated band gap energy of all films. The commercial TiO_2 and the prepared TiO_2 films had similar band gap energies of 3.20 eV and 3.19 eV, respectively, while the band gap energies of the Ag/TiO_2 samples decreased from 2.86 to 2.67 eV, inversely proportional to Ag content. This result corresponded to wavelength absorption analysis. Not only by reducing band gap energy, but the Ag dopant was also able to prevent charge recombination between electron-hole pairs. Thus, the photocatalytic reactivity's efficiency improved.

The hydrophilicity of TiO_2 and Ag/TiO_2 thin films were analysed by taking photos and measuring the contact angle of 1 mL water droplet, as shown in Fig. 4. The average water contact angle values of PET, TiO_2 , 0.01 Ag/TiO_2 , 0.05 Ag/TiO_2 , 0.1 Ag/TiO_2 and 0.2 Ag/TiO_2 thin films were 86° , 81° , 78° , 76° , 74° and 87° , respectively. It was observed that the water contact angle of the TiO_2 film was decreased when the film was doped with Ag up to 0.1 mol. The lower water contact angle, the more hydrophilicity. This result indicated that the hydrophilicity of the TiO_2 thin film can be enhanced by Ag doping. However, when 0.2 mol Ag content was incorporate in TiO_2 thin, its hydrophilicity was decreased dramatically due to the excess Ag. This is in agreement with Meng (2009) [23]. The hydrophilic Ag/TiO_2 thin film has advantages on not only photocatalysis but also on self-cleaning process. The hydrophilic film surface can adsorb more water and then generate more active hydroxyl radicals which facilitate hole and electron separation during photocatalytic reaction. Additionally, oxygen anion radicals produced from adsorbed water can accelerate the degradation of adsorbed pollutant on substrate surface.

Table 1. Band gap energy of samples.

Samples	$\lambda_{\text{cut-off}}$ (nm)	Band gap energy (eV)
TiO_2 (commercial)	388	3.20
TiO_2 (this study)	390	3.19
0.01 Ag/TiO_2	434	2.86
0.05 Ag/TiO_2	445	2.79
0.1 Ag/TiO_2	464	2.68
0.2 Ag/TiO_2	466	2.67

*commercial TiO_2 consisted of 80% anatase and 20% rutile [22]

3.2 Photodecolorization of Methylene Blue (MB)

The photocatalytic study of TiO_2 and Ag/TiO_2 thin films with the molar ratios of 0.01, 0.05, 0.10 and 0.20 were

determined by photodecolorization of 10^{-5} M MB solution under fluorescence irradiation, as shown in Fig. 5. MB concentration decreased as a function of irradiation time. The efficiency of photodecolorization decreased gradually and was constant within 14 h. The Ag/TiO_2 thin films provided better decolorization performance than the pure TiO_2 thin film. The maximum decolorization efficiency was 80%, belonging to 0.10 Ag/TiO_2 thin film. The photodecolorization rates were fit well with the first order reaction model as shown in Fig. 6. The calculated reaction rate constants (k) of TiO_2 and Ag/TiO_2 thin films with the molar ratio of 0.01, 0.05, 0.10 and 0.20 were 0.030, 0.059, 0.083, 0.129 and 0.105, [h^{-1}] respectively. Similarly to the decolorization efficiency, the 0.10 Ag/TiO_2 thin film possessed the highest k value. Thus, this study proposed 0.10 mol of Ag as the optimal amount for TiO_2 doping. Less or more than this optimal constituent, the Ag particle can act as a recombination center, resulting in the inhibition of photocatalytic activity of TiO_2 [19]. The decolorization of MB occurs by self-photosensitization under visible light irradiation which provides more electrons in the conduction band of TiO_2 . MB is then converted to cationic radical ($\text{MB}^{+\bullet}$). Subsequently, those electrons can react with adsorbed oxidants (usually O_2) to produce reactive oxygen radicals (e.g. $\text{O}_2^{\bullet-}$, $^{\bullet}\text{OOH}$, $^{\bullet}\text{OH}$) which can degrade the molecules of $\text{MB}^{+\bullet}$.



Figure 4. Hydrophilicity photos of (a) PET, (b) TiO_2 , (c) 0.01 Ag/TiO_2 , (d) 0.05 Ag/TiO_2 , (e) 0.1 Ag/TiO_2 , and (f) 0.2 Ag/TiO_2 thin films.

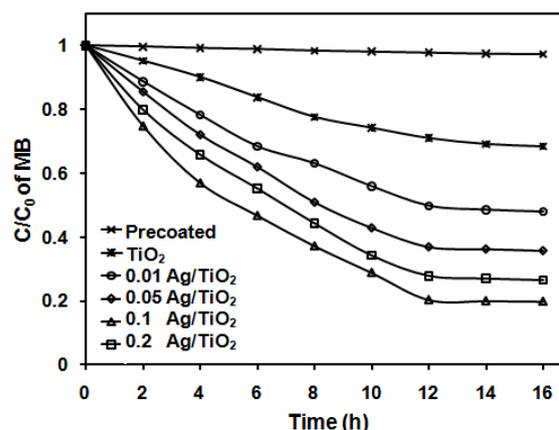


Figure 5. Photodecolorizations of MB dye by TiO_2 and Ag/TiO_2 thin films under fluorescence irradiation.

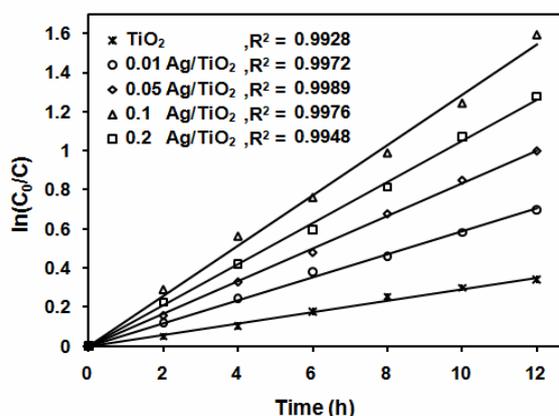


Figure 6. First order reaction rates of MB photodecolorization by TiO_2 and Ag/TiO_2 thin films under fluorescence irradiation.

3.3 Photocatalytic degradation of mixed BTEX gas

The photocatalytic degradation of mixed BTEX was tested on the TiO_2 and 0.1 Ag/ TiO_2 thin films with the initial concentration of 25 mgL^{-1} . Fig. 7(a) shows the results of the photodegradation of gaseous BTEX by pure TiO_2 thin film. This result confirms that the adsorption of BTEX gas only occurred when the light was turned off. The concentration of BTEX gas was constant within 60 min. After the light was turned on, the BTEX gas was adsorbed on the film surface and then slowly degraded during the irradiation phase. The degradation rate of xylene is the highest. Second comes ethylbenzene, followed by toluene and benzene. In comparison to the pure TiO_2 thin film,

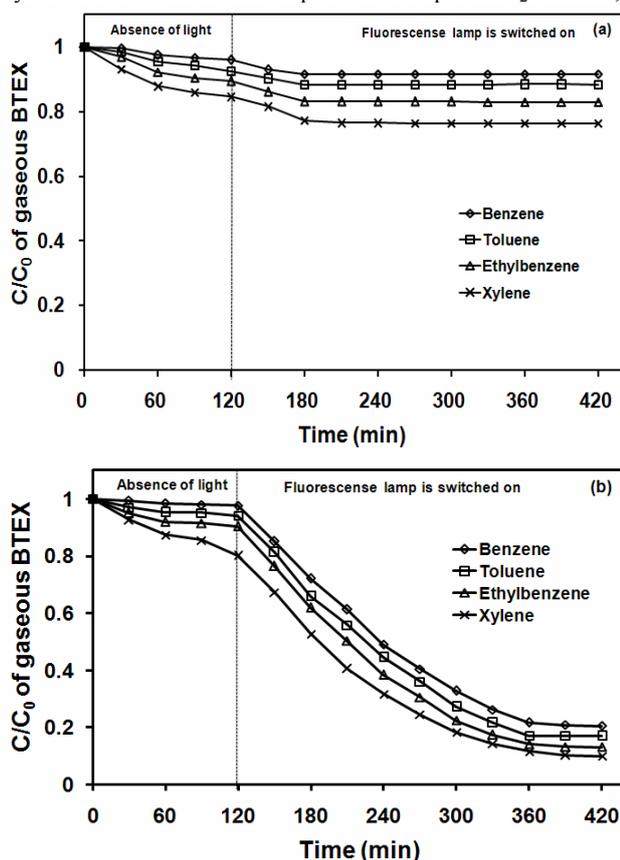


Figure 7. Photodegradation of gaseous BTEX by TiO_2 thin film on and off fluorescence irradiation.

the 0.1 Ag/ TiO_2 thin film provides higher photocatalytic degradation of gaseous BTEX as shown in Fig. 7(b). It is noticed that all gaseous BTEX can be decomposed within 240 min. The degradation efficiencies of gaseous BTEX using 0.1 Ag/ TiO_2 thin film are 79, 82, 86 and 88% for benzene, toluene, ethylbenzene and xylene, respectively. The first order reaction plots of gaseous BTEX degradation by 0.1 Ag/ TiO_2 thin film are shown in Fig. 8. The first order rate constants for degradation of benzene, toluene, ethylbenzene and xylene are 0.0061, 0.0068, 0.0079 and 0.0088 min^{-1} , respectively. It was found that xylene achieved the highest reaction rate of degradation rate and followed by ethylbenzene, toluene and benzene. The removal efficiency of BTEX was relevant to their molecular polarities. Non-polar molecules, like benzene, is hardly to be degraded because benzene is a nucleophile which has low reactivity with OH radicals produced from the photocatalysis of TiO_2 .

Fig. 9(a) and (b) show the surface morphology of TiO_2 and 0.1 Ag/ TiO_2 thin film coated on PET, respectively. With the magnification of 10,000, the surface of TiO_2 thin film looks smoother and more homogeneous than that of 0.1 Ag/ TiO_2 thin film. It is obviously seen that 0.1 Ag/ TiO_2 thin film has some agglomerated particles dispersed on the film surface, which is supposed to be the particle of Ag. The thickness of the TiO_2 and 0.1 Ag/ TiO_2 thin film can be determined from the SEM image ($\times 20,000$) in Fig. 9(c) and (d). The estimated thickness is approximately 85 and 87 nm, respectively which can be theoretically defined as thin film (thickness $< 100 \text{ nm}$) [24].

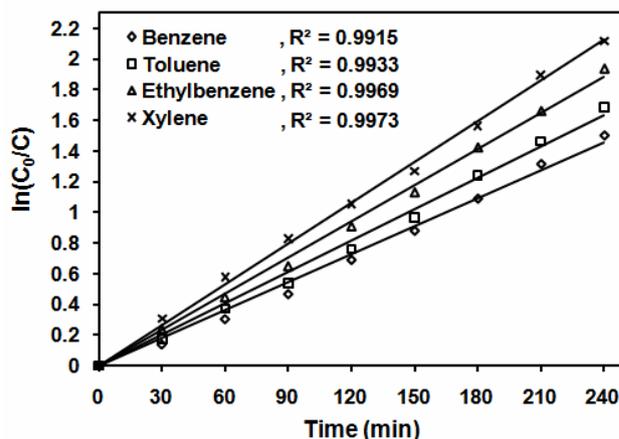


Figure 8. First order reaction rates of gaseous BTEX degradation by 0.1 Ag/ TiO_2 thin films under fluorescence irradiation.

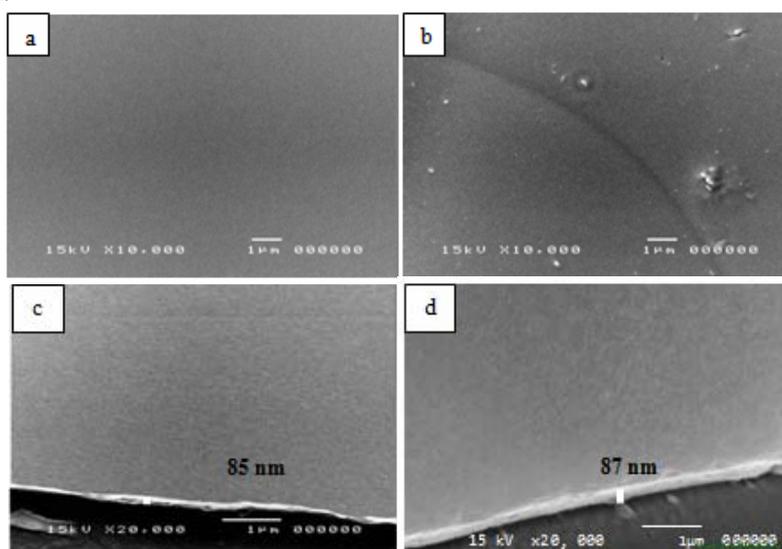


Figure 9. SEM images of thin films coated on PET ($\times 10,000$) (a) TiO_2 , (b) 0.1 Ag/ TiO_2 and ($\times 20,000$) (c) TiO_2 , (d) 0.1 Ag/ TiO_2 .

4. Conclusions

In summary, the characterizations of TiO₂ and Ag/TiO₂ thin film coated on PET substrates revealed that the simple preparation of TiO₂ and Ag/TiO₂ hybrid thin films coated on PET substrates could be achieved by sol-gel method followed by dip coating and UV activation. Doping 0.1 mol of Ag into TiO₂ thin film provides technical advantages on lowering band gap energy, preventing charge recombination and increasing hydrophilicity of the film, which can boost up the photocatalytic reactivity for both MB and gaseous BTEX photodegradation under fluorescence. Therefore, the 0.1 Ag/TiO₂ thin film has the potential to be applied in self-cleaning processes and indoor air pollution treatments.

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