



# Coating Ag on an Anatase TiO<sub>2</sub> Surface and Adsorption on a 3-Aminopropyltrimethoxysilane-Modified Al or Glass Surface

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## Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

## Article Information

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## ABSTRACT

In this study, Ag–TiO<sub>2</sub> was synthesized by reducing AgNO<sub>3</sub>. AgNO<sub>3</sub> and anatase TiO<sub>2</sub> nanoparticles (NPs) were boiled with sodium citrate, resulting in the reduction of Ag. Ag was used to coat the anatase TiO<sub>2</sub> NP surfaces. At this stage, the assembly reaction on the anatase TiO<sub>2</sub> surface was incomplete. The acidity with pH 4 or less was subsequently adjusted using dilute HCl. After processing, Ag was distributed over the entire surface of anatase TiO<sub>2</sub>. Furthermore, the synthesized Ag–TiO<sub>2</sub> could be adsorbed on an Al or glass surface using 3-aminopropyltrimethoxysilane. Al plates were used to create a substrate exhibiting surface-enhanced Raman scattering activity, and Raman intensity was measured for pyridine. Ag remained stable on the TiO<sub>2</sub> surface for over five months. The proposed method, which is cost effective and simple, can be used to prepare materials for studying the environment and so on.

**Keywords:** Energy dispersive X-ray spectroscopy; 3-aminopropyltrimethoxysilane; al; glass; Ag–TiO<sub>2</sub> nanoparticles.

## 1. INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) is frequently used in several applications. It usually exists in one of

the following three forms: anatase, rutile, or brookite. In photocatalytic studies, anatase TiO<sub>2</sub> can be observed to be more active than rutile TiO<sub>2</sub> [1] [2]. Furthermore, the photocatalytic

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activity of TiO<sub>2</sub> was observed to improve in Ag-doped TiO<sub>2</sub> nanoparticles (NPs). Ag-doped TiO<sub>2</sub> has more applications than TiO<sub>2</sub> (e.g., as a photocatalyst, in solar cells, for increasing antibacterial efficiency, and for sterilization) [3–9]. The photocatalytic efficiency of TiO<sub>2</sub> can be improved by adding transition metals, thereby extending its absorption into the visible-light region. With regard to its bactericidal action, Ag doping in TiO<sub>2</sub> not only extends its photocatalytic capability into the visible-light region but also increases its disinfection capability [6] [8]. Surface-enhanced Raman scattering (SERS) is better than other detection techniques for pollutant detection because it provides sensitivity, selectivity, cost-effectiveness, and single-molecule detection. TiO<sub>2</sub> exhibits weak SERS activity, whereas Ag NPs exhibit high SERS activity [10–12]. The methods for synthesizing Ag–TiO<sub>2</sub> include photoreduction reaction [3] [4], sol–gel method [5], hydrothermal method [6], reduction method [7] [8], and electron beam evaporation [9]. The photoreduction reaction method requires a particular ultraviolet (UV) light. Other methods require several processes and considerable amount of processing time. Further, it is desirable to develop an easy and quick method for synthesizing Ag–TiO<sub>2</sub>. A highly sensitive and reusable SERS substrate can be produced using immobilized Ag–TiO<sub>2</sub> NPs on an Al or glass surface.

This study intends to develop an easy and quick method for synthesizing Ag–TiO<sub>2</sub> without employing special equipment. The results of this study indicate that the proposed method can be used to achieve simple and easy synthesis. Furthermore, this study aims to immobilize Ag–TiO<sub>2</sub> NPs on Al or silica glass substrates, realizing the synthesis of a reusable SERS substrate for the study of environments.

## 2. Experimental

### 2.1 Preparation of the Ag–Anatase NP Solution

Anatase TiO<sub>2</sub> NPs were prepared using an aqueous anatase TiO<sub>2</sub> suspension (500 mL, 0.02%). This mixture was heated to the boiling stage under vigorous stirring for approximately 20 min before adding 5 mL of 1% aqueous AgNO<sub>3</sub> solution. Next, 5 mL of 1% sodium citrate was added after 5 min. Boiling was continued for approximately 5 min until the particle surfaces

turned black. The solution was subsequently adjusted to pH 2 or 3 by adding dilute HCl (or dilute HNO<sub>3</sub>).

### 2.2 Preparation of Ag–TiO<sub>2</sub> Adsorbed on Substrates

An Al plate was purchased and cleaned using deionized water, polished using a sponge file to remove grease from the Al surface, and washed again using deionized water. To form boehmite on the surface, the Al plate was boiled in deionized water for approximately 15 min and then functionalized by immersion in a 2% (v/v) aqueous 3-aminopropyltrimethoxysilane (APTMS) solution for 25 h at room temperature. The Al surface was dissolved by the APTMS solution because of its alkalinity (pH = 11). Therefore, to prevent this, the APTMS solution was neutralized using dilute HCl before being used to functionalize the Al substrate. The functionalized substrates were further rinsed using ultrapure water and annealed at 110°C.

The Ag–TiO<sub>2</sub> adsorbed on the substrates was prepared by the chemical assembly of the Ag–TiO<sub>2</sub> NPs on the APTMS-functionalized Al plates. These were subsequently immersed in an Ag–anatase TiO<sub>2</sub> NP solution for 50 h, which yielded a film of particles assembled on the APTMS-modified substrate.

*Glass Substrate.* Glass slides were ultrasonically cleaned in deionized water, isopropyl alcohol, acetone, and ultrapure water for 15 min each, followed by immersion in H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub>/30% NH<sub>4</sub>OH (5:1:1) for 6 h. The slides were further cleaned via sonication in ultrapure water for 20 min and then immersed in a 2% (v/v) aqueous APTMS solution for 24 h at room temperature for functionalization. The functionalized substrates were subsequently rinsed using ultrapure water and annealed at 110°C [13, 14]. These were then immersed in an Ag–anatase TiO<sub>2</sub> NP solution for 50 h. This yielded an assembly of a film of particles on the APTMS-modified substrate. The substrates were subsequently removed and kept at 150°C for 30 min.

### 2.3 Characterization

A few drops of 0.1-M pyridine, adjusted to 50 ml by dropping 0.39-ml pyridine in ultrapure water, were placed on an Al plate and covered using a glass slide, which was further sealed using a

Teflon tape. Raman spectra and images were obtained using a Raman system (NRS2100), a triple spectrometer equipped with a holographic notch filter, and a charge-coupled device detector. A solid-state laser (wavelength: 532 nm) was used for performing the Raman measurements. Furthermore, the power of the laser used on the sample was ~30 mW, and the diameter of laser spot was ~4  $\mu\text{m}$ .

Scanning electron microscopy (SEM) images were obtained using a field emission microscope (JSM6500F) operated at an accelerating voltage of 15 kV.

Furthermore, transmission electron microscopy (TEM) images were obtained using a field emission transmission electron microscope (HD-2300C) operated at an accelerating voltage of 200 kV. The APTMS and all the remaining reagents were of analytical reagent grade.

### 3. RESULTS AND DISCUSSION

The anatase  $\text{TiO}_2$  NPs were obtained from anatase  $\text{TiO}_2$  (Kanto CHEMICAL CO.INC, Japan). The particle diameter of the anatase  $\text{TiO}_2$  used in this study was 100–300 nm. The particle size decreases as the particles collide during boiling [15]. Therefore, the anatase  $\text{TiO}_2$  NPs were boiled for approximately 20 min before the addition of 1%  $\text{AgNO}_3$  and 1% sodium citrate. After approximately 3 min, the  $\text{TiO}_2$  particle surfaces turned black. Ag NPs appeared to assemble on the surfaces of the  $\text{TiO}_2$  particles. Fig. 1 depicts the TEM images of these particles (pH = 7). As seen in the X-ray spectroscopy (EDS) mapping image in Fig. 1(c), Ag NPs were adsorbed only on parts of the surfaces. Therefore, the suspension was adjusted to pH 3 using dilute HCl. Fig. 2 depicts the TEM images of the  $\text{TiO}_2$  particle surfaces at pH 3. As the EDS mapping image shows in Fig. 2(c), Ag NPs assemble on all the surfaces. Fig. 1(a) and 2(a) show TEM images of an anatase ( $\text{TiO}_2$ ) surface coated using Ag. In contrast to Fig. 1(a), Fig. 2(a) shows that the area where a heavy substance is present increases, the contrast is reduced, and many black particles are observed because of reduced permeability. From the EDS results, Ag is considered to be adsorbed on the particles. Furthermore, Fig. 1(b) and 2(b) show a high-angle annular dark-field image, where heavy atoms look brighter. Compared with Fig. 1(b), in Fig. 2(b), many bright particles are present because the part of  $\text{TiO}_2$  coating with Ag (whose atomic weight is higher than that of Ti) is heavy.

The isoelectric point of anatase  $\text{TiO}_2$  is pH = 6, and the  $\text{TiO}_2$  NPs are positively charged at pH = 5 and below [16, 17]. Figs. 3-7 show TEM images of an anatase ( $\text{TiO}_2$ ) surface coated using Ag at various pH. Reduced Ag NPs are spread over the surfaces of  $\text{TiO}_2$  NPs at pH  $\leq$  4. The reduction process of Ag NPs was performed using citric acid. Immediately after Ag seeds are formed in the initial reduction step, they form a complex with the citrate ions [18,19]. The silver citrate complex ion is an anion. Ag NPs were considered to have diffused on the  $\text{TiO}_2$  surface by electrostatic attraction when the surface of the  $\text{TiO}_2$  particles was positively charged at pH  $\leq$  5. Further, the pH of the suspension was adjusted using dilute HCl or  $\text{HNO}_3$ .

These Ag– $\text{TiO}_2$  NPs could be adsorbed on Al or glass surfaces. Because the Al surface dissolves at pH 2, the pH was adjusted to 3 using dilute HCl for the synthesis. Fig. 8(a) denotes the SEM image of adsorption of Ag– $\text{TiO}_2$  NPs on the APTMS-modified Al surface. The energy dispersive EDS pattern in Fig. 8(b) indicates that Ag– $\text{TiO}_2$  was adsorbed on the Al surface. Fig. 8(c) depicts the Raman spectra of  $\text{TiO}_2$ . The Raman shifts corresponding to anatase  $\text{TiO}_2$  were observed at approximately 144, 397, 519, and 639  $\text{cm}^{-1}$  [20–23].

The Raman intensity was measured with respect to pyridine. A few drops of 0.1-M pyridine, adjusted using ultrapure water, were dripped on an Al plate using a pipette and were then covered using a glass slide. Fig. 9 depicts the Raman spectra of the modified substrate exhibiting the most intense pyridine bands at 1,008 and 1,036  $\text{cm}^{-1}$  after the adsorption of pyridine onto the surface. The most intense pyridine bands at 1,008 and 1,036  $\text{cm}^{-1}$  exhibited almost similar intensities between 141 and 162 days after synthesis. After investigation, the Al substrate was washed using ultrapure water. The Al substrate was kept in a room without the requirement of any particular environment. This was indicated by the fact that Ag on the  $\text{TiO}_2$  surface remained stable for at least five months. When titanium oxide is irradiated with UV light, electron–hole pairs are formed, thereby simultaneously causing oxidation and reduction actions on the titanium oxide surface. Moreover, when titanium oxide is doped with metal ions, oxidation and reduction occurs in the visible range [24]. For comparison, the Ag NPs and anatase  $\text{TiO}_2$  NPs were adsorbed at separate regions on the Al substrate (see Fig. 10). Fig. 9(c) depicts the Raman spectra of this modified

substrate. The peak could not be observed because it was assumed that Ag NPs were oxidized in eight days. Therefore, Ag adsorbed

on the  $\text{TiO}_2$  surface is considered to maintain stability without any oxidation.

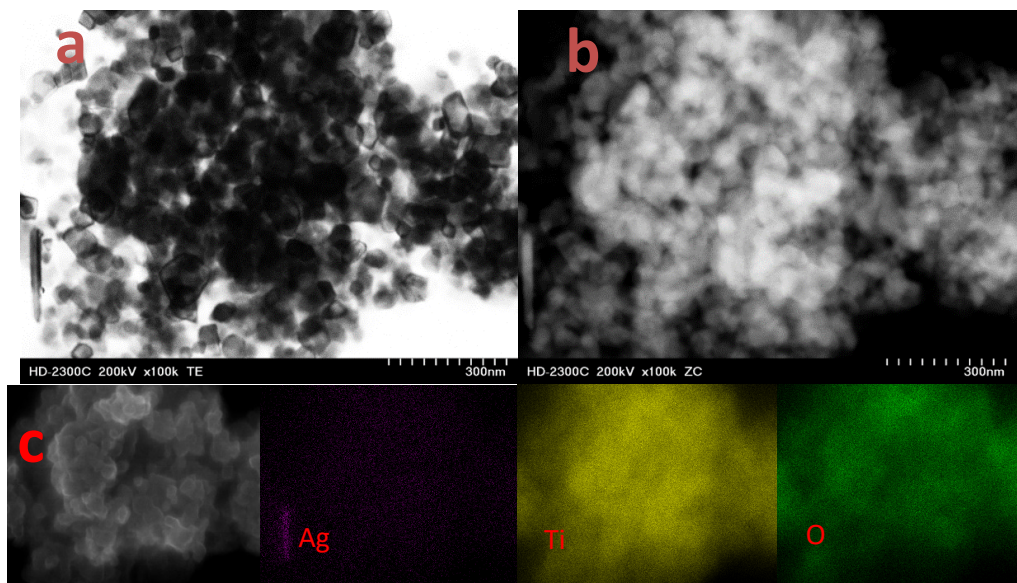


Fig. 1. (a) TEM images of an anatase ( $\text{TiO}_2$ ) surface coated using Ag at pH 7, (b) high-angle annular dark-field image of Ag- $\text{TiO}_2$ , (c) EDS mapping images (Ag, Ti, and O) of Ag- $\text{TiO}_2$

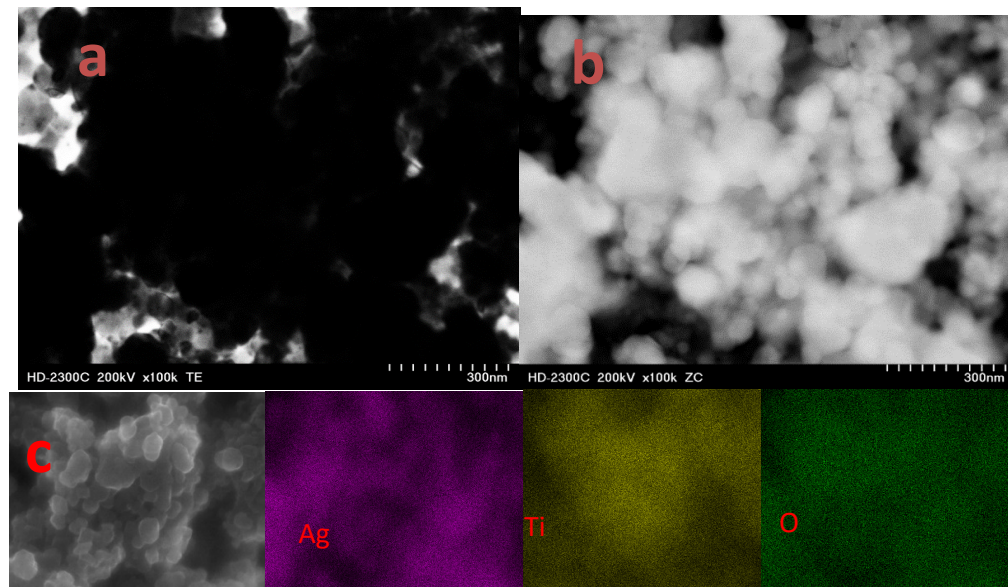
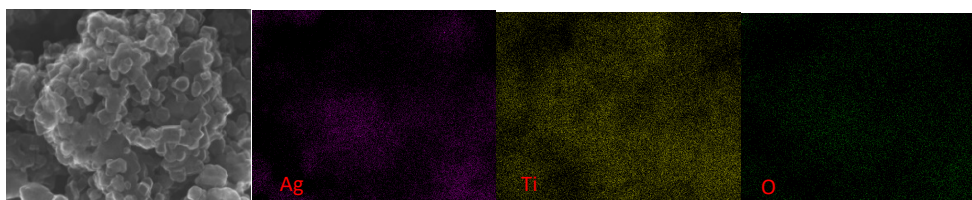
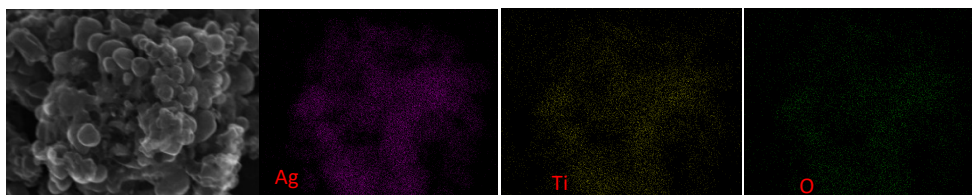


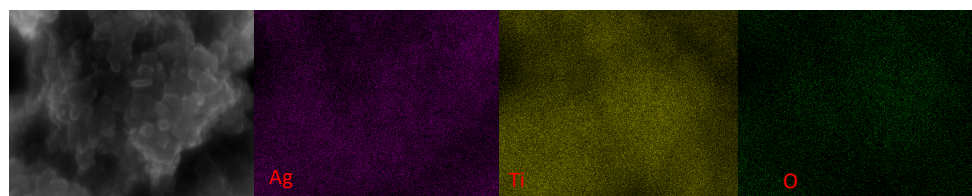
Fig. 2. (a) TEM images of an anatase ( $\text{TiO}_2$ ) surface coated using Ag at pH 3, adjusted using dilute HCl; (b) high-angle annular dark-field image of Ag- $\text{TiO}_2$ ; (c) EDS mapping images (Ag, Ti, and O) of Ag- $\text{TiO}_2$



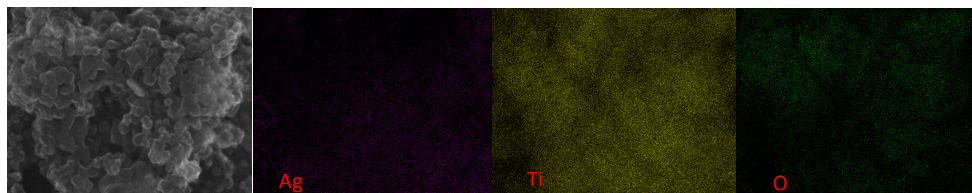
**Fig. 3.** EDX mapping images of (the element of Ag, Ti, O) of an anatase ( $\text{TiO}_2$ ) surface coated with Ag at pH = 4 adjusted by dil. HCl



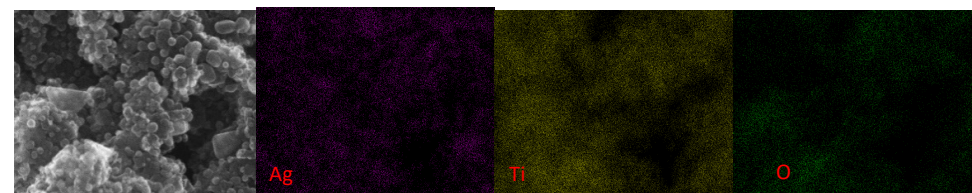
**Fig. 4.** EDX mapping images (the element of Ag, Ti, O) of an anatase ( $\text{TiO}_2$ ) surface coated with Ag at pH = 2 adjusted by dil. HCl



**Fig. 5.** EDX mapping images (the element of Ag, Ti, O) of an anatase ( $\text{TiO}_2$ ) surface coated with Ag at pH = 4 adjusted by dil.  $\text{HNO}_3$



**Fig. 6.** EDX mapping images (the element of Ag, Ti, O) of an anatase ( $\text{TiO}_2$ ) surface coated with Ag at pH = 3 adjusted by dil.  $\text{HNO}_3$



**Fig. 7.** EDX mapping images (the element of Ag, Ti, O) of an anatase ( $\text{TiO}_2$ ) surface coated with Ag at pH = 2 adjusted by dil.  $\text{HNO}_3$ .

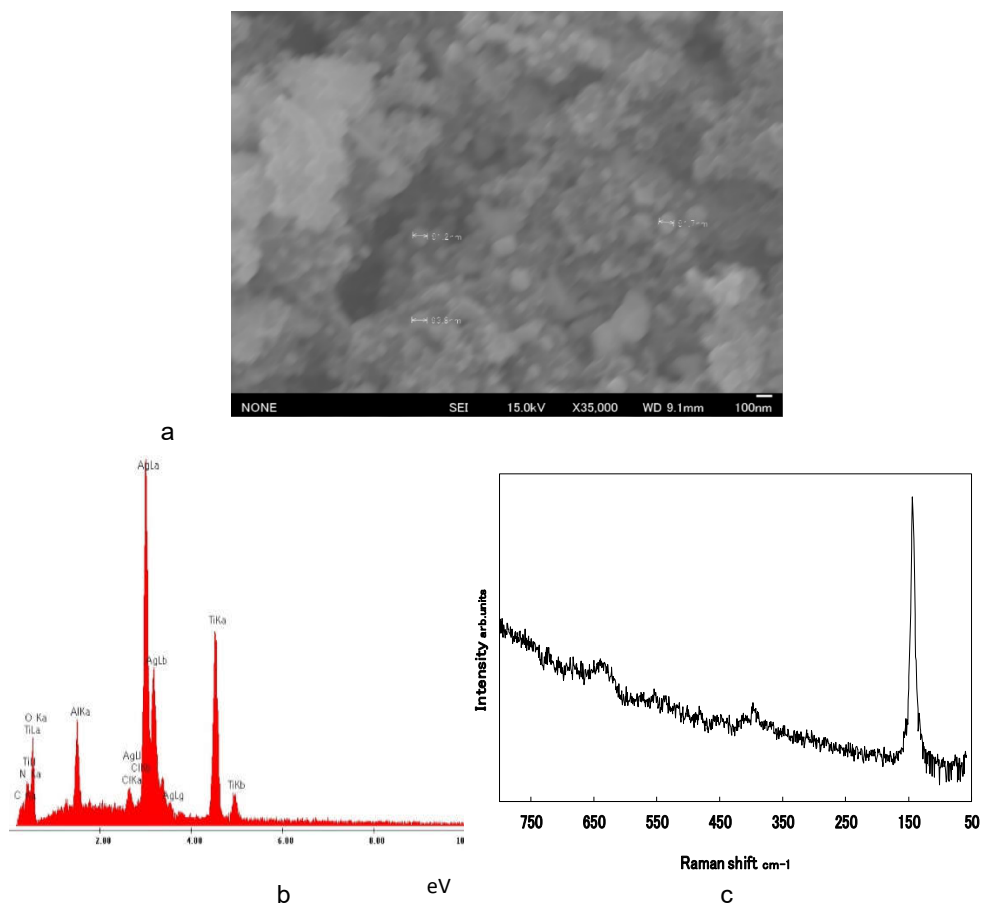


Fig. 8. (a) SEM image of the Al surface at pH 3 adjusted using dilute HCl; (b) point EDS pattern of the Al surface; (c) Raman spectra obtained from the Al surface

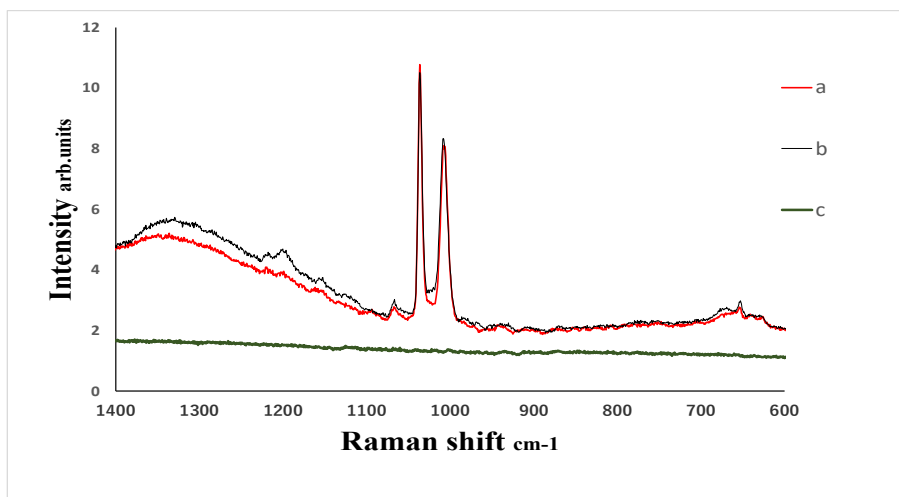
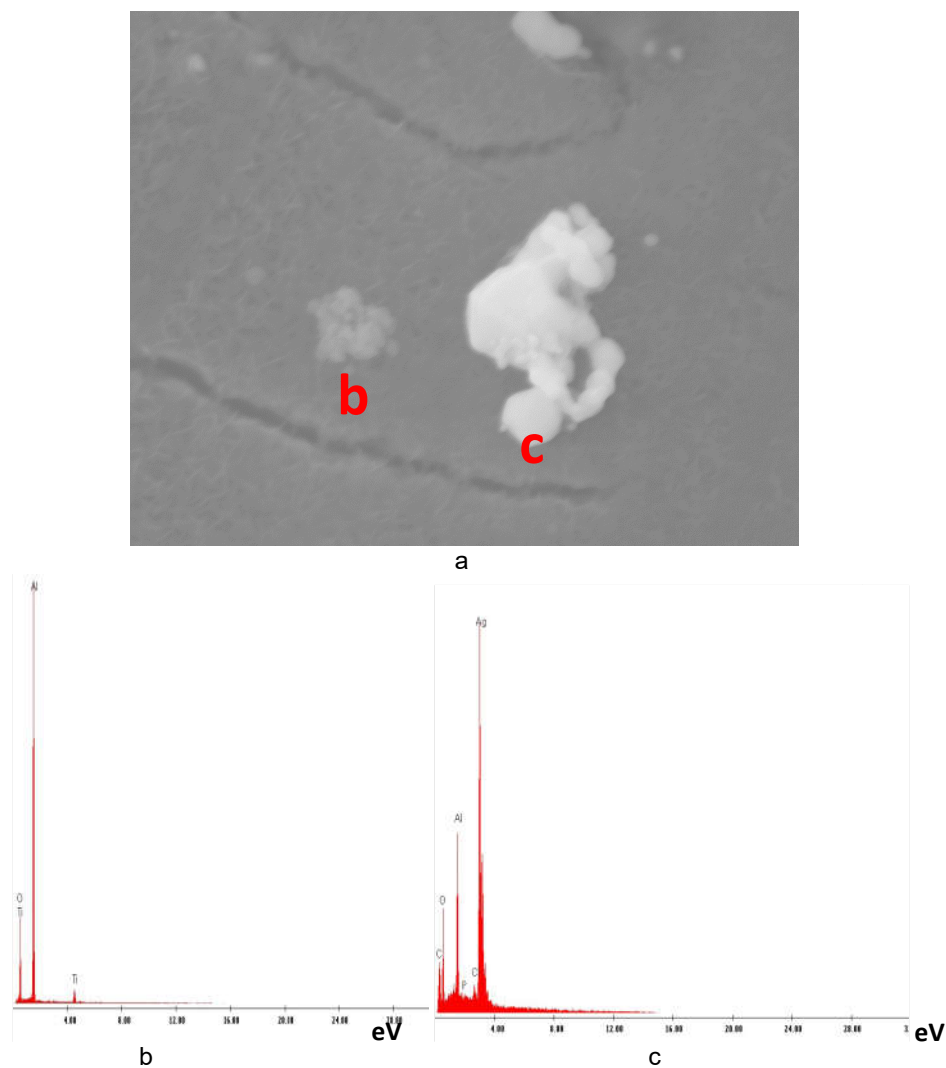


Fig. 9. SERS of pyridine—the SERS spectra obtained from the Ag-TiO<sub>2</sub>/Al substrates using pyridine as the probe molecule after (a) 141 and (b) 162 d; the SERS spectra of the substrates modified by Ag and TiO<sub>2</sub> NPs using pyridine as the probe molecule after (c) 8 d; the collection time was 20 s



**Fig. 10. SEM image of the substrates and point EDS pattern of the substrate. SEM image of the substrates. (a) Point EDS pattern of  $\text{TiO}_2$  adsorbed the substrate. (b) Point EDS pattern of Ag adsorbed the substrate. (c)**

If a drop of 0.1-M pyridine solution is cast on a SERS-active surface, a strong normal Raman signal overlapping with the SERS signal may be observed, and the experiment is therefore not conclusive. Therefore, the experiments have to be repeated with low pyridine concentrations. Fig. 11(a) shows the SERS spectra obtained from the Ag-TiO<sub>2</sub>/Al substrate using pyridine at different concentrations (0.1, 0.01, 0.001, and 0.0001 M). Moreover, the SERS substrate can prove to be reusable if the signals of the analyte disappear by proper washing. Therefore, after the investigation of 0.01-M pyridine, the Al substrate was washed using 0.1-M HCl to remove the pyridine and cleaned by sonication in

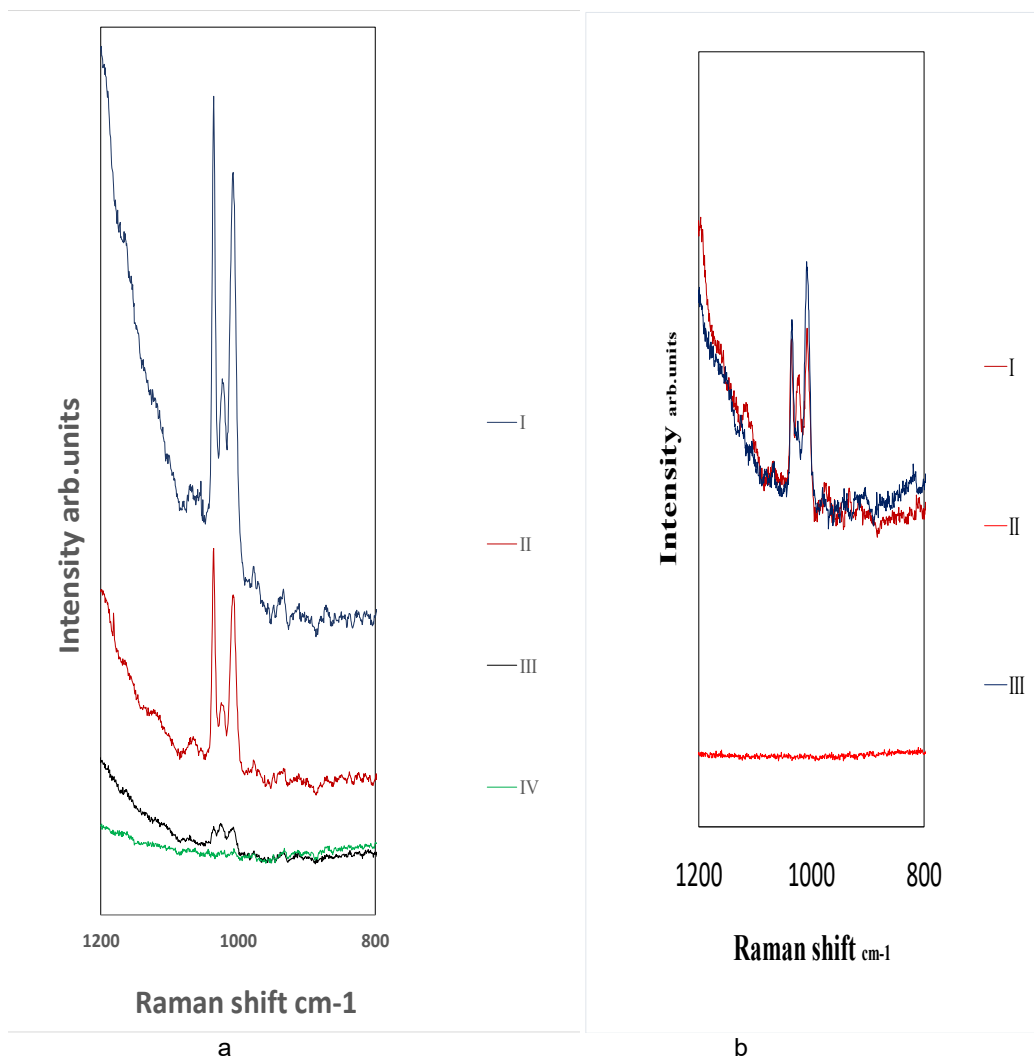
deionized water for 10 min. Fig. 11(b)II shows the SERS spectra obtained from the Ag-TiO<sub>2</sub>/Al substrate, and following this treatment, the Ag-TiO<sub>2</sub>/Al substrate signals disappeared. Next, the SERS spectra obtained from the same Ag-TiO<sub>2</sub>/Al substrate using 0.01-M pyridine was investigated once again, and the SERS signal was recovered.

Fig. 12(a) depicts an SEM image of adsorption on an APTMS-modified glass surface, where the pH was adjusted to 2 using dilute HCl for the synthesis. The EDS pattern in Fig. 12(b) indicates that Ag-TiO<sub>2</sub> was adsorbed on the glass surface. The glass surface also adsorbed

Ag–TiO<sub>2</sub> NPs whose pH was adjusted using dilute HNO<sub>3</sub> during synthesis.

This suggests that a highly sensitive and reusable SERS substrate with TiO<sub>2</sub> Ag NPs can

be produced using immobilized Ag–TiO<sub>2</sub> NPs on an Al or glass surface. This substrate can detect pollutants in the environment or succinic acid, which is a product of fumaric acid respiration in cancer cells [13].



**Fig. 11. (a) SERS of pyridine—the SERS spectra obtained from the Ag–TiO<sub>2</sub>/Al substrate using pyridine at different concentrations (0.1, 0.01, 0.001, and 0.0001 M) as the probe molecule; (I) 0.1 M, (II) 0.01 M, (III) 0.001 M, (IV) 0.0001 M. (b) The SERS spectra obtained from the Ag–TiO<sub>2</sub>/Al substrate using 0.01-M pyridine (I). Ag–TiO<sub>2</sub>/Al substrate (same substrate as that used for the investigation with 0.01-M pyridine) after washing with 0.1-M HCl and deionized water (II). SERS of pyridine—the SERS spectra obtained from the Ag–TiO<sub>2</sub>/Al substrate (following washing) with the reapplication of 0.01-M pyridine (III)**



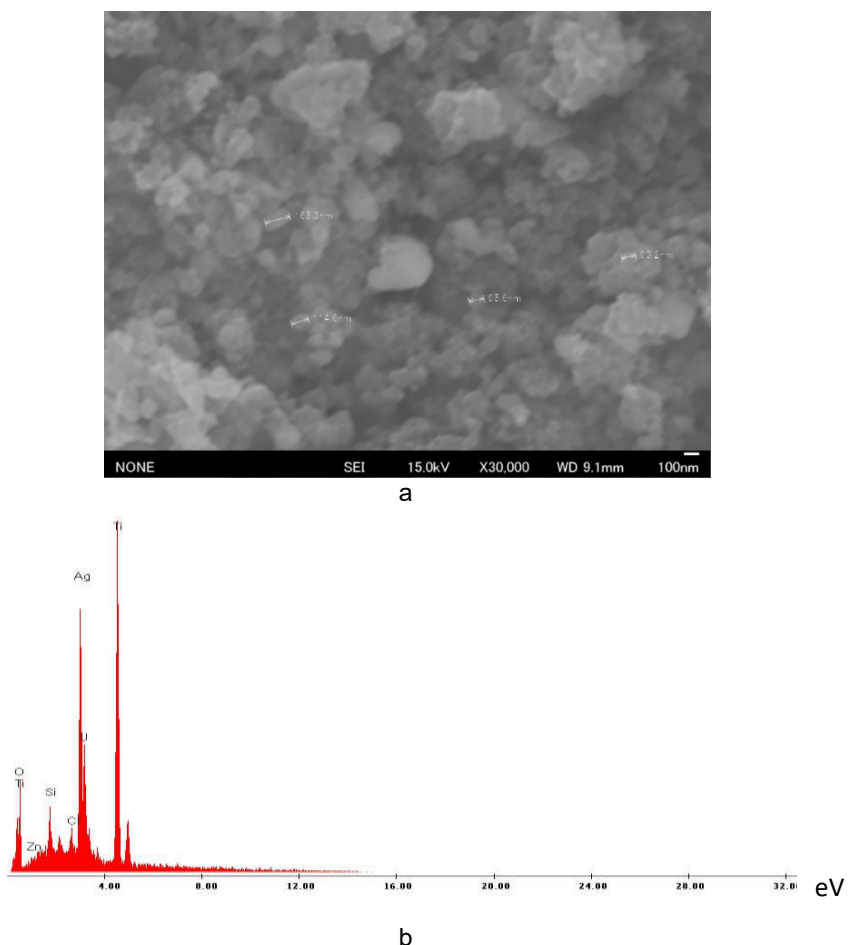


Fig. 12. (a) SEM image of the glass surface at pH 2 adjusted using dilute HCl; (b) point EDS pattern of the glass surface

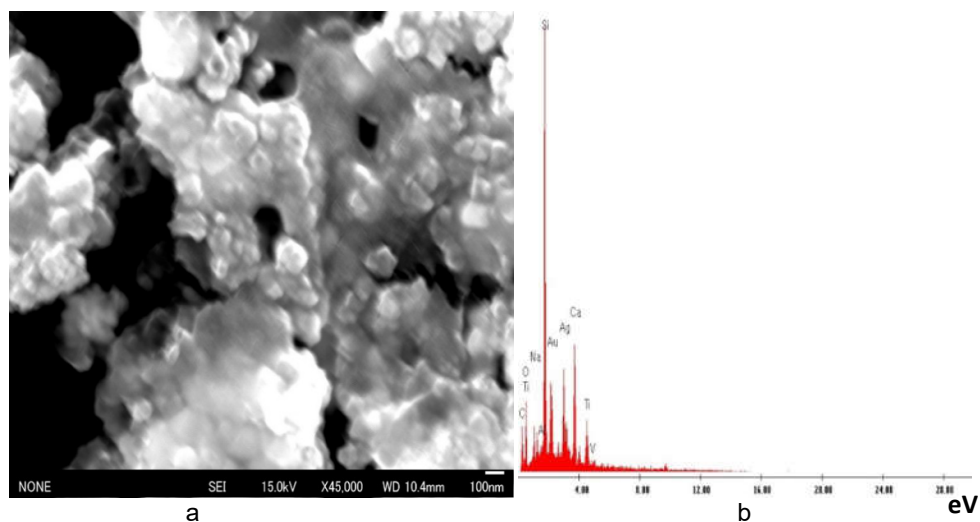


Fig. 13. (a) SEM image of the glass surface at pH 2 adjusted using dilute HNO<sub>3</sub>. (b) point EDS pattern of the glass surface.

#### 4. CONCLUSION

In this study, anatase TiO<sub>2</sub> NPs were prepared from anatase TiO<sub>2</sub> (Kanto Chemical Co. Inc.). The particle diameter of the anatase TiO<sub>2</sub> used in this study was 100–300 nm. In the case of the anatase TiO<sub>2</sub> NPs that were boiled for approximately 20 min, the final particle size was approximately 85 nm. The particle size decreased as the particles collided with each other during boiling. With the simultaneous addition of AgNO<sub>3</sub> and sodium citrate, Ag NPs were observed to reduce and assemble on the anatase TiO<sub>2</sub> NP surfaces. The pH was further adjusted to 4 or less, resulting in Ag assembly over the entire surface. The Ag–TiO<sub>2</sub> NPs could be adsorbed on the Al or glass surfaces. This substrate remained stable for more than five months.

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#### COMPETING INTERESTS

Author has declared that no competing interests exist.

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