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# Enhanced Self-Cleaning Performance of Ag-F-Codoped $TiO_2/SiO_2$ Thin Films

Byeong-Min Kim and Jung-Sik Kim†

Department of Materials Science and Engineering, University of Seoul, Seoul 02504, Republic of Korea

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**Abstract** Highly self-cleaning thin films of $TiO_2$-$SiO_2$ co-doped with Ag and F are prepared by the sol-gel method. The as-prepared thin films consist of bottom $SiO_2$ and top $TiO_2$ layers which are modified by doping with F, Ag and F-Ag elements. XRD analysis confirms that the prepared thin film is a crystalline anatase phase. UV-vis spectra show that the light absorption of Ag-F-$TiO_2/SiO_2$ thin films is tuned in the visible region. The self-cleaning properties of the prepared films are evaluated by a water contact angle measurement under UV light irradiation. The photocatalytic performances of the thin films are studied using methylene blue dye under both UV and visible light irradiation. The Ag-F-$TiO_2/SiO_2$ thin films exhibit higher photocatalytic activity under both UV and visible light compared with other samples of pure $TiO_2$, Ag-doped $TiO_2$, and F-doped $TiO_2$ films.

**Key words** photocatalyst, titanium dioxide, Ag-F-$TiO_2$ film, self-cleaning, sol-gel process.

## 1. Introduction

Titanium dioxide($TiO_2$) has become the most promising candidate for extensive application in the field of self-cleaning, photocatalysis, phototovoltaic, pigment, antibacterial and hydrogen production due to its extra ordinary properties like chemical-physical stability, thermal and electrical properties, low cost and nontoxicity.[1,2] To extend its applicability in self-cleaning surfaces, many researchers have been developing various ways to apply $TiO_2$ coating on different substrates.[3,4] Generally, $TiO_2$ and $SiO_2$ are used as high and low refractive index materials, respectively. $TiO_2$-$SiO_2$ based coatings are found to be applicable for coating various substrates due to their high, photoactivity, strong redox property, high thermal stability, high chemical durability, low thermal expansion coefficient, versatile refractive index and hydrophilicity.[5,6]

Recently, modified $TiO_2$ has attracted a great attention, because it could result in a higher photocatalytic activity compared with undoped $TiO_2$. Among various dopant species, Ag and F elements doped in $TiO_2$ showed enhancing the photocatalytic activity towards degradation of organic compounds. Ag is an extremely attractive noble metal due to its low cost, high efficiency, antimicrobial property, high oxygen adsorption reactivity and ease of preparation and its remarkable catalytic activity.[7] The deposition of Ag into $TiO_2$ has been of considerable interest for both mechanistic and applicability reasons because Ag nanoparticles can act as electron traps supporting electron-hole separation.[8,9] Visible light absorption by silver surface plasmons is considered for electron transfer to $TiO_2$ surface and thus it can be activated by visible light.

Similarly, researchers have found that the doping of nitrogen or fluorine is an effective way to enhance the photocatalytic activity of $TiO_2$.[10] Compared with N doping, F-doping can improve photocatalytic activity under both UV and visible light irradiations. F-doping converted $Ti^{4+}$ to $Ti^{3+}$ by charge compensation, and the existence of $Ti^{3+}$ could increase the photogenerated charge carrier separation rate, and enhance the photocatalytic activity.[11] The previous investigation have also indicated that surface fluorination can generate more free OH radicals and creates oxygen vacancies.[12] Also, upon F-doping in $TiO_2$, F centers are formed which helps to narrowing the band gap of $TiO_2$.[13]

Several work has been reported on Ag or F doped $TiO_2$ thin film photocatalysts[14,15] while very few studies ad-

†Corresponding author
E-Mail : jskim@uos.ac.kr (J.-S. Kim, Univ. of Seoul)

dressed self-cleaning and photocatalytic effect of Ag and F codoped $TiO_2$ thin films. Lin et al prepared F-doped $TiO_2$ loaded with Ag(Ag-F-$TiO_2$) powder by sol-gel process combined with photoreduction method and investigated the effects of Ag loading on the photocatalytic activities of F-$TiO_2$.[7] Therefore, it is necessary to understand photocatalytic performance of Ag and F co-doped $TiO_2$ thin films.

In the present work, we have synthesized Ag-F co-doped $TiO_2/SiO_2$ thin film photocatalyst by a sol-gel process. The effect of Ag and F doping on the self-cleaning and photocatalytic performance of prepared thin films were evaluated by measuring the water contact angle and photocatalytic degradation of methylene blue, respectively.

## 2. Experimental

### 2.1 Raw materials

Tetraethyl orthosilicate(TEOS, $Si[OC_2H_5]_4$) and titanium tetraisopropoxide(Ans.) (TTIP, $Ti[OCH(CH_3)_2]_4$) were purchased form Aldrich. Ethyl alcohol(EtOH, $C_2H_5OH$), Nitric acid ($HNO_3$, 64~66 %), n-butyl alcohol(n-butanol, $CH_3[CH_2]_3OH$), silver nitrate($AgNO_3$, 99.8 %), and ammonium fluoride($NH_4F$, 97 %) were purchased form Duksan. Hydrochloric acid(HCl, 36.5~38 %) and isopropyl alcohol (IPA, $C_3H_8O$) was purchased from J. T. Baker and Dong-Woo Fine-Chem, respectively.

### 2.2 Preparation of $TiO_2/SiO_2$-based thin films

The thin films of Ag, F and Ag-F co-doped $TiO_2/SiO_2$ double layer were prepared by a sol-gel method. Initially, $SiO_2$ thin film was prepared according to a previous report.[16] $SiO_2$-sol was aged for 2 days and then used to coat the glass substrate using a spin coater. After spin coating, the $SiO_2$-coated glass substrate was annealed at 400 °C for 1hr.

The $TiO_2$ sol was prepared by mixing titanium tetra-isopropoxide with ethanol, n-butanol, deionized water, and HCl. Similarly, Ag-$TiO_2$, F-$TiO_2$ and Ag-F-$TiO_2$ sol were prepared using precursors such as $AgNO_3$ and $NH_4F$. $TiO_2$ sol, Ag-$TiO_2$ sol, F-$TiO_2$ sol and Ag-F-$TiO_2$ sol were aged for 12hr, then each sol was spin coated on a glass substrate using a spin coater and annealed at 500 °C for 1 hr. Table 1 represents the molar ratio of chemical precursors used to prepare sols. The prepared thin films of $TiO_2/SiO_2$, Ag-$TiO_2/SiO_2$, F-$TiO_2/SiO_2$ and Ag-F-$TiO_2/SiO_2$ were denoted as TS, ATS, FTS, and AFTS, respectively.

### 2.3 Materials characterization

The XRD patterns of thin films were acquired on an X-ray diffraction(New D8-Advance, Bruker-AXS) with a 2θ range of 20~80°. The optical properties of the thin films were studied on a UV-Vis spectrometer(S-4100, SCINCO). The surface morphology of the samples was investigated using a scanning electron microscopy(Field Emission S-4700, Hitachi) and transmission electron microscopy(TECNAI F20 G2, FEI). The XPS measurement was carried out on an X-ray photoelectron spectroscopy(VG ESCALAB 220i, Thermo Scientific). Surface hydrophilicity of the films was quantified from measurements of the water contact angle. Experiments were performed at room temperature using a goniometer (Surface tech, GSTD, Korea) attached to a camera. Water contact angles were measured on the thin film surface by dropping water droplets(2 $\mu L$) at pH 5.7. The photo-induced hydrophilicity of the films was measured using a UV lamp(Daytime CFL 20W Black-light, Korea). The peak wavelength of a UV-lamp was 365 nm.

### 2.4 Photocatalytic reaction measurement

The photocatalytic activity was evaluated for degradation of methylene blue(MB) solution under UV and visible light irradiation. The thin films($2.5 \times 2.5$ cm$^2$) were dipped into 5 mL MB solution(2ppm). Prior to the photocatalytic reaction was carried out, the thin film was kept in the dark under magnetic stirring for 1 h for the saturation adsorption of MB on the coatings. UV lamp (Day time CFL 20W Black light, Korea) and incandescent bulb (NB-220-C 200W, Lanxi China) with ultraviolet light filter(Kenko zeta UV L41, Japan) were used for UV and visible light irradiation, respectively. The concentration of MB aqueous solution was determined every 15 min with a UV-Vis spectrometer(S-4100, SCINCO).

**Table 1.** Molar ratios of chemical precursors.

| Coating materials | Molar ratio |
|---|---|
| $SiO_2$ | TEOS : $H_2O$ : HCl : IPA = 1 : 4 : 0.03 : 20 |
| $TiO_2$(TS) | TTIP : EtOH : $H_2O$ : HCl : n-butanol = 1 : 20 : 1 : 0.35 : 1 |
| Ag-$TiO_2$(ATS) | TTIP : EtOH : $H_2O$ : $HNO_3$ : n-butanol : $AgNO_3$ = 1 : 20 : 1 : 0.35 : 1 : 0.03 |
| F-$TiO_2$(FTS) | TTIP : EtOH : $H_2O$ : $HNO_3$ : n-butanol : $NH_4F$ = 1 : 20 : 1 : 0.35 : 1 : 0.04 |
| Ag-F-$TiO_2$(AFTS) | TTIP : EtOH : $H_2O$ : $HNO_3$ : n-butanol : $AgNO_3$ : $NH_4F$ = 1 : 20 : 1 : 0.35 : 1 : 0.03 : 0.04 |

## 3. Results and Discussion

### 3.1 XRD analysis

The XRD patterns of thin films are shown in Fig. 1. The obtained diffraction patterns are crystalline in nature and clearly matched with the anatase phase $TiO_2$(JCPDS 21-1272). No diffraction patterns of rutile or brookite were detected in these samples. In case of Ag containing samples(Ag-$TiO_2$ and Ag-F-$TiO_2$), no any peak of silver was detected in the diffraction patterns. This may be due to the low concentration of silver below the detection limit. Also, F-doping did not cause any shift in peak position of $TiO_2$ phase because the ionic radius of fluorine atom(0.133 nm) is almost similar to the substituted oxygen atom(0.132 nm).[13] The crystallite size of the samples were estimated using the Debye-Scherrer equation. The crystallite sizes calculated for TS, ATS, FTS and AFTS were about 18.99 nm, 18.88 nm, 19.08 nm and 19.10 nm, respectively. Our XRD results are in good agreement with previous reports and it was found that the Ag and F doping in $TiO_2$ does not affects crystal structure of $TiO_2$ thin films.[17]

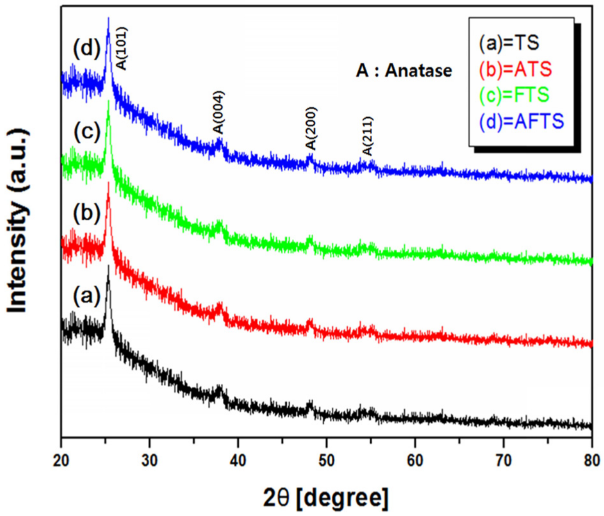


**Fig. 1.** XRD patterns of $TiO_2$, Ag-$TiO_2$, F-$TiO_2$ and Ag-F-$TiO_2$ thin films.

### 3.2 Optical properties

The optical absorption spectra of the thin films are shown in Fig. 2. The optical absorption of $TiO_2$ thin film was in the UV region. ATS thin film showed strong absorption peak at 401 nm which is due to the dipole resonance of silver nanoparticles.[18,19] No any significant shift was observed for F-doped $TiO_2$ thin films. Previous reports suggest that the optical properties of $TiO_2$ are not affected by F-doping.[20] The absorption edge of AFTS samples shows significant red shift in the visible light region. This can be attributed to the surface plasmon resonance effect of silver nanoparticles and F centers generated by substituted oxygen vacancies with F dopant. The UV-Vis transmittance spectra of the thin films are shown in Fig. 3. The transmittance values observed for thin film samples were about 75 %, 72 %, 69 %, and 65 % for TS, ATS, FTS, and AFTS sample, respectively.

### 3.3 Morphological properties

SEM images of all thin film samples are shown in Fig. 4. Almost spherical particles of few nanometer in size were detected in all thin film samples. As shown in images, F and Ag containing samples also shows uniform porous structure of the thin film. Fig. 3(e) shows cross-sectional view of a representative AFTS sample. The thickness of $SiO_2$ and $TiO_2$ layer were found to be 215 nm and 74 nm, respectively.

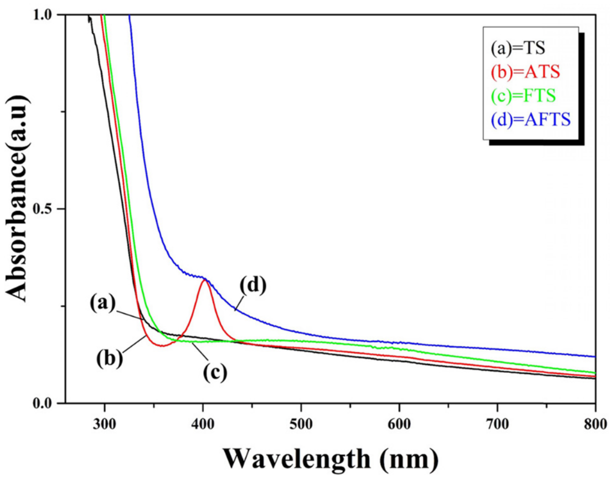


**Fig. 2.** UV-Vis absorbance spectra of $TiO_2$, Ag-$TiO_2$, F-$TiO_2$ and Ag-F-$TiO_2$ thin films.

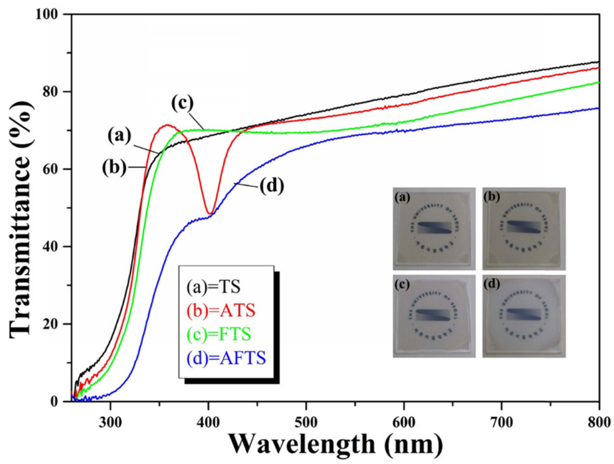


**Fig. 3.** UV-vis transmittance spectra of $TiO_2$, Ag-$TiO_2$, F-$TiO_2$ and Ag-F-$TiO_2$ thin films.

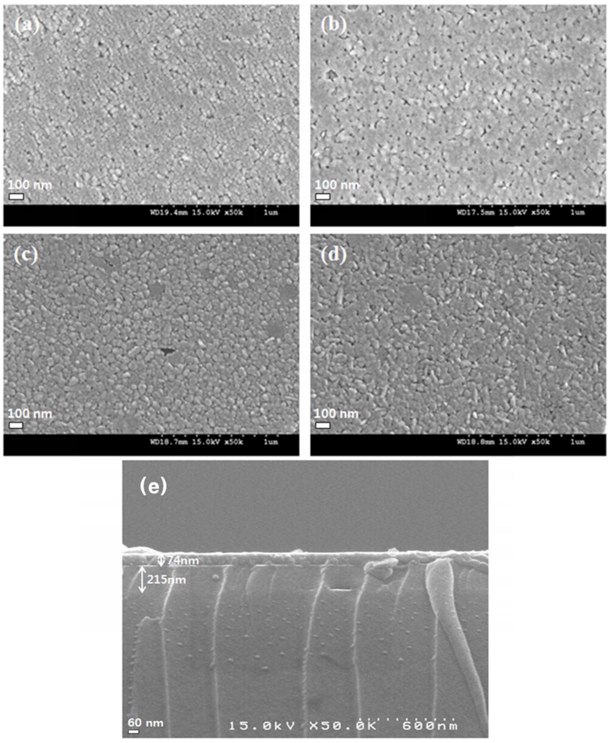


**Fig. 4.** SEM surface images of (a) TS, (b) ATS, (c) FTS, (d) AFTS, and (e) cross section of AFTS films.

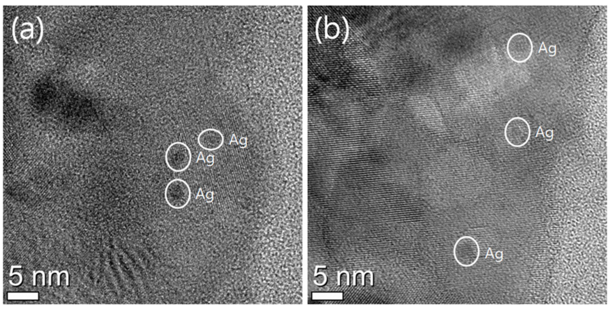


**Fig. 5.** TEM images of (a) ATS and (b) AFTS films.

Fig. 5 shows TEM images of ATS and AFTS samples. TEM images clearly shows that the Ag NPs are uniformly dispersed on the surface of $TiO_2$. The size of Ag and $TiO_2$ NPs were found to be 2 nm and 12 nm, respectively.

### 3.4 XPS analysis

The chemical state of Ti, O, F, and Ag were analyzed by XPS measurement as shown in Fig. 6. For $TiO_2$, Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks are detected at 458.49 eV and 464.28 eV, respectively. The splitting between the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ is 5.79 eV, indicating a normal state of $Ti^{4+}$ in the sample.[21] The peak observed at 530 eV is assigned to lattice oxygen of $TiO_2$. Fig. 6(b) shows the XPS of ATS sample in which the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ binding energy regions are found at 367.8 and 373.8 eV, respectively. The corresponding spin energy separation is 6.0 eV. This is the characteristic of metallic Ag, confirming that the Ag present in the metallic state.[22] The XPS of FTS and AFTS is shown in Fig. 6(c-d). The binding energy peak at 684.3 eV indicates that the fluorine is present in the thin films sample in the form of $TiF_4$ and/or physically adsorbed $F^-$ on $TiO_2$. Similarly, the peak at 688 eV could assigned to nonstoichiometric solid solution of F in $TiO_2$ of the $TiO_{2-x}F_x$ type.[23] Fig. 7 shows high resolution XPS spectra of O1s configuration for TS, ATS, FTS, and AFTS samples. The Ti-O peak intensity was in the order of AFTS < ATS < FTS < TS, while the surface hydroxyl peak intensity was in the order of TS < FTS < ATS < AFTS. The higher hydroxyl density was found for AFTS sample which might be beneficial to trap holes reaching the surface region of the film. This leads to the enhancement of both the charge transfer efficiency and photocatalytic activity.

### 3.5 Photo-induced hydrophilicity

Hydrophilicity of the prepared thin films were studied using water contact angle measurements under UV light irradiation. Fig. 8 shows the contact angles of all thin film samples. Before UV light irradiation, the nature of thin films was hydrophobic and the water contact angles of all thin films were in the range of 21-24$^o$. After UV light irradiation, the water contact angles decreased to about 4$^o$ within 5 min of UV irradiation. All thin film samples showed super hydrophilicity upon UV light irradiation.

### 3.6 Photocatalytic activity

In order to evaluate the self-cleaning activity of the films and to give an example of potential applications, photocatalytic activity of the thin films was evaluated by photocatalytic degradation of methylene blue aqueous solution under UV and visible light irradiation. The concentration of MB solution under dark conditions (without light) didn't change. Also, in presence of light irradiation and without thin films, the concentration of MB solution remains constant. Therefore, the degradation of MB solution can be occurred by both light irradiation and photocatalytic thin film.

Fig. 9 and Fig. 10 show the MB degradation profiles for all samples(TS, ATS, FTS, and AFTS coating films) under UV and visible light irradiation, respectively. Upon visible light irradiation, pure $TiO_2$ sample did not show any photo-activity, but other samples of ATS, FTS and AFTS showed photocatalytic activities because of formed F centers[13] and surface plasmon resonance effect of Ag dopant.[24] It is shown that the photo-activity of AFTS thin film under UV as well as visible light was higher

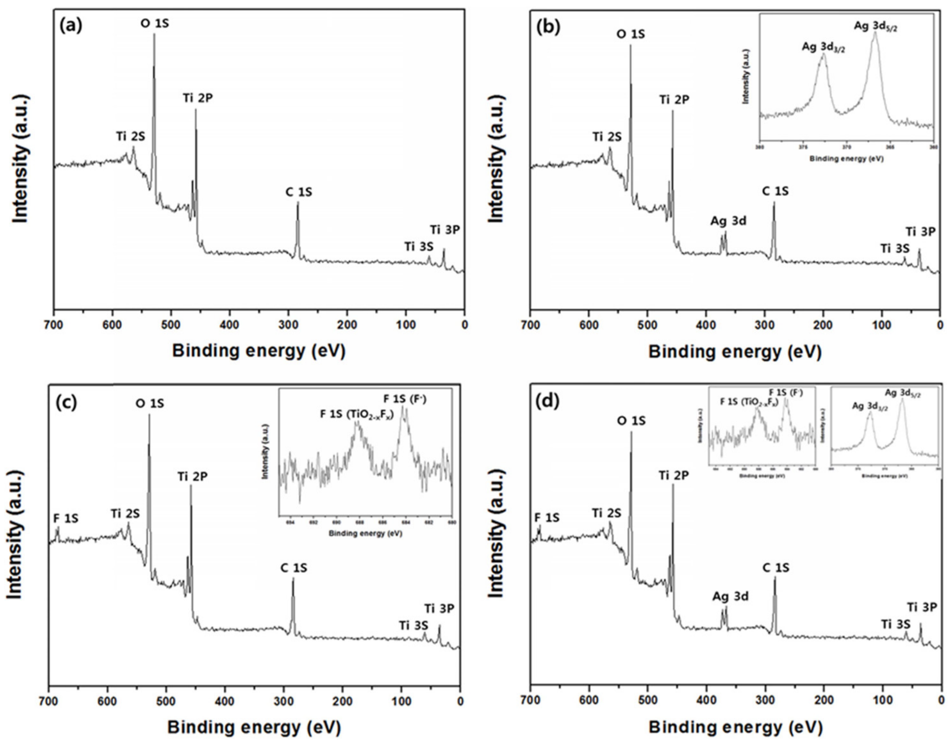


**Fig. 6.** Survey XPS spectra of (a) TS, (b) ATS, (c) FTS, and (d) AFTS films(Inset: high-resolution XPS spectra of Ag 3d and F 1S).

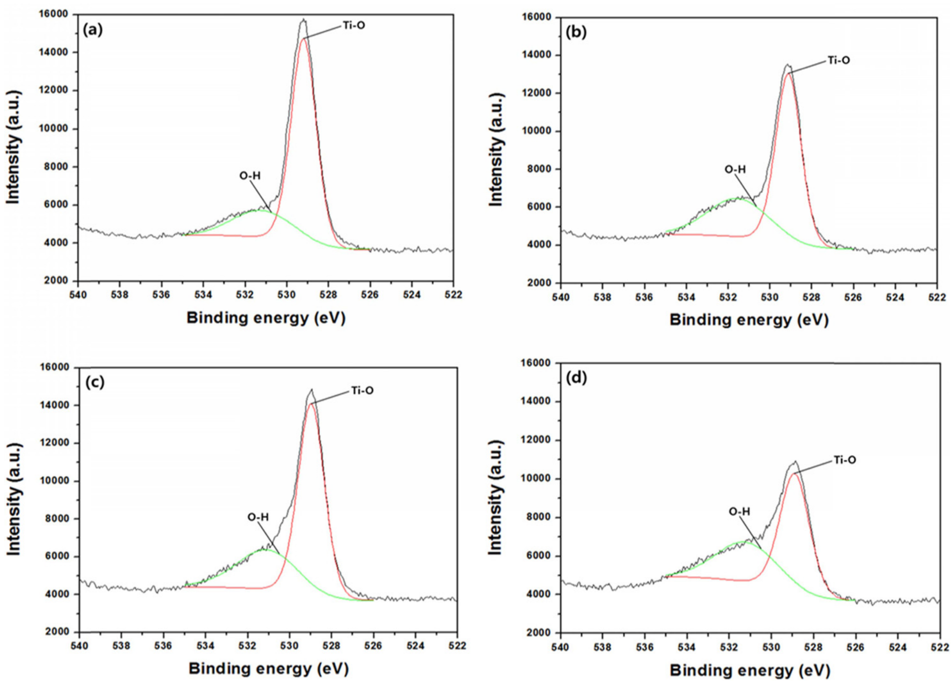


**Fig. 7.** High-resolution XPS spectra of O 1S for (a) TS, (b) ATS, (c) FTS, and (d) AFTS films.

than that of other samples. In agreement with previous researches, the incorporation of Ag on $F-TiO_2$ is a promising way to enhance the photocatalytic performance.[25) The $F-TiO_2$ thin film showed lower photocatalytic activity than the $Ag-TiO_2$ thin film under UV and visible light irradiation. The photocatalytic activity was high in

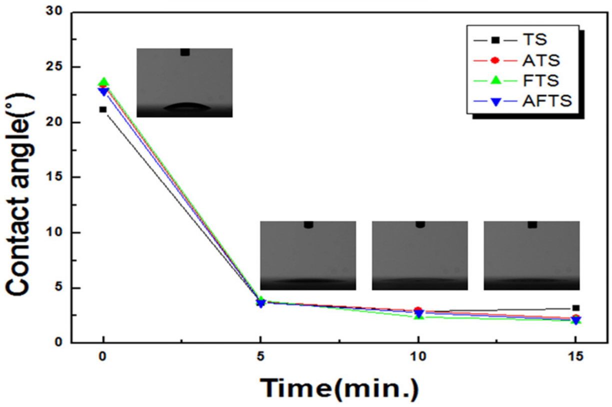


**Fig. 8.** Contact angles of photocatalysts($TiO_2$, Ag-$TiO_2$, F-$TiO_2$, and Ag-F-$TiO_2$)/$SiO_2$ under UV light irradiation.

the order of AFTS > TS > FTS > ATS under UV and AFTS > ATS > FTS > TS under visible light irradiation, respectively.

The enhanced photocatalytic activity of the AFTS thin film may be due to the difference in Fermi level of Ag and F-$TiO_2$. As the Fermi level of Ag is lower than that of F-$TiO_2$, the photo-induced electrons can transfer to the Ag particles loaded on the surface of $TiO_2$. Then, the transferred electrons are trapped by Ag and separated effectively. Ultimately, more reactive oxygen species are generated due to the photo-generated charge carriers and enhance the photocatalytic activity.[26] In addition, the surface plasmon resonance of Ag particles on F-$TiO_2$ is excited by visible light, enhancing the surface electron excitation and photo-generated charge carrier separation. The combined effect of Ag played an important role to transfer electrons from the sample surface to adsorbed $O_2$, and to inject photo-excited electrons into the F-$TiO_2$ conduction band, producing separated electrons and holes, which can react with adsorbates.

It has been reported that in the F doped $TiO_2$, doped F can convert $Ti^{4+}$ to $Ti^{3+}$ by charge compensation.[27] Upon light irradiation, photo-generated electrons accumulate at the lower lying surface state of $Ti^{3+}$, while holes accumulate at the valence band of $TiO_2$. The photo-generated electrons could easily diffuse after doping fluorine, and then captured by Ag.[28] The hydroxyl density of AFTS was higher than that of other samples, so the AFTS sample is efficient to trap holes reaching the surface region of the thin film, which ultimately enhance photocatalytic activity by promoting charge transportation.

## 4. Conclusions

$TiO_2/SiO_2$ thin films doped with F, Ag and Ag-F were successfully prepared by a sol-gel method, followed by spin coating. Optical analysis confirmed that the Ag-F-$TiO_2/SiO_2$ coating film showed good visible light absorption. All prepared thin films of (Ag-$TiO_2$, F-$TiO_2$, and Ag-F-$TiO_2$)/$SiO_2$ showed excellent self-cleaning and photocatalytic properties. Self-cleaning performance of Ag-F-$TiO_2/SiO_2$ thin film was higher than other samples under UV and visible light. This higher self-cleaning performance of Ag-F-$TiO_2/SiO_2$ film was mainly attributed to the synergetic effect of F and Ag dopant, enhancing the formation of oxygen vacancies and the separation of electron-hole pairs.

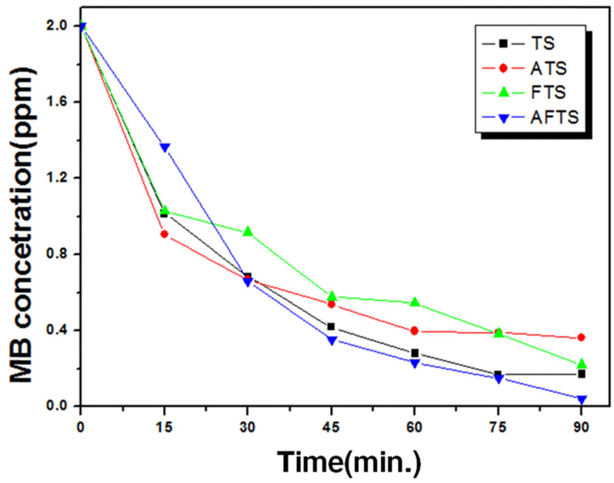


**Fig. 9.** Comparisons of photo-decomposition for MB solution with photocatalysts($TiO_2$, Ag-$TiO_2$, F-$TiO_2$, Ag-F-$TiO_2$)/$SiO_2$ under UV light irradiation.

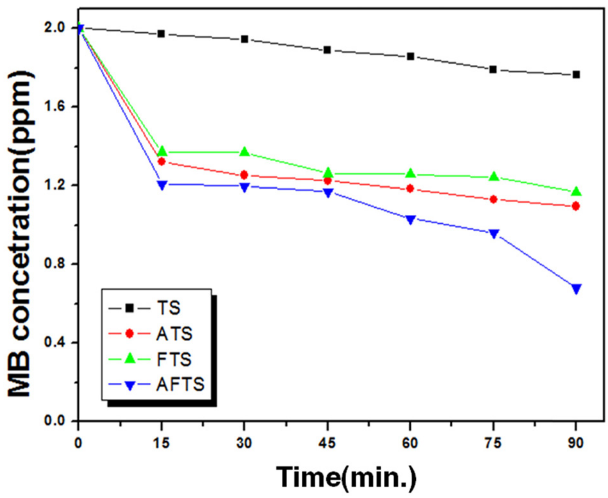


**Fig. 10.** Comparisons of photo-decomposition for MB solution with photocatalysts($TiO_2$, Ag-$TiO_2$, F-$TiO_2$, and Ag-F-$TiO_2$)/$SiO_2$ under visible light irradiation.

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## References

1. S. Banerjee, D. D. Dionysiou and S. C. Pillai, Appl. Catal. B Environ. **176-177**, 396 (2015).
2. H. M. Yadav, J.-S. Kim and S. H. Pawar, Korean J. Chem. Eng., **33**, 1989 (2016).
3. W.-J. Lee, Y.-B. Choi and D.-S. Bae, Korean J. Mater. Res., **27**, 289 (2017).
4. L. Zhou, S. Yan, B. Tian, J. Zhang and M. Anpo, Mater. Lett., **60**, 396 (2006).
5. H. M. Yadav, T. V. Kolekar, S. H. Pawar and J.-S. Kim, J. Mater. Sci.: Mater. Med. 27: **57**, 1 (2016).
6. M. Houmard, G. Berthomé, J. C. Joud and M. Langlet, Surf. Sci., **605**, 456 (2011).
7. X. Lin, F. Rong, D. Fu and C. Yuan, Powder Technol., **219**, 173 (2012).
8. B.-M. Kim and J.-S. Kim, Korean J. Mater. Res., **26**, 73 (2016).
9. E. Albiter, M. A. Valenzuela, S. Alfaro, G. Valverde-Aguilar and F. M. Martinez-Pallares, J. Saudi Chem. Soc., **19**, 563 (2015).
10. A. M. Asiri, M. S. Al-Amoudi, S. A. Bazaid, A. A. Adam, K. A. Alamry and S. Anandan, J. Saudi Chem. Soc., **18**, 155 (2014).
11. J. C. Yu, J. Yu, W. Ho, Z. Jiang and L. Zhang, Chem. Mater., **14**, 3808 (2002).
12. D. Li, H. Haneda, N. K. Labhsetwar, S. Hishita and N. Ohashi, Chem. Phys. Lett., **401**, 579 (2005).
13. D. Li, H. Haneda, S. Hishita, N. Ohashi and N. K. Labhsetwar, J. Fluor. Chem., **126**, 69 (2005).
14. D. J. R. Gutierrez, N. R. Mathews and S. S. Martinez, J. Photochem. Photobiol. A: Chem., **262**, 57 (2013).
15. J. Xu, Y. Ao, D. Fu and C. Yuan, Appl. Surf. Sci., **254**, 3033 (2008).
16. B.-M. Kim, H. M. Yadav, J.-S. Kim, J. Coat. Technol. Res., **13**, 905 (2016).
17. S. C. Chan and M. A. Barteau, Top. Catal., **54**, 378 (2011).
18. I. Pastoriza-Santos and L. M. Liz-Marzán, Nano Lett., **2**, 903 (2002).
19. S. P. Deshmukh, R. K. Dhokale, H. M. Yadav, S. N. Achary, S. D. Delekar, Appl. Surf. Sci., **273**, 676 (2013).
20. T. Yamaki, T. Umebayashi, T. Sumita, S. Yamamoto, M. Maekawa, A. Kawasuso and H. Itoh, Nucl. Instrum. Methods Phys. Res., Sect. B, **206**, 254 (2003).
21. D. K. Kim and W. Y. Maeng, Korean J. Mater. Res., **26**, 271 (2016).
22. X. Yang, Y. Wang, L. Xu, X. Yu and Y. Guo, J. Phys. Chem. C, **112**, 11481 (2008).
23. C. Trapalis, N. Todorova, T. Giannakopoulou, G. Romanos, T. Vaimakis and J. Yu, Int. J. Photoenergy, **2008**, 534038 (2008).
24. H. M. Sung-Suh, J. R. Choi, H. J. Hah, S. M. Koo and Y. C. Bae, J. Photochem. Photobiol. A: Chem., **163**, 37 (2004).
25. X. Lin, F. Rong, D. Fu and C. Yuan, Powder Technol., **219**, 173 (2012).
26. M. Jakob, H. Levanon and P. V. Kamat, Nano Lett., **3**, 353 (2003).
27. Y. Wu, H. Liu, J. Zhang and F. Chen, J. Phys. Chem. C, **113**, 14689 (2009).
28. S. N. Subbarao, Y. H. Yun, R. Kershaw and K. Dwight, Inorg. Chem., **18**, 488 (1979).