Effective adsorption of Ag–TiO_2using aCu-containing solution

ABSTRACT

Titanium dioxide is hard to coat on glass or boehmite at low pH.In this study, a method to coat titanium dioxide functionalized by Ag on the glass surfaces using aCu-containing solution is proposed. This method facilitated the coatingof titanium dioxide functionalized by Ag on glass surfacesusing 3-aminopropyltrimethoxysilane (APTMS).Resultsshowed that Ag–TiO_2 nanoparticles can be coated on Al and glass surfaces. Furthermore, they can be coated on boehmite at low pH without using APTMS.

Keywords: 3-aminopropyltrimethoxysilane; Copper (II) nitrate; Boehmite; Glass; AnataseTiO_2 nanoparticles: Ag–TiO_2 nanoparticles

1. Introduction

Titanium dioxide (TiO_2) is an important material because it is widely used in several applications. Typically, TiO_2has three forms: anatase, rutile, and brookite. Anatase TiO_2has better photocatalytic properties than rutile TiO_2[1, 2]. TiO_2nanoparticles (NPs) are used in several applications such as photocatalysts, self-sustained fuel cells, biocides, solar cells, oxygen reduction catalysts, and optoelectronic devices. The photocatalytic activity of TiO_2can be improved in Ag-doped TiO_2NPs. Ag-doped TiO_2can be used in more applications than TiO_2 (e.g., as a photocatalyst, in solar cells, andto enhance the antibacterial efficiency ofsterilization) [3–~~10~~12]. The enhanced photocatalytic activity of TiO_2 doped with transition metals can be attributed to the increasein its absorption in the visible-light region. Additionally, TiO_2doping with Ag also increases its disinfection capability [8]. Especially with the emergence of new variants of SARS-CoV-2. In recent work, antimicrobial cotton fabrics were developing with Ag/TiO_2 nanoparticles synthesized.[12]TiO_2 or Ag–TiO_2can be used for applications, such as bactericidal applications, by coating them on a glass substrate. This method allows the reuse of the material. The resultant solution should be at low pH, which induces a stable dispersion of the nanoparticles. The electrostatic potential on a surface, called zeta potential, is an important factor. Anatase TiO_2 stably disperses in a strongly acidic medium at pH ≤2. However, it is difficult to coat anatase TiO_2on glass using 3-aminopropyltrimethoxysilane(APTMS) at low pH, because the protons in the surface SiAOH groups were not detached and created a negatively charged surface, which is not enough capable of attracting positively charged TiO_2 NPs[~~11~~13]. This study examines coating anatase TiO_2 on glass surfaces using APTMS. In this study, $Cu(NO_3)_2$ was added to aid the adsorption of anatase TiO_2 on glass plates treated with APTMS to form a self-assembled monolayer at ~20°C. Ag–TiO_2coating on glass surfaces was also investigated. Furthermore adding $Cu(NO_3)_2$ enabled Ag–TiO_2NPs to be successfully coated on boehmite without APTMS.

2. Experimental

2.1. Preparation of anataseTiO_2 NPs, Ag–anatase TiO_2 NPs, andsolution containing Cu ions

Anatase TiO_2 NPs were prepared using an aqueous anatase TiO_2 suspension (500 mL, 0.02%). This mixture was heated to the boiling stage under vigorous stirring for ~20 min.

Ag–anatase TiO_2 NPs were prepared using an aqueous anatase TiO_2 suspension (500 mL, 0.02%). This mixture was heated to the boiling stage under vigorous stirring for ~20 min before adding an aqueous $AgNO_3$solution (5 mL, 1%). Next, sodium citrate(5 mL, 1%) was added after 5 min of the addition of the $AgNO_3$ solution. Boiling was continued for ~5 min until the particle surfaces turned black.

An aqueous $Cu(NO_3)_2$solution (200 mL, 0.01%) was boiledfor ~2min, anda sodium citratesolution (2 mL, 1%) was added to the solution,after which the color of the solution became deepblue. The

final productis a Cu-citriccomplex ion-containing solution.
The pH of the solution was subsequently adjusted to 2–3 by adding diluted HNO_3.

2.2. Preparation of Ag–$TiO_2$and TiO_2adsorbed on substrates

An Al plate whichpurchased from KENIS LIMITEDwas cleaned using deionized water, sonicatedusing a neutral detergent for 15 min to remove grease from its surface, and sonicated again in deionized water for 20 min. To form a boehmite layer on the Al surface, the Al plate was boiled in deionized water for ~15 min.

The Al plate was then functionalized by immersing it in an aqueousAPTMS solution (2% (v/v)) for 25 h at ~20 °C. APTMS can dissolve the Al plate because of its alkalinity (pH = 11). To prevent this, the APTMS solution was neutralized using diluted HCl solution before using it to functionalize the Al substrate. The functionalized substrates were then rinsed using deionized water and annealed at 110°C.

The Ag–TiO_2 adsorbed on the substrates was prepared by a chemical assembly of Ag–anatase TiO_2 NPs on the prepared boehmite Al surface. This was conducted by immersing the platein an Ag–anatase TiO_2 NP solution for 50h until the NPswere deposited on the surface.

Ag–TiO_2 adsorbed on the substrates was also prepared by a chemical assembly of the Ag–TiO_2 NPs on the APTMS-functionalized Al plates. These plates were immersed in an Ag–anatase TiO_2 NP solution for 50h until a film of the NPsis formed on the APTMS-modified substrate.

Glass slides were ultrasonically cleaned in deionized water, isopropyl alcohol, acetone, and deionized water for 15 min each followed by immersion in H_2O/H_2O_2/30% NH_4OH (5:1:1) for 16 h. For functionalization, the slides were further cleaned by sonication in deionized water for 15 min and then immersed in an aqueous APTMS solution (2% (v/v)) for 24 h at room temperature. The functionalized substrates were subsequently rinsed using deionized water and annealed at 110°C [14,15]~~[12, 13]~~. Some of them were then immersed in a TiO_2 NP solution for 75 h. The other substrates were immersed in an Ag–anatase TiO_2 NP solution for 75 h until a film of particles was formed on the APTMS-modified substrate.

2.3. Characterization

Using a field emission microscope (JSM6500F) operated at an accelerating voltage of 15 kV, scanning electron microscopy (SEM) images were obtained.Transmission electron microscopy (TEM) images were obtainedusing a field emission transmission electron microscope (HD-2300C) operated at an accelerating voltage of 200 kV.

2.4. Materials and methods

1) Materials

AnataseTiO$_2$ NPs were obtained from anatase TiO_2(Kanto Chemical Co. Inc, Japan). The particle diameter of the anatase TiO_2 used in this study was 100–300 nm. The following reagents were obtained: 3-aminopropyltrimethoxysilane (Tokyo Chemical Industry Co., Ltd. Japan), sodium citrate(Wako PureChemical Corporation. Japan), $AgNO_3$ (YONEYAMA YAKUHIN KOGYOU Co., Ltd. Japan), and $Cu(NO_3)_2$(Kanto Chemical Co. Inc, Japan); all reagents were of analytical grades.

2) Methods of preparing Ag–TiO_2

The particle size of anatase TiO_2 decreases during boiling because of the collision of the particles [10]. Thus, the anatase TiO_2 NPs were boiled for ~20 min to decrease their particle size. A part of the solution was then added to a solution containing a mixture of $AgNO_3$ (1%) and sodium citrate (1%). After ~3 min, the surfaces of the TiO_2 particles turned black. Diluted HNO_3 was then added for adjusting the pH to 2–3 because acidic conditions promote the deposition of Ag NPs on the TiO_2 surfaces. Ag remains stable on the TiO_2 surface for over 5 months [1~~4~~6].

3. Results and discussion

Figure 1(a)shows the TEM images of the prepared Ag–TiO_2particles after adjusting the pH of the solution to 3 using diluted HNO_3. The X-ray spectroscopy (EDS) pattern in Figure 1(b)confirms a successful adsorption of Ag NPs on all surfaces.

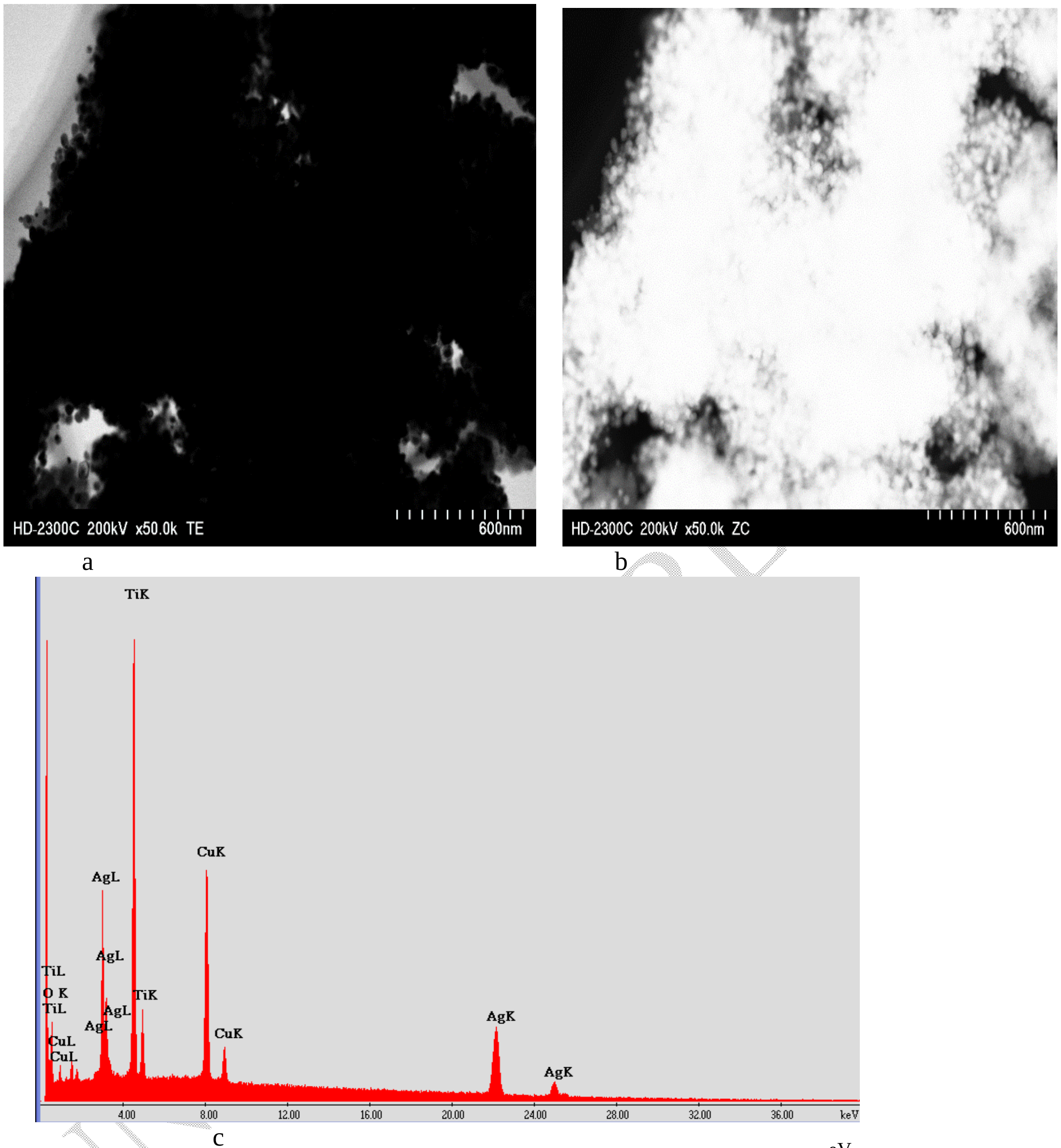

Fig. 1. (a) TEM images of an anatase (TiO_2) surface coated using Ag at pH 3, (b) high-angle annular dark-field image of Ag–TiO_2, (c) point EDS pattern of the TiO_2 surface. The copper signal is from the TEM sample grid.

Figures 2–5 show that the developed Ag–TiO_2 NPs could be adsorbed on Al or glass surfaces. Because Al dissolves at a pH = 2, the pH was adjustedto 3 using diluted HNO_3 for the synthesis. Figure 2(a) shows the SEM image of the Ag–TiO_2 NP adsorption on the APTMS-modified Al surface. The energy dispersive EDS pattern in Figure 2(b) indicates that Ag–TiO_2 was adsorbed on the Al surface.However, only a small deposit was observed on the Al surface,which was not modified by APTMS,with the boehmite layer.

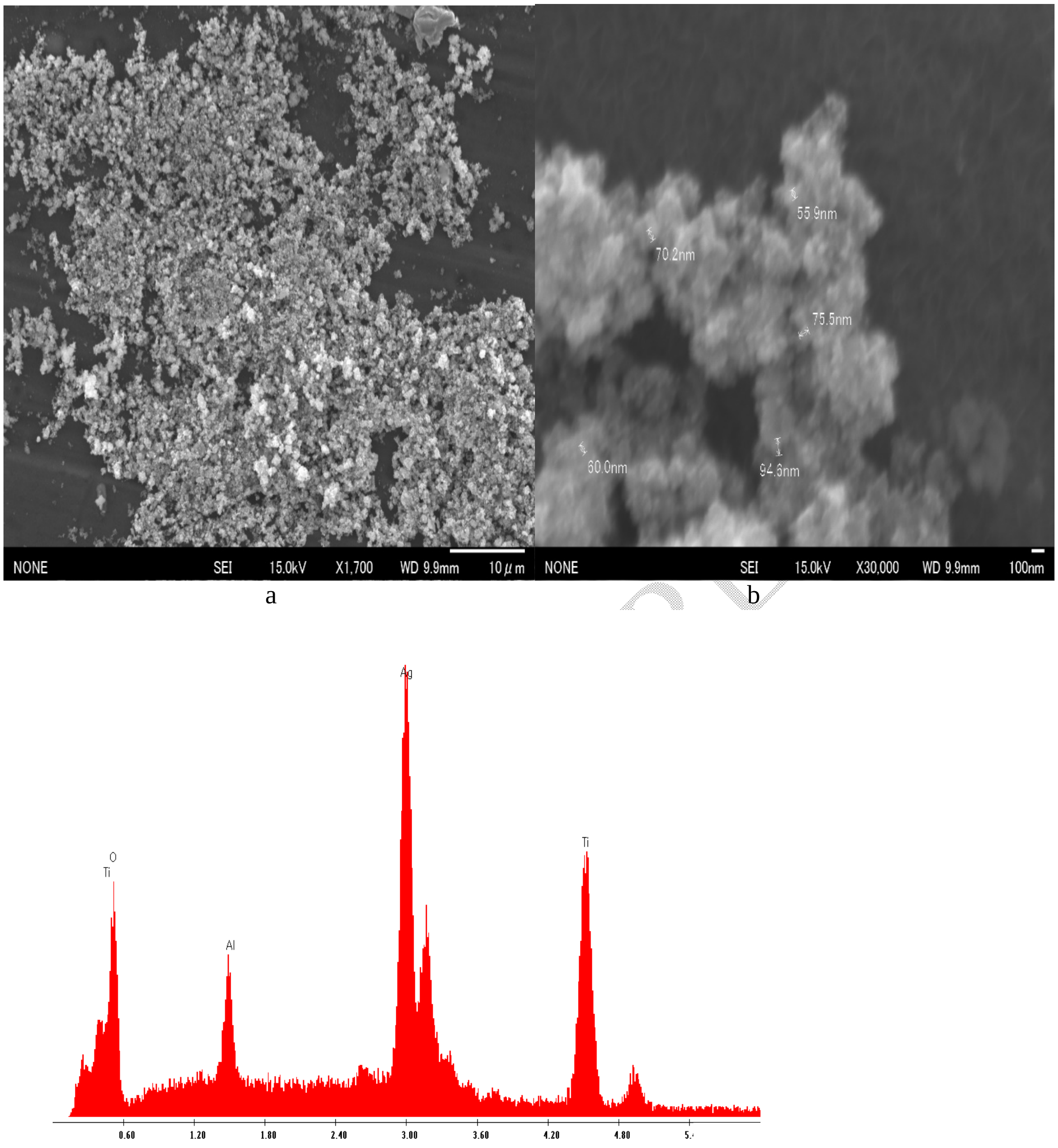

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Fig. 2.(a)(b) SEM image of the Al surfacefunctionalized with APTMS at pH 3 adjusted using dilute HNO_3; (c) point EDS pattern of the Al surface

Figure 3(a) denotes the SEM image of the Ag–TiO_2 NP adsorption on the Al surface with a boehmite layer. The energy dispersive EDS pattern in Figure 3(b) indicates that only Ag was adsorbed on the Al surface.

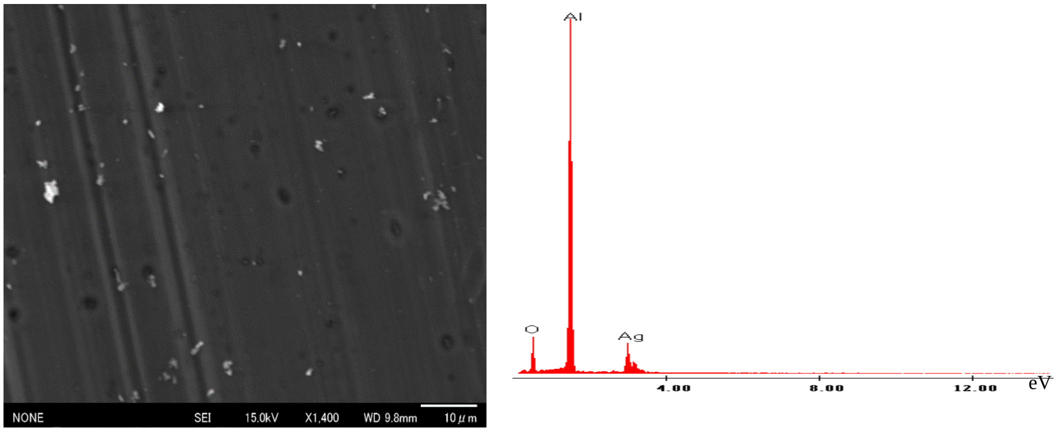

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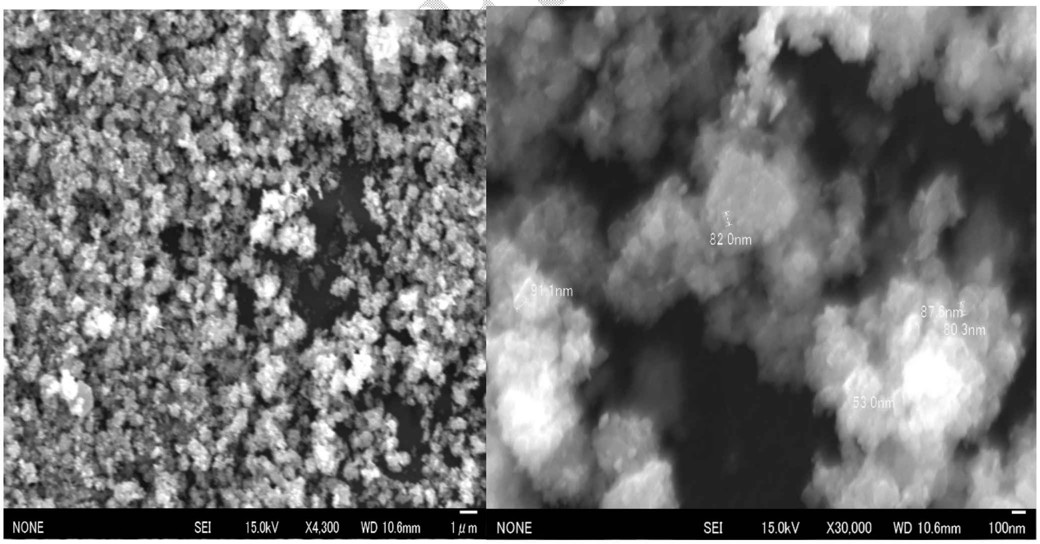
Fig. 3.(a) SEM image of the Al surfaceat pH 3 adjusted using dilute HNO_3, which coated by Ag-TiO_2 solution without copper ion. ;(b) point EDS pattern of the Al surface

Next,the Al surface with a boehmite layer that was immersed in a solution containing a mixture ofAg–TiO_2 and $Cu(NO_3)_2$was examined.Figure 4(a) shows the SEM image of the adsorption of Ag–TiO_2 NPs on the Al surface with the boehmite layer. Many Ag–TiO_2 particles were observed on Al surface. The energy dispersive EDS pattern in Figure 4(b) indicates that Ag–TiO_2 was adsorbed on the Al surface.



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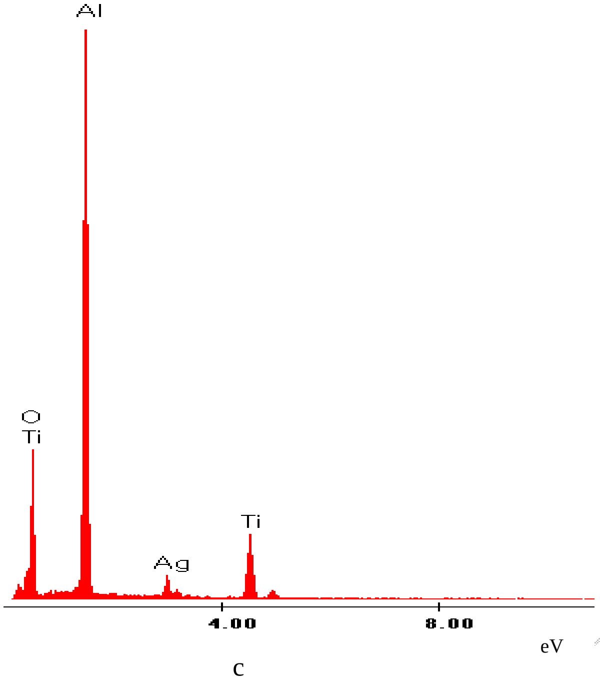

Fig. 4.(a)(b) SEM image of the Al surface at pH 3 adjusted using dilute HNO_3, which coated by aqueous Ag-TiO_2 solution including copper ion; (c) point EDS pattern of the Al surface.

As shown in Table 1, taking from the reference [~~15~~17], the Cu-citric complex ion is changed from a negative charge at pH 5–7 to a positive charge at pH 2–4. At pH 2–4, the Cu-citric complex ion is formed $[CuH_2C_6H_5O_7]^{+}$. However, an electron is released from Ag–TiO_2 surface. Then, the following reaction occur [Cu(Ligand)]+ e^{-} $\rightarrow Cu^{0}$ + Ligand^{-}.[~~15~~17]Cu prevents Ag present in Ag–TiO_2 surface from dissolving by the law of ionization tendency (Figure5).

Table 1. Citric Acid Complexes That Were Formed at Different pH Values and Their Dissociation Constants

p H	complex	Dissociation constant $(K_{dis})^{a}[L^{2}/mol^{2}]$
2-4	$[CuH_2C_6H_5O_7]^{+}$	1.0×10^{-6}
4-5	$[CuH_2C_6H_5O_7]$	1.0×10^{-7}
5-7	$[CuC_6H_5O_7]^{-}$	7.4×10^{-6}
7-11	$[Cu(OH)C_6H_5O_7]^{2-}$ $[CuC_6H_4O_7]^{2-}$	1.8×10^{-18} 1.5×10^{-16}
>11	$[Cu(OH)C_6H_4O_7]^{3-}$	1.8×10^{-18}

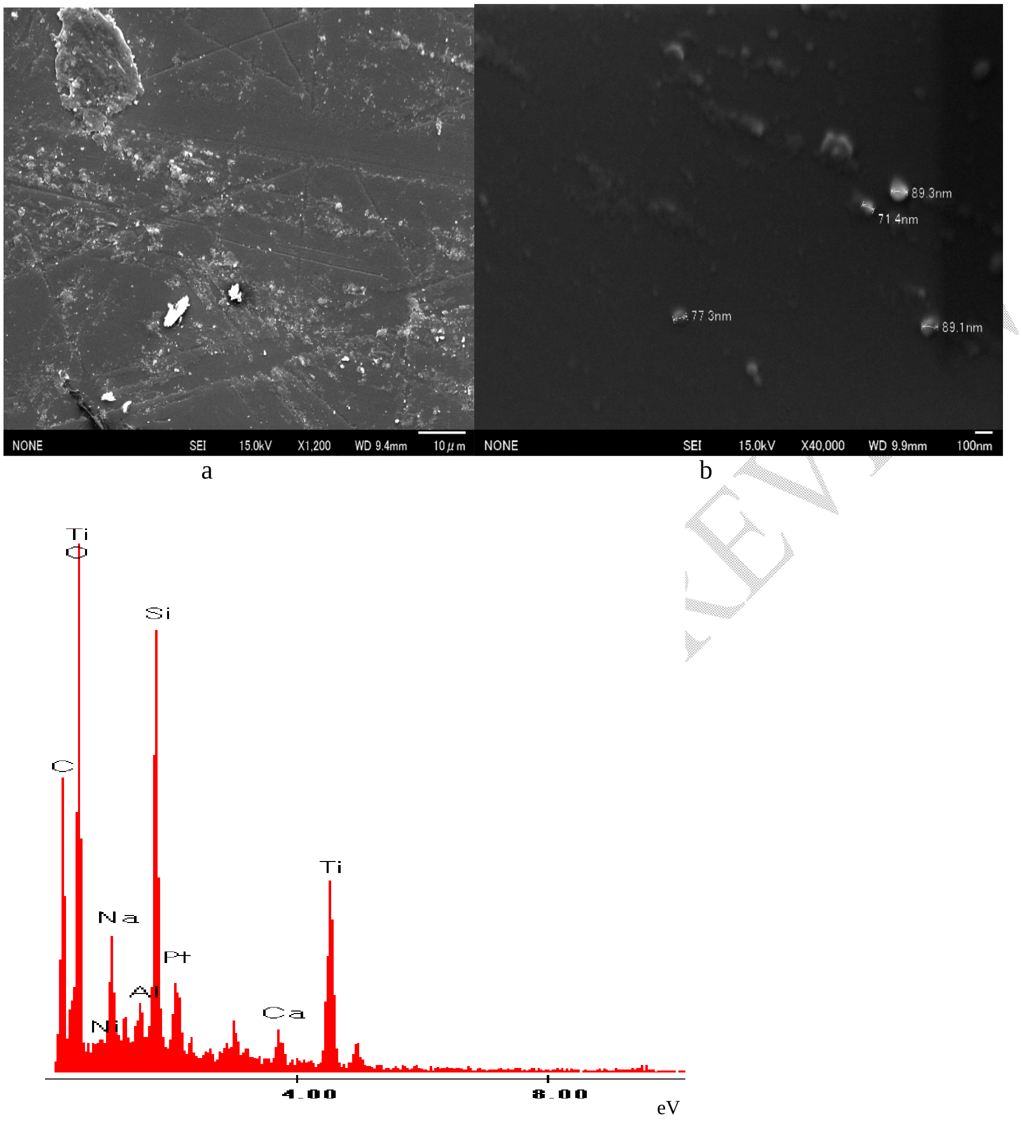

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Fig. 5.(a)(b) SEM image of the glass surface at pH 2 adjusted using dilute HNO_3, which coated by aqueous anatase(TiO_2) solution including copper ion; (c) point EDS pattern of the glass surface.

When HNO_3 was added to the solution, the morphology of the Cu-citric complex ion changed; the Cu-citric complex ion changes similar to the abovementioned reason. Several OH groups of the boehmite were present on the surfaceof the boehmite, which may serve as a proton conductor for the electrochemical reactions in aqueous environments.Cu donated its valence electrons to OH groups ($–OH_2^+$)and changed to Cu^{2+}. Then,the positively charged Ag–TiO_2 bonded to boehmite.Furthermore, Cu^{2+} was recovered by citric acid and became $[CuC_6H_5O_7]^-$.The color of the mixed solution before adding HNO_3 was deep brown; after adding HNO_3, the solution first turned light green, and after leaving turned deep brown when the solution was recovered,whichreason is considered for gradual recovery of the solutions' original color of dark blue ($[CuC_6H_5O_7]^-$) from light blue ($[CuH_2C_6H_5O_7]^+$)(Figure6) [~~15~~17].

a b

Fig.6. The color of the mixed solutionincludingCu-citric complex ion.
(a)The color of the mixed solution before adding HNO_3(b)The color of the mixed solution after adding HNO_3

Thus, the Ag–TiO_2 NPs can be deposited on the surfaces at either pH = 3 or 2.This suggests that Ag–TiO_2 was bonded to boehmite.

Next, coating anatase TiO_2 on an ATMPS-functionalized glass surface was examined. The surface isoelectric point of anatase $TiO_2$was observed at a pH = 6 [~~16~~18]. Hence, under more acidicconditions, hydrogen ions were adsorbed on the OH groups, resulting in a buildup of positive charges. Conversely, under alkaline conditions, the OH groups dissociate from the surface, resulting in a buildup of negative charges. Hence, anatase TiO_2 will be stably dispersed in a strong acidic solution with a pH = 2 or less [~~17~~19]. However, the anatase TiO_2 NPs were found to slightly deposit on the glass surfaces at a pH = 2.In this case, protons in the surface SiAOH groups were not detached, and a complete negatively charged surface was not created, which was incapable of attracting positively charged TiO_2 NPs.[~~18~~20].Therefore, the ATMPS-functionalized glass surface was immersed in a solution containing a mixture ofanataseTiO_2 and $Cu(NO_3)_2$. However, TiO_2that were not coated by Ag cannot irradiate electron.Figure 5(a) illustrates the SEM image of the adsorption of TiO_2 NPs on the glass surface. The energy dispersive EDS pattern in Figure 5(b) indicates that TiO_2 was adsorbed on the APTMS-modified glass surface as some TiO_2 NPs were observed.

Next, Ag–TiO_2 was used instead of TiO_2. The ATMPS-functionalized glass surface was immersed in a solution containing a mixture of Ag–TiO_2 and $Cu(NO_3)_2$. Figure 7(a) shows the SEM image of Ag–TiO_2 NP adsorption on the glass surface. The energy dispersive EDS pattern in Figure 7(b) indicates that Ag–TiO_2 was adsorbed on the APTMS-modified glass surface. A considerable amount of Ag–TiO_2 NPs was observed on the surface.Because negative charge accumulates around the positively charged APTMS due to electron released from Cu,such as the reason before .Therefore, positively charged Ag–TiO_2 was deposited on glass surface.For comparison,Figure 7(c) shows the SEM image of Ag–TiO_2 NP adsorption on the glass surface immersed in a solution that does not contain $Cu(NO_3)_2$. Ag-TiO_2NPdeposits were few.

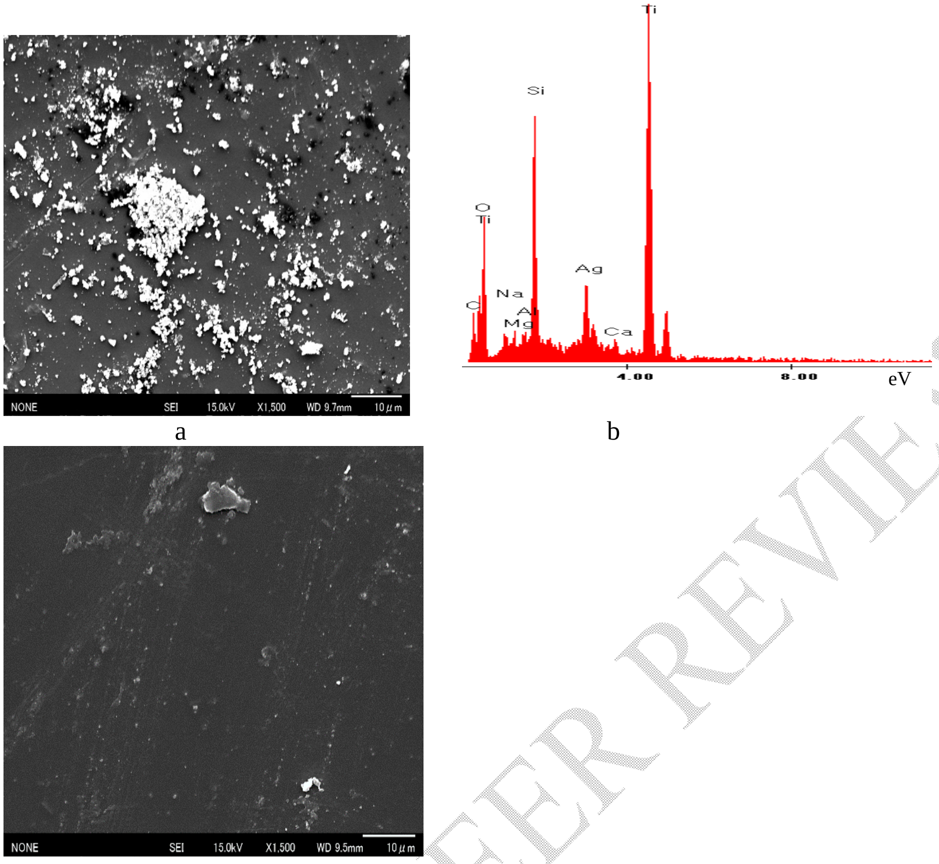

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Fig. 7. (a) SEM image of the glass surface at pH 2 adjusted using dilute HNO_3, which coated by Ag-TiO_2 solution including copper ion; (b) point EDS pattern of the glass surface;(c) SEM image of the glass surface at pH 2 adjusted using dilute HNO3, which coated by Ag-TiO2 solution without copper ion.

4. Conclusions

In this study, TiO_2 and Ag–TiO_2were adsorbed on Al and glass surfaces using a solution containingCu ions. The Cu ionsenhanced the adsorption of Ag–TiO_2on Al and glass surfaces.Negative charge accumulates around the positively charged APTMS by irradiation electron from Ag-TiO2. And Cu acts not to dissolve Ag form Ag-TiO2 surface by law of ionization tendency, such as the reason before. This can be attributed to the buildup of negative charges, which occurred after the addition of $HNO_3$to the solution as a result of its reaction with Cu.Producing substrates that have localized surface plasmon resonance and antibacterial effects is easy using this method.

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