Since January 2020 Elsevier has created a COVID-19 resource centre with free information in English and Mandarin on the novel coronavirus COVID-19. The COVID-19 resource centre is hosted on Elsevier Connect, the company's public news and information website.

Elsevier hereby grants permission to make all its COVID-19-related research that is available on the COVID-19 resource centre - including this research content - immediately available in PubMed Central and other publicly funded repositories, such as the WHO COVID database with rights for unrestricted research re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for free by Elsevier for as long as the COVID-19 resource centre remains active.
Advanced removal of *C. famata* in bioaerosols by simultaneous adsorption and photocatalytic oxidation of Cu-doped TiO$_2$/PU under visible irradiation

Thanh-Dong Pham, Byeong-Kyu Lee

Department of Civil and Environmental Engineering, University of Ulsan, Daehakro 93, Namgu, Ulsan 680-749, Republic of Korea

**Highlights**

- Cu doping was used to enhance the photocatalytic activity of TiO$_2$ photocatalyst.
- Titania was deposited on porous polyurethane by using the bridging role of silicon.
- Use of the porous polyurethane increased the adsorption ability of the photocatalyst.
- Both PU and TiO$_2$/PU removed *C. famata* from aerosols under visible light via adsorption.
- Under visible light, Cu–TiO$_2$/PU removed *C. famata* via both adsorption and photo-oxidization.

**Abstract**

Polyurethane (PU), a honeycomb structure material, was used as a substrate onto which TiO$_2$ and Cu–TiO$_2$ were deposited in order to integrate the adsorption property to the photocatalysts. TiO$_2$ deposited on PU (TiO$_2$/PU) and Cu-doped TiO$_2$ deposited on PU (Cu–TiO$_2$/PU) were synthesized and applied to the removal of *Candida famata* (*C. famata*), a frequently encountered airborne yeast. The removal capacities of *C. famata* by PU, TiO$_2$/PU, and Cu–TiO$_2$/PU were $1.5 \times 10^5$, $3.2 \times 10^5$, and $6.9 \times 10^6$ (CFU/cm$^3$) under dark condition and $1.5 \times 10^5$, $3.3 \times 10^5$, and $1.8 \times 10^6$ (CFU/cm$^3$) under visible light irradiation, respectively. PU and TiO$_2$/PU seemed to exhibit only an adsorption ability for removing *C. famata* in aerosols under both dark and visible light. The *C. famata* removal capacity of Cu–TiO$_2$/PU under visible light was increased 2.6-fold compared to that under dark condition. This significant increase was attributed to the Cu dopant, which enhanced the electron–hole separation efficiency and capacity of TiO$_2$, resulting in the high photocatalytic activity of Cu–TiO$_2$/PU under visible light.

**1. Introduction**

Exposure to a wide class of bioaerosols, containing microorganisms (bacteria, fungi, viruses, pollens), their fragments and the by-products of their metabolism, can result in various adverse effects to human health including infectious diseases, respiratory pathologies and allergic reactions [1,2]. Such adverse effects have been increasing recently with examples such as severe acute respiratory syndrome (SARS) in 2003 and influenza (H1N1) in 2009 [3]. In addition, the population and resistance of species in bioaerosols or biohazards have also been increasing rapidly, possibly due to...
increased environmental pollution originated from human activities. Therefore, numerous studies have been conducted to develop powerful technologies and devices for biohazard control [3–6]. Traditional control methods to eliminate the microorganisms in the aerosol environment include uses of activated charcoal filters and high efficiency particulate air (HEPA) filters with or without UV radiation [4]. Electrostatic field and ozonizers have also been used to inactivate airborne microorganisms [3]. However, organic matter, both dust and microorganism fractions, tends to accumulate in the filters, which in turn become an emission source of microorganisms under certain conditions such as suitable temperature, humidity and presence of nutrients. The disadvantages of using UV irradiation, electrostatic field and ozonizers include high operating costs, high energy consumption, safety issues and the generation of toxic by-products. Therefore, the photocatalytic process combined with adsorption power has been proposed as a potential technology to overcome these limitations. In addition, visible light is progressively replacing UV light in many applications [7,8]. Thus, the study continuously utilizes visible light as a potential source to initiate for photocatalysis processes.

Photocatalysts can inactivate a wide range of harmful microorganisms such as viruses, bacteria, fungi and algae, as well as cancer cells or protozoa [9]. TiO₂ has been widely used as a photocatalyst for the disinfection of aqueous liquid phases due to its superior characteristics such as exceptional optical and electronic properties, chemical stability, non-toxicity and low cost [10–18]. Recently, the removal of biological airborne pollutants using TiO₂ as photocatalyst has also been reported [19]. As the provided energy is higher than the band gap energy of TiO₂, electron–hole pairs can be generated on the surface of the photocatalyst and the resulting electrons and holes can react with water and/or oxygen to produce oxidative species, including hydroxyl radical and superoxide radicals [19]. These oxidative species, which are all highly reactive, can then participate in the oxidation reactions to decompose organic compounds contained in microorganisms absorbed on the photocatalyst surface, leading to the mineralization of the microorganism’s cells or their death [9]. However, the practical use of TiO₂ has been limited by the following three major issues: (1) low photocatalytic efficiency due to fast recombination of the photogenerated electrons and holes of TiO₂ [22]; Cu doping also decreased the band gap energy of TiO₂ and hence the energy requirement for electron–hole pair generation of TiO₂. Then, the Cu-doped TiO₂ was deposited on glass fiber to overcome the disadvantages of TiO₂ powder. The Cu-doped TiO₂/glass fiber exhibited high photocatalytic disinfection activity against Escherichia coli in bioaerosol even under visible light irradiation [22]. However, the synthesized Cu-doped TiO₂/glass fiber photocatalysts mainly exhibited photocatalytic oxidation properties to inactivate bacteria. The low adsorption properties of the photocatalyst were attributed to the low surface area of the glass fiber substrate. Therefore, in the present study, we investigate a new high surface area substrate onto which the Cu-doped TiO₂ is deposited in order to integrate the adsorption properties of the photocatalyst. Polyurethane (PU) foam, a polymer composed of a chain of organic units joined by urethane links with a honeycomb structure and high surface area, could be a suitable substrate for the deposition of Cu-doped TiO₂ [23,24]. The resulting Cu–TiO₂/PU photocatalyst is expected to exhibit high bioaerosol removal efficiency by combining both adsorption and photocatalytic oxidation activities. In our previous study, the Cu-doped TiO₂/glass fiber exhibited a significant disinfection activity to remove E. coli in bioaerosols. However, the wide diversity of the bioaerosol world is exemplified by the different structure of each strain, and hence different resistance to photocatalytic oxidation and adsorption. The present study, therefore, examines the bioaerosol removal efficiency of Cu–TiO₂/PU, which could be fabricated as a dual adsorption/photocatalytic material, against Candida famata, a frequently encountered airborne yeast, as a new microorganism target [25]. It is hoped that the experimental results will lead to the adsorption and photocatalytic purification of bioaerosols under visible light irradiation.

2. Experimental and analysis

2.1. Material preparation and characterization

Before the TiO₂ photocatalyst was deposited on the PU substrate, pristine PU was activated to introduce isocyanate groups (NCO) on its surface. Silicon in γ-aminopropyl triethoxysilane (APTES) was used as a bridge element to silanize titanium by creating a Si–O–Ti bond. Then, TiO₂ was deposited on the PU surface, based on the urea bond formed from the reaction of the isocyanate group in the activated PU with the amino group (NH₂) in the silanized titanium. Scheme 1 shows the four-step material preparation

![Scheme 1. Material preparation processes.](image)
processes: pre-treatment of pristine PU, silanization process, coating TiO₂ on activated PU and synthesis of Cu–TiO₂/PU.

2.1.1. Pre-treatment of pristine PU

Pristine honeycomb PU foams (2 cm × 2 cm × 3 cm) were cleaned under strong ultrasonication condition for 20 min each in toluene and ethanol solutions, dried at 40 °C under vacuum for 2 h and then placed in a mixed solution of toluene (50 mL), toluene-2,4-diisocyanate (TDI) (5 mL), and anhydrous triethylamine (2 mL) in a 150 mL flask. The solution containing PU was stirred continuously and heated to 60 °C for 1 h under nitrogen as a protective gas in order to introduce isocyanate groups (NCO) on the surface of the PU [26]. After this procedure, the PU containing isocyanate groups (activated PU) was washed repeatedly with toluene and dried in nitrogen gas at 60 °C for 4 h.

2.1.2. Silanization process

To prepare for the silanization titanium, 5 mL titanium tetraisopropoxide (TTIP) solution was slowly dropped into a flask containing 100 mL toluene under stirring condition [27]. Then, 100 mL toluene containing 4% APTES was added to the flask. The mixture flask was stirred continuously for 1 h and then kept in an oven at 40 °C for 4 h to silanize the titanium. The final product was a colloid solution of titanosiloxane.

2.1.3. TiO₂ coating process

The activated PU was immersed in the titanosiloxane solution at 40 °C for 1 h, after which the TiO₂ coated on PU was slowly washed with 100 mL distilled water, dried at 80 °C for 2 h, and calcined in protective nitrogen gas at 200 °C for 2 h to obtain the TiO₂/PU photocatalysts.

2.1.4. Synthesis Cu–TiO₂/PU

A 0.1 M Cu(NO₃)₂ solution was slowly dropped onto TiO₂/PU after the immersing process to synthesize Cu–TiO₂/PU photocatalysts. The addition volume of Cu(NO₃)₂ was adjusted to synthesize Cu–TiO₂/PU materials with 6% weight fractions of Cu/TiO₂. Then, the Cu–TiO₂/PU was cleaned using 50 mL of 1 M oxalic acid solution. The obtained material was continuously irradiated with an UV-C light (60 W) for 5 h and calcined in protective nitrogen gas at 200 °C for 2 h to afford Cu–TiO₂/PU photocatalyst.

2.1.5. Analysis of physicochemical properties

A Nicolet 380 spectrometer was used to obtain Fourier transform infrared spectroscopy (FTIR) spectra of the pristine PU, activated PU, TiO₂/PU and Cu–TiO₂/PU materials. A Thermo Fisher K-Alpha X-ray Photoelectron Spectrometer system was used to obtain X-ray photoelectron spectroscopy spectra (XPS) of TiO₂/PU and Cu–TiO₂/PU to determine the chemical composition of the synthesized materials. A Hitachi S-4700 scanning electron microscope (SEM) was used to determine the surface morphology of the PU, TiO₂/PU and Cu–TiO₂/PU. An energy dispersive X-ray spectrometer was integrated to the Hitachi S-4700 SEM to determine X-ray mapping images of Cu and Ti in the Cu–TiO₂/PU. An Evolution 300 spectrophotometer (UV-1700 Shimadzu) was used to measure the UV–Vis absorption spectra of the shredded pristine PU, TiO₂/PU and Cu–TiO₂/PU.

2.2. Yeast removal methods

2.2.1. Yeast cultivation

C. famata (obtained from an environmental bioengineering laboratory at the University of Ulsan, Korea) was cultivated at 30 °C in YPD medium (0.5% yeast extract, 1% peptone and 2% glucose) for 48 h. Then, 400 mL cultured yeast was centrifuged at 500 rpm for 3 min to obtain 200 mL condensed yeast for use as the yeast source for each removal experiment.

2.2.2. Experimental model design

An experimental model was designed to test the yeast removal efficiency using the synthesized materials (Fig. 1). Fresh air (input air) was pumped into the condensed yeast solution to incite the yeast in the condensed yeast solution and was diffused into aerosol to generate an atmospheric yeast stream that was pumped to two similar volume pipes. The atmospheric yeast in pipe 1 was directed to phosphate buffer saline (PBS) solution (5) by pump (4). The atmospheric yeast in pipe 2 was directed to pass through the reaction chamber by pump (10) (Fig. 1). The top and bottom of the reaction chamber were made of quartz so that the experimental light could easily pass through the reaction chamber walls and irradiate the synthesized materials inside. The reaction chamber was isolated in a cask with a dark cover that ensured no light penetration to prevent any interference with the photocatalytic activities. Two 20 W fluorescent bulbs (1200 lm) were placed at the top of the reaction chamber.}

![Fig. 1. Experimental model for C. famata removal tests.](image-url)
and bottom of the isolated cask to generate visible light with power density of 0.025 W/cm² for the photocatalytic activities.

2.2.3. Yeast removal capacity

PU, TiO$_2$/PU and Cu–TiO$_2$/PU were used as photocatalytic and adsorption materials for the yeast removal experiments. The light bulbs in the isolated cask could be turned off or on to create dark or visible light condition, respectively. The flow rate of the two pumps was maintained almost constant at 2 L/min during each experiment so that almost the same amount of yeast passed through pipes 1 and 2 (Fig. 1). The yeast in pipe 1, for absorption into PBS solution (5), was considered as the input yeast amount of the yeast removal processes. The remaining yeast in pipe 2, which passed through the reaction chamber, was absorbed into the PBS solution (11) to determine the output yeast amount of the yeast removal processes. According to the count method reported by White et al., the amount of the viable yeast (C. famata) in the PBS solution was determined by counting colony-forming unit (CFU) on agar plates [28]. The reaction time, which was similar to the working time of the pumps, was adjusted to control the input yeast amount for each removal experiment. The yeast removal capacities by using pristine PU, TiO$_2$/PU and Cu–TiO$_2$/PU as photocatalytic and adsorption materials (having volume of 12 cm$^3$) under dark and visible light conditions were calculated by Eq. (I):

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

In the control experiments, the reaction chamber was kept empty but other procedures were similar to the previous yeast removal experiments. The amount of yeast absorbed on the solutions (5) and (11) was compared to verify the hypothesis, assuming that the yeast passing through pipe 1, considered as the input yeast amount, was almost the same as that passing through pipe 2 used for the yeast removal experiments.

3. Results and discussion

3.1. Material characterization

3.1.1. TiO$_2$ coating

Fig. 2 shows the FTIR spectrum results of pristine PU, activated PU and TiO$_2$/PU. The FTIR bands and their assigned vibrations are shown in Table 1. The FTIR spectra indicate that the urethane group (–NH–CO–O–), which contains N–H, C–N, C=O and C–O bonds, in the pristine PU was successfully converted to an isocyanate group (–N=C=O) in the activated PU. The Si–O–Ti bond recorded in the FTIR spectra of TiO$_2$/PU confirmed the silanization process between TTIP and APTES to create titanosiloxane (Scheme 1). As compared to the FTIR spectrum of the activated PU, the FTIR spectrum of TiO$_2$/PU showed a strong increase in the N–H and C=O adsorption peaks, which are typical peaks of the urea group (–NH–CO–NH–). However, the isocyanate peak in TiO$_2$/PU greatly decreased as compared to that of the activated PU. The peak intensity change revealed the successful formation of the urea linkage based on reaction between the isocyanate group of the activated PU and the amine group of the titanosiloxane (Scheme 1). Therefore, titania was successfully coated on the surface of PU by using the bridging role of APTES. Silicon in APTES

| Wavenumber (cm$^{-1}$) | Materials | Assigned vibrations | References |
|------------------------|-----------|---------------------|------------|
| 3400–3250              | C         | N–H                 | [53,54]    |
| 2950–2850              | A, B, C   | C=O                 | [55]       |
| 2250                   | B, C      | N=O=C=O             | [56]       |
| 1730                   | A, C      | C=O                 | [53,54]    |
| 1600                   | A, B, C   | C=N                 | [53,54]    |
| 1510, 1240             | A, C      | C=Si                | [57]       |
| 1200                   | C         | C=Si                | [58]       |
| 1100, 790              | C         | Si–O–Si             | [58]       |
| 970                    | C         | Si–O–Ti             | [58]       |
| 570, 670               | C         | Ti–O–Ti             | [16]       |

Note: A – pristine PU, B – activated PU, C – TiO$_2$/PU.
could link to titania in TTIP via the Si–O–Ti bond. The amine group in the APTES could react with the isocyanate group in the activated PU to create a urea linkage. The FTIR spectra of the TiO$_2$/PU exhibited adsorption peaks at 670 and 570 cm$^{-1}$, which were assigned to vibrations of the Ti–O–Ti bond. The peaks indicated that TiO$_2$ was coated on the surface of PU based on reaction between titanium alkoxide and H$_2$O.

3.1.2. Cu dopant

Fig. 3 shows the high-resolution XPS spectrum of the Cu 2p$_{3/2}$ peak of Cu in Cu–TiO$_2$/PU. The Gaussian multiplex shapes were applied to fit the Cu 2p$_{3/2}$ peak to determine the state of copper in Cu–TiO$_2$/PU. The peak analysis result revealed two components of copper in Cu–TiO$_2$/PU: Cu$^+$ in Cu$_2$O (932.3 eV) and Cu$^{2+}$ in CuO (933.5 eV) [29]. CuO in Cu–TiO$_2$/PU was produced from thermal decomposition of Cu(NO$_3$)$_2$ during UV irradiation or calcination processes [22]. The UV irradiation (photo-reduction) and oxalic acid, rolled as a cleaner for the cleaning process, could reduce Cu$^{2+}$ into Cu$^+$ during the decomposition of Cu(NO$_3$)$_2$ to form Cu$_2$O [30–33]. Lin et al. reported that the Cu$^{2+}$ cations could penetrate into the TiO$_2$ lattice and substitute the Ti$^{4+}$ cations, leading to formation of Cu–O–Ti bonds [34]. The substitution of Cu$^{2+}$ into TiO$_2$ lattice was confirmed by XRD analysis (see Supplementary material). The substitution could also lead to the formation of Cu$^+$ in TiO$_2$ lattice. Therefore, the elemental states of the Cu dopant in Cu–TiO$_2$/PU included Cu$^+$ and Cu$^{2+}$, most of which existed in Cu$_2$O and CuO forms, respectively, which are physically adsorbed on the TiO$_2$ surface. Another Cu$^+$ existed in the TiO$_2$ lattice in the form of Cu–O–Ti bonds.

3.1.3. Morphology and surface area

Fig. 4A shows that the pristine PU contained pores sized from 100 to 300 µm. Since, TiO$_2$ was smoothly and thinly coated on the PU surface in TiO$_2$/PU, the TiO$_2$ layer did not greatly affect the pore size change of the PU substrate (Fig. 4B). The SEM features of Cu–TiO$_2$/PU exhibited small Cu$_2$O and CuO particles that were deposited with good dispersion on the TiO$_2$ layer (Fig. 4C). Fig. 4D shows the mixed mapping of Ti and Cu elements in the Cu–TiO$_2$/PU material. The elemental mapping clearly shows that the Ti and Cu elements were deposited almost evenly or alternately on the PU frame, which may have caused the distinct photocatalytic activity of Cu–TiO$_2$/PU for bioaerosol removal.

The BET surface area of the synthesized TiO$_2$/PU was 111.4 m$^2$/g, which was much higher than that of PU (31.3 m$^2$/g) or TiO$_2$ commercial powder (AEROXIDE TiO$_2$ P25) obtained from Evonik Degussa Corporation (60 m$^2$/g) [35]. The high surface area indicates that the immobilization process of TiO$_2$ onto the surface of PU, which could minimize the coagulation of the TiO$_2$ particles, strongly enhanced the surface area of TiO$_2$. In addition, during
TiO₂/PU preparation process, several silicon of APTES could substitute Ti⁴⁺ ions in TiO₂ lattice to form Si–O–Ti bond (Table 1) contributing to enhancement in surface area and porosity of TiO₂/PU [36]. Thus, the surface area of TiO₂/PU could be higher than that of pure TiO₂. The BET surface area of the synthesized Cu–TiO₂/PU was 166.3 m²/g, which was higher than that of PU or TiO₂/PU. This strong improvement in the surface area was attributed to significant deposition of small Cu₂O and CuO particles on the TiO₂ layer (Fig. 4C). The distribution of the particles increased the degree of surface roughness leading to increase in the surface areas of the Cu–TiO₂/PU.

3.1.4. Light adsorption ability
The UV–Vis adsorption spectra of PU, TiO₂/PU and Cu–TiO₂/PU are shown in Fig. 5. As compared to TiO₂/PU and Cu–TiO₂/PU, PU did not exhibit any adsorption ability for light in the wavelength range from 300 to 700 nm. The UV–Vis adsorption spectrum of TiO₂/PU exhibited an adsorption edge at 390 nm. However, it did not exhibit any noticeable adsorption in the visible region, which corresponds to the light adsorption properties of TiO₂ [37]. As compared to the UV–Vis adsorption spectrum of TiO₂/PU, that of Cu–TiO₂/PU, however, not only showed a red shift of the absorption edge but also exhibited higher adsorption ability in the visible region. The red shift of the absorption edge for Cu–TiO₂/PU was possibly due to the absorption role of CuO in the synthesized material. Pham and Lee reported that a composite material, containing TiO₂ and CuO, could create a suitable semiconductor–semiconductor system that decreased the band gap energy of TiO₂ leading to a red shift of the absorption edge of the synthesized material [22]. The direct interfacial electron transfer from the valence band of TiO₂ to the valence band and conduction band of CuO also led to the red shift of the absorption edge for Cu–TiO₂/PU [38]. The strong enhancement of the light adsorption ability of Cu–TiO₂/PU was attributed to the Cu dopant, which increases the light-harvesting ability of TiO₂ within the visible light region [39]. This enhanced visible light absorbance of Cu–TiO₂/PU is expected to considerably increase the photocatalytic activity of the synthesized material in the visible light region.

3.2. Yeast removal
The control experimental results (data not shown) indicated that when the reaction chamber was empty, the yeast amounts absorbed into the PBS solutions (5) and (11) were similar and that the yeast amounts passing through pipes 1 and 2 were similar. Therefore, the hypothesis that the yeast in pipe 1 could be considered as the input yeast amount of the yeast removal experiment was verified. The aerosol yeast removal capacities by PU, TiO₂/PU and Cu–TiO₂/PU under dark and visible light over the input yeast concentration range of 500–5 × 10⁵ (CFU) are shown in Figs. 6 and 7. The yeast removal capacities initially increased with increasing input yeast to a maximum but then plateaued with further increase in input yeast. Table 2 shows the stable maximum yeast removal capacities by PU, TiO₂/PU and Cu–TiO₂/PU under dark and visible light.

3.2.1. Yeast removal by PU
The maximum removal capacity of the aerosolized yeast by PU was similar under both dark and visible light conditions: 1.5 × 10⁵ (CFU/cm²) (Table 2). This result indicated that PU only acted as an absorbent in removing the aerosolized yeast under both dark and visible light conditions. The reported yeast removal mechanism indicates that a microorganism is adhered into an adsorbent. Kara et al. reported that removal of a microorganism is a complex process affected by many parameters such as the chemical and physical properties of the adsorbent, the microorganism’s characteristics and the environmental conditions [40]. The porous structure and large surface area of the PU are favorable for the adsorption of airborne microorganisms [41]. Yeast can be adhered on the inner surface of the pores of PU by van der Waals force [42]. The yeast adsorption mechanism by PU is also due to its hydrophobicity and non-polarity. Most previous studies reported that microorganisms tend to attach to hydrophobic and non-polar materials [41,43]. Li et al. reported that hydrophobic interaction between the yeast cell surface and the adsorbent surface can enable the cell to overcome the repulsive forces within a certain distance from the adsorbent and yeast [41].

3.2.2. Yeast removal by TiO₂/PU
The maximum removal capacity of the aerosolized yeast by TiO₂/PU under visible light condition was 3.3 × 10⁵ (CFU/cm²), which was only slight increased from the capacity of 3.2 × 10⁵ under dark light condition. This was due to the TiO₂ photocatalysts wide band gap energy of approximately 3.2 eV, which required excitation light with a wavelength lower than 388 nm to excite for the photocatalytic process. Therefore, visible light could not significantly excite the electron–hole pairs necessary for TiO₂/PU to develop any photocatalytic activity to remove the aerosolized yeast. Thus, TiO₂/PU only exhibited an adsorption ability to remove the aerosolized yeast under both dark and visible light conditions. The maximum removal capacity of the aerosolized yeast by TiO₂/PU was twice that of PU, which was attributed to the much higher surface area of TiO₂/PU (111.4 m²/g) compared to that of PU (31.3 m²/g). Li et al. reported that the surface area is one of main factors affecting the increased adsorption ability of microorganisms by an adsorbent [41]. The van der Waals force, which could adhere the yeast into the inner surface of pores of TiO₂/PU, contributed strongly to the adsorption process [42]. The SiO₂ component in the TiO₂/PU could enhance the free energy or charge density on the surface of TiO₂/PU [41,42]. This charge density increase could increase the electrostatic interaction between the surface of the TiO₂/PU and the charges on the cell wall of the yeast, thereby increasing the adhesion between the yeast and TiO₂/PU [44]. Therefore, the yeast adsorption ability of TiO₂/PU was higher than that of PU.

3.2.3. Yeast removal by Cu–TiO₂/PU
The maximum removal capacity of the aerosolized yeast by Cu–TiO₂/PU under dark condition was 6.9 × 10⁵ (CFU/cm³), which
Fig. 6. Yeast removal capacities by PU (A), TiO$_2$/PU (B) and Cu–TiO$_2$/PU (C) under dark condition.

Fig. 7. Yeast removal capacities by PU (A), TiO$_2$/PU (B) and Cu–TiO$_2$/PU (C) under visible light condition.
was approximately five- and two-fold higher than that by PU and TiO\textsubscript{2}/PU, respectively. This significant enhancement was firstly due to the increased surface area of Cu–TiO\textsubscript{2}/PU (166.3 m\textsuperscript{2}/g), which was much higher than that of PU (31.3 m\textsuperscript{2}/g) and TiO\textsubscript{2}/PU (111.4 m\textsuperscript{2}/g). Kara et al. reported that the rough surface of an adsorbent could promote adhesion of the microorganisms [40]. Therefore, the higher surface roughness of Cu–TiO\textsubscript{2}/PU (Fig. 4C), as compared to PU (Fig. 4A) and TiO\textsubscript{2}/PU (Fig. 4B), may also have enhanced the yeast removal capacity by Cu–TiO\textsubscript{2}/PU. In addition, the Cu\textsuperscript{2+} ions existing on the surface of Cu–TiO\textsubscript{2}/PU may have killed the yeast and thus increased the yeast removal capacity of the synthesized Cu–TiO\textsubscript{2}/PU [17,45].

The maximum yeast removal capacity by Cu–TiO\textsubscript{2}/PU of 1.8 × 10\textsuperscript{5} (CFU/cm\textsuperscript{3}) under visible light was approximately three-fold higher than that under dark condition. This significant enhancement was attributed to the photocatalytic activity of Cu–TiO\textsubscript{2}/PU under visible light as the excitation sources. The greatly increased photocatalytic activity even under visible light could be attributed to the role of the Cu dopant in Cu–TiO\textsubscript{2}/PU. The doped Cu could defect into the TiO\textsubscript{2} lattice leading to reduction of Ti\textsuperscript{4+} ions into Ti\textsuperscript{3+} ions. The formation of Ti\textsuperscript{3+} in the TiO\textsubscript{2} lattice was confirmed by XPS analysis of titanium (see Supplementary material). Thus, in Cu–TiO\textsubscript{2}/PU, the titanium was found to exist in the forms of Ti\textsuperscript{3+} and Ti\textsuperscript{4+}, while copper existed in the forms Cu\textsuperscript{+} and Cu\textsuperscript{2+}. All these different ionic states of titanium and copper created a mixture of different Fermi levels as shown in Fig. 8 [21,46,47]. When considering the mixture of Fermi levels, the low energy levels provided by incident visible light could be utilized to transfer electrons from the valence band (VB) to the intermediate Fermi levels of Cu\textsuperscript{+}, Cu\textsuperscript{2+}, and Ti\textsuperscript{3+}, and finally, to the Ti\textsuperscript{4+} conduction band (CB), in series (Fig. 8). CuO and Cu\textsubscript{2}O oxides existing on the surface of Cu–TiO\textsubscript{2}/PU could also act as electron sinks to inhibit the recombination of the photo-generated electrons with holes, thus increasing the lifetime of the photo-generated electrons or electron–hole pair separation efficiency [48]. In addition, Ti\textsuperscript{3+} could more easily generate excited electrons than Ti\textsuperscript{4+} because the electron number of Ti\textsuperscript{3+} (19) is higher than that of Ti\textsuperscript{4+} (18). Thus, Cu doping, which led to formation of Ti\textsuperscript{3+} in TiO\textsubscript{2} lattice, could increase the electron–hole separation capacity of the synthesized Cu–TiO\textsubscript{2}/PU photocatalyst [22,49]. Therefore, as compared to TiO\textsubscript{2}, Cu–TiO\textsubscript{2}/PU exhibited an increase in the electron–hole pair separation efficiency and capacity even under visible light irradiation. The lifetime of the photo-generated electrons in Cu–TiO\textsubscript{2}/PU was also prolonged longer than that in TiO\textsubscript{2}/PU. Thus, electron–hole pairs were easily generated and could exist for a longer time when Cu–TiO\textsubscript{2}/PU was irradiated by visible light. The photo-generated electron–hole pairs then reacted with water and molecular oxygen absorbed on the surface of the Cu–TiO\textsubscript{2}/PU material, leading to the formation of oxy radicals such as hydroxyl radicals (•OH) and superoxide radical anions (•O\textsubscript{2}–) [17,49–51]. The formed oxy radicals could cause destruction of the outer cell wall of the yeast, oxidation of coenzyme A and hence inhibition of cell respiration, oxidation of unsaturated phospholipids in the yeast cell membrane, leakage of intracellular K\textsuperscript{+} ions and detrimental effects on DNA and RNA, leading to inactivation or death of the yeast [5,45,50]. After destruction of the outer cell wall of the yeast by oxy radicals, the Cu ions could also permeate inside the cell wall, leading to mutation of key biochemical processes inside of the cell and finally resulting in the death of the yeast cell [50]. In addition, the CuO and Cu\textsubscript{2}O distributed on surface of TiO\textsubscript{2} could also disinfect a certain amount of C. famata via a mechanism called “contact killing” [52].

### 4. Conclusion

The photocatalytic activity of TiO\textsubscript{2} was successfully enhanced by the addition of Cu dopant, which acted as both a defecting and an intermediate agent to increase the electron–hole separation efficiency and capacity of TiO\textsubscript{2}. The adsorption ability was also successfully integrated into the metal-doped TiO\textsubscript{2} by using PU as a substrate for the coating process. The yeast removal capacity of the photocatalysts decreased in the order of Cu–TiO\textsubscript{2}/PU > TiO\textsubscript{2}/PU > PU under both dark and visible light conditions. The removal of the aerosolized yeast under dark condition was mainly attributed to the adsorption ability, which depended on the surface area, surface roughness, polarity, and hydrophobicity of the synthesized materials. The aerosolized yeast removal capacity was highest for Cu–TiO\textsubscript{2}/PU under visible light condition, at a level 2.6-fold higher than that under dark condition. The greatly enhanced removal capacity of the aerosolized yeast under visible light by Cu–TiO\textsubscript{2}/PU was mainly due to a combination of the photocatalytic activity and the adsorption ability of the synthesized photocatalysts. Under visible light, the Cu–TiO\textsubscript{2}/PU photocatalyst could produce oxy radicals, which participated in many oxidation processes to decompose important organic components of yeast and thereby kill the yeast.

### Acknowledgments

This work was supported by a grant from the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT and Future Planning (2013R1A2A2A03013138).

### 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.2015.10.100.
[54] R.M. Hodlur, M.K. Rabina, Self-assembled graphene layers on polyurethane foam as a highly pressure sensitive conducting composite, Compos. Sci. Technol. 90 (2014) 160–165.

[55] C. Pulgarina, J. Kiwi, V. Nadtochenko, Mechanism of photocatalytic bacterial inactivation on TiO₂ films involving cell-wall damage and lysis, Appl. Catal. B 128 (2012) 179–183.

[56] U. Sebenik, M. Krajnc, Influence of the soft segment length and content on the synthesis and properties of isocyanate-terminated urethane prepolymers, Int. J. Adhes. Adhes. 27 (2007) 527–535.

[57] J. Wang, C.H. Lua, J.R. Xiong, Self-cleaning and depollution of fiber reinforced cement materials modified by neutral TiO₂/SiO₂ hydrosol photoactive coatings, Appl. Surf. Sci. 298 (2014) 19–25.

[58] B. Cui, H. Peng, H. Xia, X. Guo, H. Guo, Magnetically recoverable core–shell nanocomposites Fe₂O₃@SiO₂@TiO₂–Ag with enhanced photocatalytic activity and antibacterial activity, Sep. Purif. Technol. 103 (2013) 251–257.