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Novel integrated approach of adsorption and photo-oxidation using Ag–TiO₂/PU for bioaerosol removal under visible light

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HIGHLIGHTS

- The photocatalytic activity of TiO₂ was enhanced by Ag metal doping.
- TiO₂ and Ag-doped TiO₂ were coated on porous polyurethane (PU) using C–Si–O–Ti bonds.
- Increased adsorption ability of the photocatalyst was due to the porosity of the PU.
- Removal of E. coli from an aerosol was only by adsorption with PU and TiO₂/PU.
- Under visible light, E. coli was removed by adsorption and photo-oxidation with Ag–TiO₂/PU.

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ABSTRACT

We investigated a novel approach by synthesizing an integrated material, which could act as both adsorbent and photocatalytic material, for bioaerosol purification under visible light conditions. Ag was used as a dopant agent to enhance photocatalytic activity of TiO₂, leading to high photocatalytic activity of the doped TiO₂ even under visible light. Under visible light, the doped TiO₂ photocatalyst could produce oxy radicals, oxidative agents, that participate in oxidation reactions to decompose important organic components of bacteria, leading to death or removal of bacteria from an aerosol. Adsorption property was integrated into the enhanced TiO₂ photocatalyst by using polyurethane (PU), a honeycomb structure material, as a substrate for coating process of the doped TiO₂. Three materials including pristine PU, TiO₂ coating on PU (TiO₂/PU), and Ag-doped TiO₂ coating on PU (Ag–TiO₂/PU) were used to remove Escherichia coli in an aerosol under visible light. Under dark conditions, the removal capacities of E. coli in the aerosol by PU, TiO₂/PU, and Ag–TiO₂/PU were 1.2 × 10⁵, 2.7 × 10⁵, and 6.2 × 10⁵ (CFU/cm³), respectively. Under visible light irradiation, the removal capacities of E. coli in an aerosol by PU, TiO₂/PU, and Ag–TiO₂/PU were 1.2 × 10⁵, 2.7 × 10⁵, and 1.8 × 10⁶ (CFU/cm³), respectively. The improvement of the removal capacity by TiO₂/PU and Ag–TiO₂/PU, versus PU, is due to adsorption alone and the combination of adsorption plus photocatalytic activity, respectively.

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1. Introduction

A bioaerosol is usually defined as a suspension of airborne particles that contain living organisms or material released from living organisms, including bacteria, fungi, and viruses, and their derivatives, such as endotoxin, glucans, and mycotoxin [1]. Exposure to bioaerosols may be associated with a wide range of adverse health effects to humans including allergies, lung impairments, asthma exacerbation, and infectious diseases [2,3]. Recently, outbreaks of infectious diseases, such as “severe acute respiratory syndrome” (SARS) in 2003 and H1N1 influenza in 2009 have prompted global concerns about airborne biological exposure [4]. Bioaerosol exposure can occur in many different human working situations, including healthcare facilities, schools, office buildings, and restaurants [2]. Thus, it is of great importance to develop powerful bioaerosol control technologies to eliminate adverse health effects of bioaerosols to human.

Over the years, many studies have been conducted to develop bioaerosol control technologies [5–10]. The technologies can be categorized into two main methods: adsorption and disinfection methods. In the adsorption method, filters, such as high efficiency particulate air (HEPA) filter, or adsorbent materials such as carbon nanotubes (CNT) or activated carbon can effectively trap microorganisms to eliminate them from the air stream [5,6]. However, the trapped or adsorbed microorganisms are not inactivated and thus...
could reproduce under certain suitable conditions [11]. In the disinfection methods, typically UV irradiation and UV-induced photocatalysis (e.g., TiO2) are used to decompose organics leading to the death of the microorganism [7,8,12]. However, high-energy consumption and safety issues are the main problems concerning the use of UV irradiation. To overcome the disadvantages of using UV as excitation source, numerous strategies have been carried out to improve the photocatalytic activity of TiO2 as an effective photocatalyst under visible light irradiation [13–16]. Among these strategies, metals or non-metals as doping agents to enhance the photocatalytic activity of TiO2 have been frequently used [17–21]. In our previous studies, we used Ag as a doping and sensitization to enhance the photocatalytic activity of TiO2 deposited on glass fiber [22–24]. The synthesized photocatalysts exhibited high photocatalytic disinfection activity in removing Escherichia coli (E. coli) and Staphylococcus (Staph) in bioaerosols under visible light. However, the glass fiber used as the substrate for the deposition of the enhanced TiO2 has a low surface area and low adsorption ability. Thus, the photocatalytic activity of the enhanced TiO2 was not maximally exhibited. Thus, a more suitable substrate, with properties such as higher adsorption capacity, strong adherence with the enhanced TiO2, non-degradation, and oxidative resistance during the photocatalytic process, is needed to replace the glass fiber substrate for the deposition of the enhanced TiO2.

Polyurethane (PU), a polymer composed of a chain of organic units joined by urethane links, has been used widely in adhesives and coatings of various materials, e.g., textiles, metals, and plastics, because of its good flexibility, elasticity, surface resistance, and age resistance [25,26]. Among many PU types, honeycomb-structure PU has the highest surface area [27]. Thus, honeycomb-structure PU could be a suitable substrate for coating with the enhanced TiO2.

In the present study, Ag was used as a doping agent to enhance the photocatalytic activity of TiO2. Pristine PU was activated to improve its surface properties before using it as a substrate for the coating process with the enhanced TiO2. The combination of the enhanced TiO2 photocatalyst and the PU, having a high surface area, was expected to create a novel approach that could exhibit both adsorption and photo-oxidation properties for bioaerosol purification processes even under visible light, having lower energy consumption and higher safety than UV lights. The characteristics of the PU, TiO2/PU, and Ag–TiO2/PU were compared in this study to investigate the effects of PU, TiO2, and Ag in the integrated material’s properties. Additionally, the removal capacities for E. coli in an aerosol by PU, TiO2/PU, and Ag–TiO2/PU were compared to demonstrate the distinct properties of Ag–TiO2/PU in the bioaerosol purification process. The distinct obtained properties of the synthesized Ag–TiO2/PU could be further applied for disinfection in the healthcare facilities, where the existence of bioaerosol creates significant human health issues.

2. Materials and methods

2.1. Material preparation

2.1.1. Pre-treatment of pristine PU

A honeycomb PU piece (2 × 2 × 3 cm) was ultrasonicated for 20 min in toluene and ethanol to remove residuals on its surface, and then the cleaned PU was dried at 40 °C under vacuum for 2 h. The dried PU was placed in a mixed solution of toluene (50 mL), toluene-2,4-diisocyanate (TDI) (5 mL), and anhydrous triethyamine (2 mL) in a 150-mL flask, and stirred continuously. The solution was then heated at 60 °C for 1 h under nitrogen to introduce isocyanate groups (NCO) on the surface of the PU (reaction 1) [28]. After this procedure, the material was washed repeatedly with toluene and dried under nitrogen gas for 4 h at 60 °C.

\[
\begin{align*}
\text{PU} - \text{N} = \text{C} + & \text{O} - \text{Si} - \text{O} - \text{H} \quad + \quad \text{R}_1 - \text{O} - \text{Ti} - \text{O} - \text{R}_2 \\
\text{OR}_1 & \text{OR}_2 \\
\text{H}_2\text{N} - \text{C}_2\text{H}_4 - & \text{Si} - \text{O} - \text{H} \quad \rightarrow \quad \text{H}_2\text{N} - \text{C}_2\text{H}_4 - & \text{Si} - \text{O} - \text{Ti} - \text{O} - \text{R}_2 \\
\text{OR}_1 & \text{OR}_2
\end{align*}
\]

2.1.2. Silanization of titania

Based on reported methods for the silanization of titania [29], 5 mL tetra isopropyl ortho titinate (TIOIT) was added into a flask containing 100 mL toluene and was stirred. Then, 100 mL of 4% γ-aminopropyl triethoxysilane (APTES) in toluene was then added to the flask and the mixture was stirred continuously for 1 h. The silanized solution was then kept in oven at 40 °C for 4 h to produce a colloidal solution of titanosiloxane. The mechanism of the silanization is illustrated in reaction (2).

2.1.3. Synthesis TiO2/PU

The activated PU, containing NCO groups, was then immersed in the colloidal titanosiloxane solution at 40 °C for 1 h. The chemical reaction of the coating of titanosiloxane onto polyurethane is illustrated in reaction (3).
The titanosiloxane coated on PU was taken out and then slowly washed with distilled water for hydrolysis of the alkyl groups (R₁ and R₂) to produce TiO₂/PU. Then, the TiO₂/PU was dried at 80 °C for 2 h and calcined under nitrogen gas at 200 °C for 2 h to obtain the TiO₂/PU photocatalyst.

2.1.4. Synthesis Ag–TiO₂/PU

A 0.1 M AgNO₃ solution was added slowly drop-wise onto titanosiloxane coated on PU. The addition volume of AgNO₃ was adjusted to synthesize Ag–TiO₂/PU materials with 6 wt% of Ag/TiO₂ in the Ag–TiO₂/PU. The Ag–TiO₂/PU was irradiated with a UV light (60 W) for 5 h to photo-reduce the AgNO₃. Then, the irradiated Ag–TiO₂/PU was annealed under nitrogen at 200 °C for 2 h to produce the Ag–TiO₂/PU photocatalyst.

2.2. Characterization

The surface morphologies of the PU, TiO₂/PU, and Ag–TiO₂/PU were observed with a Hitachi S-4700 scanning electron microscope (SEM). An energy dispersive X-ray spectrometer was connected to the SEM to determine X-ray mapping images of Ag and Ti in the Ag–TiO₂/PU. Fourier-transform infrared spectroscopy (FTIR) spectra of the pristine PU, activated PU, TiO₂/PU, and Ag–TiO₂/PU materials were obtained by a Nicolet 380 spectrometer. The surface area (S_BET) of the PU, TiO₂/PU, and Ag–TiO₂/PU materials was determined using the N₂-BET isotherm. The UV–vis absorption spectra of shredded PU, TiO₂/PU, and Ag–TiO₂/PU were measured using an Evolution 300 spectrophotometer (UV-1700 Shimadzu). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Fisher Kx model to determine the chemical composition of the synthesized materials.

2.3. E. coli removal experiments

An E. coli Top10 source was obtained from the environmental bioengineering laboratory at the University of Ulsan, Korea. E. coli were cultivated in 400 mL Luria-Bertani (LB) medium containing tryptone (10 g/L), yeast extract (5 g/L), and NaCl (5 g/L). The LB medium was kept at 37 °C for 12 h on a rotary shaker to culture the E. coli. Then, 400 mL of cultivated E. coli was centrifuged (500 rpm, 3 min) to get 200 mL concentrated E. coli for use as a solution source to create air containing E. coli for the removal experiments.

PU, TiO₂/PU, and Ag–TiO₂/PU were used as photocatalyst and adsorbent materials for E. coli removal tests under both dark and visible light conditions. An experimental model was designed to test the E. coli removal efficiency using the PU, TiO₂/PU, and Ag–TiO₂/PU materials (Fig. 1).

Air containing E. coli from source (1) was passed through pipe 1 and pipe 2, which have similar volumes, by the suction force generated from pumps (2) and (8). During each experiment, flow rates of two pumps (2) and (8) were kept at 2 L/min. Thus, the E. coli amount passing through pipe 1 and pipe 2 were assumed to be almost the same. The E. coli passing through pipe 1, which were absorbed into Tris-buffered saline (TBS) solution (3), could be considered as the input E. coli amount of the E. coli removal experiment. The E. coli in pipe 2 were oriented to pass through reaction chamber (5), which was entirely in an isolated cask. The top and bottom of the reaction chamber were made of quartz so that the experimental light could easily reach the materials put inside the reaction chamber. The isolated cask has a dark cover to prevent outside light reaching into the cask. The visible light used to irradiate for the photocatalytic activity experiment was from two 20 W white light bulbs (EFTR 20EX-D, Kumho Co., Ltd.), placed at the top and bottom of the isolated cask. The distance between the light source and the photocatalyst was 20 cm. The power density in the isolated cask was 0.05 W/cm². The remaining E. coli passing through the reaction chamber were absorbed into solution (9) to determine the E. coli 'output' amount from the removal experiment. The E. coli removal capacities using PU, TiO₂/PU, and Ag–TiO₂/PU as photocatalytic and adsorbent materials were calculated with Eq. (1):

\[
\text{E. coli removal capacity (CFU/cm}^3\text{) = } \frac{\text{Input E. coli – Output E. coli}}{\text{Material volume (12 cm}^3\text{)}}
\]

The input E. coli was adjusted by altering the reaction time, which is similar to the working time of pumps, to determine maximum E. coli removal capacity by the PU, TiO₂/PU, and Ag–TiO₂/PU materials under dark and visible light conditions. Control experiments were also performed to confirm that the E. coli in pipe 1 is considered the E. coli input amount for the removal experiment. In the control experiments, the reaction chamber was kept empty (with no photocatalytic or adsorbent material) and other procedures were similar to the E. coli removal experiments.

3. Results and discussion

3.1. Physicochemical properties

3.1.1. FTIR analysis

The FTIR spectra confirmed the presence of urethane groups (–NH–CO–O–), containing N–H, C–N, C=O, and C–O bonds, in the pristine PU (Fig. 2 [30,31]). Compared with the FTIR spectra of the pristine PU, the FTIR result of the activated PU showed a decrease in the adsorption peaks of N–H, C–N, C=O, and C–O bonds.

Fig. 1. Schematic diagram of the E. coli removal experiment.
and the new occurrence of an isocyanate (–N=C=O) peak (Fig. 2) [32]. This indicated that the urethane group in pristine PU had been converted into an isocyanate group in the activated PU. The chemical reaction to introduce isocyanate group onto PU surface is shown in Fig. 3.

Fig. 4 shows the FTIR analysis results of the activated PU, TiO2/PU, and Ag–TiO2/PU. The adsorption peaks of Ti–O–Ti were also observed at 670 and 570 cm⁻¹ in the FTIR spectra of TiO2/PU and Ag–TiO2/PU, respectively [33]. These results indicated that TiO2 was formed on the PU surface. In the FTIR spectra of the TiO2/PU and Ag–TiO2/PU, the adsorption peaks of Si–O–Si, corresponding to the occurrence of SiO2 on the surface of the PU, were also observed. Also, the adsorption peaks indicating C–Si and Si–O–Ti bonds were seen at 1240 cm⁻¹ and 970 cm⁻¹, respectively (Fig. 4) [34,35]. These peaks indicated that the silanization process of titania to produce titanosiloxane occurred successfully based on the reaction between tetra isopropyl ortho titanate and γ-aminopropyl triethoxysilane (reaction 1). Compared with the FTIR result of the activated PU, the FTIR peaks of TiO2/PU and Ag–TiO2/PU showed strong increases in the N–H and C=O adsorption peaks, which are typical peaks of the urea group (–NH–CO–NH–) [36]. Additionally, the isocyanate peaks in the TiO2/PU and Ag–TiO2/PU greatly decreased, compared with the activated PU. This indicates that urea linkage was formed successfully based on the reaction between the isocyanate groups in the activated PU and the amine groups of the titanosiloxane (reaction 2). Thus, TiO2 was deposited successfully on the surface of PU in both TiO2/PU and Ag–TiO2/PU based on bridge role of silicone, which bonds TiO2 and PU by a C–Si–O–Ti link.

3.1.2. XPS analysis

Fig. 5 shows the high-resolution XPS spectra of the Ag 3d peaks of Ag in Ag–TiO2/PU. Gaussian multi-peak shapes were applied to fit the Ag 3d peaks to determine the state of the silver in the Ag–TiO2/PU. The spectrum analysis indicated that the states of the Ag in Ag–TiO2/PU were Ag⁰ and Ag⁺. The peaks observed at 374.1 and 368.1 eV are characteristic peaks of Ag metallic (Ag⁰) [37]. The formation of Ag⁰ could be due to photo-reduction and thermal decomposition of AgNO3 during the irradiation and calcination processes [17,22]. The peaks observed at 373.3 and 367.3 eV are characteristic peaks of Ag⁺ [38]. Atla et al. reported that Ag⁺ ions, which were adsorbed on TiO2 surface, could be anchored to the external-surface of TiO2 by Ti–O–Ag bonds via photo-deposition processes [17,39]. Because the peak intensity and peak area of Ag⁰ peaks were much higher than those of Ag⁺ peaks, the concentration of Ag⁰ in Ag–TiO2/PU was much higher than that of Ag⁺ (Fig. 5).

Fig. 6 shows the high-resolution XPS spectra of Si 2p peaks of silicon in TiO2/PU and Ag–TiO2/PU. Based on the Gaussian multi-peak shapes, the Si 2p peaks of silicon in TiO2/PU consisted of three different peaks, at 103.8, 102.7 and 101.9 eV, which were attributed to the binding energy of Si–O–Si, Si–O–Ti, and C–Si–O bonds, respectively [40,41]. The peak of Si–O–Si bond was identified by the occurrence of SiO2 layer in TiO2/PU. The occurrence of Si–O–Ti and C–Si–O peaks confirmed the conclusion, from the FTIR analysis, that silicon acted as bridge element to bond TiO2 with the polyurethane substrate. Thus, the surface chemical composition of TiO2/PU could contain three main layers: a TiO2 layer, a SiO2 layer, and the PU substrate. The TiO2 layer could bond to PU substrate by C–Si–O–Ti links (Fig. 7). The Si 2p peaks of silicon in Ag–TiO2/PU also consisted of three different peaks – at 103.7, 102.4, and 101.9 eV – which were attributed to the binding energy of Si 2p in Si–O–Si, Si–O–Ti, and C–Si–O bonds, respectively. The peak position of the C–Si–O bond was identified by the occurrence of SiO2 layer in TiO2/PU. The occurrence of Si–O–Ti and C–Si–O peaks confirmed the conclusion, from the FTIR analysis, that silicon acted as bridge element to bond TiO2 with the polyurethane substrate. Thus, the surface chemical composition of TiO2/PU could contain three main layers: a TiO2 layer, a SiO2 layer, and the PU substrate. The TiO2 layer could bond to PU substrate by C–Si–O–Ti links (Fig. 7). The Si 2p peaks of silicon in Ag–TiO2/PU also consisted of three different peaks – at 103.7, 102.4, and 101.9 eV – which were attributed to the binding energy of Si 2p in Si–O–Si, Si–O–Ti, and C–Si–O bonds, respectively. The peak position of the C–Si–O bond was shifted 0.1 and 0.3 (eV) into the lower binding energy region, respectively (Fig. 6). These peak shifts could be due to Ag particles deposited on
the surface of the TiO₂ layer [22]. The electron clouds of silicon in Si–O–Si and Si–O–Ti bonds could be stretched due to plasmon resonance of Ag particles, leading to the shift of their typical peaks into the lower binding energy region. On the other hand, the plasmon resonance of Ag may not be strong enough to stretch the electron cloud of silicon in the C–Si–O bond because the Ag particles are too far from the bond (Fig. 7).

3.1.3. Surface morphology and surface area

Fig. 8A shows that the PU exhibited a honeycomb mesoporous structure with a pore size ranging from 100 to 300 μm. In the TiO₂/PU, TiO₂ was uniformly coated on the PU surface (Fig. 8B). In the Ag–TiO₂/PU, small Ag particles were well dispersed and deposited on the TiO₂ layer (Fig. 8C). The mix mapping results of Ag and Ti elements of Ag–TiO₂/PU, as shown in Fig. 8D, indicate that Ti and Ag were almost evenly deposited over the whole PU frame. This could lead to a distinct photocatalytic activity of Ag–TiO₂/PU for bioaerosol removal.

The BET surface areas of the PU, TiO₂/PU, and Ag–TiO₂/PU were 30.46, 110.93, and 186.56 m²/g, respectively. These results indicated that the BET surface areas of TiO₂ and Ag–TiO₂ photocatalysts were successfully enhanced by using honeycomb PU as a substrate. The BET surface area of the synthesized TiO₂/PU is not only greatly higher than that of the PU but also much higher than the surface area of commercial TiO₂ powder, which is approximately 60 m²/g [42]. This result indicates that the immobilization process of TiO₂ onto surface of PU by C–Si–O–Ti bond greatly increased the surface area of TiO₂. Because of deposition of small Ag particles on TiO₂ layer, the Ag–TiO₂/PU exhibited the highest BET surface area.

3.1.4. UV–vis absorption spectra

Fig. 9 shows the UV–vis adsorption spectra of PU, TiO₂/PU, and Ag–TiO₂/PU in the range 300–700 nm. As compared with TiO₂/PU and Ag–TiO₂/PU, PU did not exhibit noticeable light absorption ability in the visible range. The TiO₂/PU seems to have inherited the light absorption properties of TiO₂, with the absorption edge around 370 nm [43]. Compared with TiO₂/PU, the Ag–TiO₂/PU exhibited a red shift of the absorption edge. In the visible region (400–700 nm), the light adsorption ability of Ag–TiO₂/PU was also much higher than that of TiO₂/PU. The result is explained by light absorption characteristic of the Ag particles, which were deposited on the TiO₂ surface [18,39]. The plasmon resonance of Ag could excite electrons to move out of the valence band of TiO₂. Thus, the electrons in the valence band of TiO₂ could be readily generated under certain excitation conditions, leading to the red shift of the absorption edge of the Ag–TiO₂/PU. Ag could act as an intermediate agent to transfer excited electrons from the valence band to the conduction band of TiO₂ [43]. Additionally, Ag particles could also act as electron sinks to prevent the recombination of the excited electrons in the conduction band and holes in the valence band of TiO₂ [22]. Therefore, the visible light absorption...
of the Ag–TiO₂/PU was significantly improved by the Ag particles. Because Ag–TiO₂/PU is easily excited by visible light and prevented from recombination of the electrons and holes, the photocatalytic activity is expected to increase even under visible-light irradiation.

3.2. E. coli removal

According to the results of control experiments (data not shown), the E. coli absorbed into solution (5) were similar to those in solution (11). This study assumed that the E. coli amounts passing through pipe 1 and pipe 2, shown in Fig. 1, were similar. This was confirmed by checking the count of the E. coli that passed through both pipes. The E. coli absorbed into the TBS solution (5) is considered as the E. coli input of the E. coli removal experiment. When the input E. coli was adjusted ranging from 500 to 5 × 10⁷ (CFU), the removal capacities of E. coli in aerosol by PU, TiO₂/PU and Ag–TiO₂/PU under dark and visible light conditions are shown in Fig. 10. It is clear that the E. coli removal capacities also increased with increasing E. coli input (Fig. 10). However, when the input E. coli increased to a certain degree, the E. coli removal capacities seemed to become stable. Table 1 shows maximum E. coli removal capacities under given experimental conditions (input E. coli, room temperature and humidity) by PU, TiO₂/PU, and Ag–TiO₂/PU under dark and visible light conditions.

3.2.1. E. coli removal under dark conditions

The maximum E. coli removal capacities by PU, TiO₂/PU, and Ag–TiO₂/PU under dark condition were 1.2 × 10⁵, 2.7 × 10⁵ (2.25

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**Fig. 7.** The surface chemical composition of the TiO₂/PU and Ag–TiO₂/PU.

**Fig. 8.** SEM of activated PU (A), TiO₂/PU (B), Ag–TiO₂/PU (C) and mapping of Ag and Ti in Ag–TiO₂/PU (D).

**Fig. 9.** UV–vis absorption spectra of PU, TiO₂/PU, and Ag–TiO₂/PU.
times of that by PU), and $6.2 \times 10^5$ (5.17 times of that by PU) CFU/cm$^3$, respectively. Under dark conditions, E. coli removal could be mainly attributed to the adsorption abilities of the PU, TiO$_2$/PU, and Ag–TiO$_2$/PU adsorbents. The PU, TiO$_2$/PU, and Ag–TiO$_2$/PU could act as adsorbents, leading to removal of E. coli from the aerosol. Such adsorption is based on interactions between the cells and the adsorbent surface including van der Waals forces, electrostatic and hydrophobic interactions [44]. These interactions depend greatly on the characteristics of the adsorbent surface, such as pore structure, surface area, roughness, surface charge, chemical structure, and hydrophobicity [44,45]. It is clear that the maximum E. coli removal capacity by the PU, TiO$_2$/PU, and Ag–TiO$_2$/PU were positively related to the specific surface area of the adsorbents. The identified specific surface areas of PU, TiO$_2$/PU, and Ag–TiO$_2$/PU were 30.46, 110.93, and 186.56 m$^2$/g, respectively. These results indicate that specific surface area would be a major factor contributing to the adsorption capacity of bacteria by the synthesized materials. However, the bacterial adsorption capacities were not exactly in proportion with the specific surface area of adsorbents, because of differences in the surface properties of the different adsorbents. Different surface properties of the adsorbents, such as the hydrophobicity of the PU, positive charged surface of the TiO$_2$/PU and Ag–TiO$_2$/PU, and the surface roughness of the Ag–TiO$_2$/PU can lead to different interactions between bacterial cells and adsorbent surface, resulting in different bacterial adsorption capacities by different adsorbents. Tijing et al. reported that PU was a hydrophobic material [46]. Thus, a hydrophobic interaction between PU and bacteria could also contribute to the bacterial adsorption capacity of PU [47]. Several previous studies have reported that materials containing metal, TiO$_2$, and SiO$_2$ on the surface could have numerous positive charges on their surface [44,46]. Thus, the electrostatic interactions between the negative charges on the cell wall of E. coli and the positive charges on the surface of TiO$_2$/PU or Ag–TiO$_2$/PU could also contribute to the bacterial adsorption capacity of the adsorbents. In addition, the surface roughness of an adsorbent could promote bacterial adhesion, and thus the surface roughness of Ag–TiO$_2$/PU (Fig. 8C) could be another factor contributing to the increase in E. coli adsorption capacity of the material [48].

3.2.2. E. coli removal under visible light conditions

The maximum E. coli removal capacities by PU, TiO$_2$/PU, and Ag–TiO$_2$/PU under visible light conditions were $1.2 \times 10^5$, $2.8 \times 10^5$ (2.33 times that by PU), and $1.8 \times 10^6$ (15.0 times that

![Fig. 10. E. coli removal capacities by PU under dark (A) and visible light (B), TiO$_2$/PU under dark (C) and visible light (D), Ag–TiO$_2$/PU under dark (E) and visible light (F).](image-url)
by PU) CFU/cm³, respectively. The maximum E. coli removal capacity by PU and TiO₂/PU under visible light condition did not exhibit any significant increase as compared with those under dark conditions. These results indicated that the PU and TiO₂/PU exhibited only or almost only an adsorption capability to remove E. coli from the aerosol under visible light conditions. Because PU is non-photocatalytic and an inert material in visible light, it exhibits only adsorption properties to remove E. coli from the aerosol under visible light. Although TiO₂/PU does inhibit the photocatalytic properties of TiO₂, the band gap energy of TiO₂ is approximately 3.2 eV, which requires irradiation with a wavelength shorter than 388 nm to excite electrons for photocatalytic processes. Thus, visible light, which has wavelengths in range from 400 to 700 nm is not a sufficiently energetic light source to allow photocatalytic processes of TiO₂. Thus, the visible light irradiation showed no noticeable effect on the E. coli removal capacity beyond its adsorption removal capacity for TiO₂/PU.

The maximum E. coli removal capacity by Ag–TiO₂/PU under visible light conditions was approximately three times higher than that under dark conditions. This increase could be due to the role of the Ag dopant that could enhance the photocatalytic activity of the TiO₂. As explained in Section 3.1.4, the Ag dopant could enhance electron–hole separation efficiency and separation capacity of TiO₂. When the Ag–TiO₂/PU was irradiated even by visible light, the electron–hole pairs could be generated easily. Then, the photo-generated electron–hole pairs of Ag–TiO₂/PU could react with water and molecular oxygen adsorbed on the material surface, leading to the formation of oxy radicals, such as hydroxyl radicals (OH) and superoxide radical anions (O₂⁻), which are highly reactive. The generated oxy radicals could cause destruction of the outer cell wall and unsaturated phospholipids in the cell membrane of the bacteria, leading to significant disorder in cell permeability and decomposition of the cell walls, resulting in bacterial death [49]. Chen et al. reported that the oxy radicals could also oxidize intracellular coenzyme A (CoA), leading to inhibiting cell respiration and subsequently causing the death of the bacteria [8]. The generated oxy radicals could also decompose the nucleic acids, and affect the replication of DNA and many cellular functions, resulting in bacterial death [50]. Thus, the Ag–TiO₂/PU could exhibit photocatalytic activity even under visible light to generate highly oxidative radicals, which could participate in oxidation processes to decompose important organic components of bacteria, resulting in death or removal of the bacteria from the aerosol [22]. Jin et al. reported that Ag ions did not have obvious toxicity to bacteria under dark conditions [51]. However, Ag ions could exhibit a significant bacterial disinfection effect under light conditions. The Ag ion can interact with the thiol groups of L-cysteine residues inside of the cell to affect many key biochemical processes, resulting in bacterial death.

4. Conclusions

The synthesized PU and TiO₂/PU materials only exhibited adsorption ability to remove E. coli from an aerosol under both dark and visible light conditions. This bacterial adsorption capacity could be mainly attributed to interactions between the bacterial cells and the adsorbent surface, involving van der Waals, electrostatic and hydrophobic interactions. The specific surface area of the PU and TiO₂/PU was the main factor affecting their maximum E. coli adsorption capacity.

We first synthesized Ag–TiO₂/PU, a highly adsorbent and photocatalytic material, using Ag as a doping agent to enhance the photocatalytic activity of TiO₂/PU. As compared with PU and TiO₂/PU, the Ag–TiO₂/PU exhibited much improved removal capacity (15 and 3 times, respectively) of E. coli in the aerosol. This was partly because the Ag–TiO₂/PU had the highest specific surface area and surface roughness. The main reason for the greatly improved E. coli removal capacity by Ag–TiO₂/PU was Ag dopant effect. Thus, this study identified that the Ag–TiO₂/PU showed greatly improved photocatalytic activity even under visible light to produce oxy radicals, which could decompose vital organic components of bacteria, leading to death or removal of bacterial from the aerosol. Thus, Ag–TiO₂/PU could be used effectively and economically for both adsorption and photo-oxidation removal of E. coli from an aerosol even under visible light irradiation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2015.04.055.

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Table 1

| Materials Conditions | PU | TiO₂/PU | Ag–TiO₂/PU |
|----------------------|----|---------|------------|
|                      | Dark | Vis-light | Dark | Vis-light | Dark | Vis-light |
| Maximum removal (CFU/cm³) | 1.2 × 10⁶ | 1.2 × 10⁶ | 2.7 × 10⁶ | 2.8 × 10⁶ | 6.2 × 10⁶ | 1.8 × 10⁶ |

Note: The synthesized PU and TiO₂/PU materials only exhibited adsorption ability to remove E. coli from an aerosol under both dark and visible light conditions. This bacterial adsorption capacity could be mainly attributed to interactions between the bacterial cells and the adsorbent surface, involving van der Waals, electrostatic and hydrophobic interactions. The specific surface area of the PU and TiO₂/PU was the main factor affecting their maximum E. coli adsorption capacity.
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