



Stabilizing Ag Nanoparticles Using Anatase TiO₂ and Cu on Al Surface

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Author's contribution

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

Article Information

DOI: 10.9734/AJOPACS/2020/v8i430123

Editor(s):

- (1) Prof. Luigi Casella, Università di Pavia, Italy.
(2) Dr. Natt Makul, Phranakhon Rajabhat University, Thailand.

Reviewers:

- (1) Nidia García González, Tecnológico de Estudios Superiores de Jocotitlán, Mexico.
(2) Thamer Mutlag Jasim, Al Hady College University, Iraq.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/62625>

Received 25 August 2020

Accepted 31 October 2020

Published 12 November 2020

Original Research Article

ABSTRACT

Chemical adsorption of anatase TiO₂, silver nanoparticles (Ag NPs), and Cu particles (Cu Ps) on aluminum (Al) surface yielded an active surface-enhanced Raman scattering (SERS) substrate. TiO₂ is known to reduce both silver (Ag) and copper (Cu). In an oxidizing environment, Ag NPs remain unoxidized since Cu has a more negative redox potential than Ag. Ag is therefore protected by Cu from getting oxidized. Although Ag NPs exhibit better SERS activity than Au NPs, Ag is relatively easier to oxidize, limiting the development of Ag-based nanomaterials. Therefore, despite the poor SERS activity of Au nanoparticles than that of Ag nanoparticles, Au nanoparticles have been widely used. Herein, the stabilization of Ag nanoparticles by incorporating a reductive process using anatase TiO₂ is reported. The fabricated substrates bearing anatase, Ag NPs, and Cu Ps were stable, as seen by Raman spectra, and remained unchanged for more than 2 months.

Keywords: SERS; Raman; APTMS; Al; TiO₂ Ag nanoparticles.

1. INTRODUCTION

Titanium dioxide (TiO₂) is frequently used in a wide range of applications, including

decontamination, sterilization, and deodorization, and in the removal of NO_x gases, among others. Moreover, nanosized TiO₂ can be applied in photocatalysts, solar cells, and gas sensors,

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among others. TiO₂ usually exists in one of the following 3 forms: anatase, rutile, or brookite. In photocatalytic studies, anatase is generally more active than crystalline rutile [1-9]. It has also been experimentally found that Ag particles in Ag-doped TiO₂ increase the bactericidal efficiency of the TiO₂ by acting as electron traps. [8] This study aims to immobilize a mixture of Ag and TiO₂ NPs on Al substrate, while keeping the Ag NPs stable to oxidation. However, the 2 sets of NPs were seen to adsorb at disparate regions on the Al substrate. Therefore, Cu Ps were added to the mixture. In this case, the Ag and anatase TiO₂ NPs assembled on the surface of the Cu Ps. The anatase TiO₂ NPs reduced not only Ag⁺ to Ag⁰ but also the Cu. [10] Herein, a mixture of anatase TiO₂, Ag and Cu particles was adsorbed onto an aluminum plate.

Surface-enhanced Raman scattering (SERS) is a useful technique for the structural analysis of trace substances and has been recently used to study the effects of surface plasmons on both Au and Ag NPs [11-16]. Herein, Al plates were used to create a substrate with SERS activity, and the Raman intensity was measured with respect to pyridine [11,12]. SERS is observed because the metal NPs are coordinated by the pyridine through the lone pair on the nitrogen. Raman shifts were observed at approximately 1036 and 1008 cm⁻¹ when pyridine was adsorbed on the prepared substrates [11,17].

Ag is prone to oxidation and has only a limited use in the development of nanomaterials [18]. The development of stable Ag NPs is necessary to make advances in the field of chemical analysis. Methods to stabilize Ag NPs have already been developed using thiols or through the electrolytic polymerization of poly(2-vinylpyridine) [11,18]. Previously, a research based on the electrolytic polymerization using poly(2-vinylpyridine) was reported [11]. However, electrolytic polymerization cannot be used in the stabilization of Ag NPs that are immobilized on glass and other nonmetals. Herein, the SERS activity of the substrate was used to monitor the stabilization of Ag NPs on an Al substrate through reduction by anatase. The substrate remained unchanged for more than 2 months after coating with Ag NPs, Cu, and anatase TiO₂, suggesting that it is possible to maintain the SERS activity of unstable Au NPs by association with anatase TiO₂.

2. MATERIALS AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

3-aminopropyl trimethoxysilane (APTMS) and all other reagents were of analytical reagent grade. The electrostatic potential on a surface, zeta potential, is an important factor for the synthesis of TiO₂ NPs because if 2 approaching particles are sufficiently repelled by their surface charges, they will remain in a state of dispersion. Anatase TiO₂ can be dispersed in a strongly acidic medium at a pH of 2 or less and the particles do not cohere [19,20]. However, an Al surface dissolves at a pH of 2 or less, and resultantly, it was found that a pH of 3 was the optimum pH to adsorb anatase onto an Al surface without particle coherence.

2.1 Preparation of the Anatase NP Solution

Anatase TiO₂ NPs were synthesized using aqueous anatase TiO₂ solution (500 mL, 0.02%) adjusted to pH 3 by dilute HCl. The solution was then heated boiling under vigorous stirring for about 20 min, as the particle diameter can be changed by increasing the boiling time [21].

2.2 Preparation of SERS-active Substrates

SERS-active substrates were prepared by the chemical assembly of Ag NPs on APTMS-functionalized Al plates [11,12].

Ag NPs were synthesized according to a known method [11,12]. An aqueous AgNO₃ solution (200 mL, 0.01%) was heated to boiling under vigorous stirring, and aqueous trisodium citrate solution (1.0 mL, 1%) was added. The color of the solution changed within several minutes. The yellow solution was then used for future chemical assembly (solution 1).

The Cu citrate complexes were synthesized according to the same procedure using Cu instead of Au. Aqueous Cu(NO₃)₂ solution (100 mL, 0.01%) was heated to boiling with vigorous stirring, and aqueous trisodium citrate solution (1.0 mL, 1%) was added. The resulting solution was heated with further stirring for 15 min (solution 2). The color of the solution changed to blue after several minutes.

Al plate was cleaned by boiling in deionized water for approximately 15 min and then functionalized by immersion in a 2% (v/v) aqueous APTMS solution that had been neutralized using dilute HCl for 25 h at room temperature. It was found that the APTMS solution was alkaline with a pH of 11, which dissolved the Al surface. Therefore, to prevent this, APTMS solution was neutralized by dilute HCl and then used to functionalize the Al substrate [11].

The functionalized substrates were then rinsed with ultrapure water and annealed at 110°C before they were immersed in a mixture of solution 1: solution 2: anataseTiO₂ NPs solution (2:1:1) for 50 h (adjusted to pH 3 by dilute HCl). This yielded a substrate with a film of particles assembled on the APTMS modified substrate.

Another substrate: An Al plate was cleaned by boiling in deionized water for approximately 15 min. After the Al plate became boehmite, it was immersed in a mixture of solution 1: solution 2: anataseTiO₂ NPs solution (2:1:1) for 50 h (adjusted to pH 3 by dilute HCl).

Glass substrate: The glass slide was ultrasonically cleaned in deionized water, isopropyl alcohol, acetone, and ultrapure water, each for 15 min, followed by cleaning in H₂O:H₂O₂:30% NH₄OH (5:1:1) for 3 h. The slides were further cleaned by 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. Dilute HCl was added to adjust the pH to 2 during the coating process.

2.3 Characterization

Raman spectra were obtained using a Raman spectrophotometer (JASCO NRS-2100), a triple-spectrometer instrument equipped with a holographic notch filter, and a charge-coupled device detector. A solid-state laser ($\lambda = 532$ nm) was used for the Raman measurements at a power of approximately 21 mW with a spot size of approximately 4 μ m in diameter. Scanning electron microscope (SEM) images were obtained using a field emission microscope (JSM6500F) operated at an accelerating voltage of 15 kV.

3. RESULTS AND DISCUSSION

It is known that Ag particles in Ag-doped TiO₂ increase the bactericidal efficiency of TiO₂.

Moreover, anatase TiO₂ can reduce Ag⁺ to Ag⁰. Therefore, adsorbing both Ag and anatase NPs at the same place on an Al substrate would be beneficial to increasing the stability of the Ag NPs. Here, the Al plate was cleaned and functionalized with APTMS as described above. However, immersion of the substrate in a 1:1 solution of Ag NPs/anatase TiO₂ NPs for 50 h (adjusted to pH 3 by dilute HCl) yielded an uneven coating. The Ag and anatase TiO₂ NPs were adsorbed at separate regions on the Al substrate.

In the second experiment, the immobilization of both Cu and anatase TiO₂ NPs at the same place on an Al substrate was attempted. The substrate was cleaned and functionalized as before and then immersed in a 1:1 solution of Cu Ps/anatase TiO₂ NPs for 50 h (adjusted to pH 3 by dilute HCl). Fig. 1 shows an SEM image of the substrate and the point EDS pattern clearly show that the TiO₂ NPs are located on the Cu Ps. Also, it could be identified nanoparticles on the particle from this SEM image, too.

To characterize the uniformity of the surface SERS signal, Raman experiment was performed following adsorption of pyridine onto the surface. Fig. 2 shows the Raman spectra of the substrates, using the most intense pyridine bands at 1008 and 1036 cm⁻¹. [11] The intensity of the symmetric ring stretching modes is at 1008 cm⁻¹, and the intensity of the pyridine ring is at 1036 cm⁻¹. Fig. 3 shows that the Raman intensity from the Cu/TiO₂/Al substrate was very low.

Having established that the TiO₂ NPs adsorb onto the Cu Ps, a further experiment to include Ag NPs was attempted using a similar procedure. SEM was used to characterize the SERS substrate, and Fig. 3 shows the image and the EDS result. As SEM image shows some nanoparticles on particles. It appears that the Ag NPs and anatase TiO₂ NPs are both assembled onto the Cu Ps.

Anatase TiO₂ is known to reduce Ag⁺ to Ag⁰, but it can also reduce Cu. The redox potential of Cu is more negative than that of Ag. Therefore, when exposed to an oxidizing environment, Cu is preferentially oxidized before Ag. Therefore, the anatase protects the Ag⁰ from any oxidation. Fig. 4 shows the Raman spectra of the modified substrate using the most intense pyridine bands at 1008 and at 1036 cm⁻¹ after pyridine was adsorbed onto the surface. The intensity of the

symmetric ring stretching modes at 1008 cm^{-1} did not change, even after more than 2 months. However, the intensity was found to drop to half in 93 days.

The intensity of the symmetric ring stretching mode is 1008 cm^{-1} and the intensity of the

pyridine ring mode is 1036 cm^{-1} . [11] Fig. 5 shows the reproducibility of the SERS spectra obtained from the Ag, Cu, TiO_2/Al substrate after 68 days. The average spectrum and standard deviations have been calculated from the spectra in Fig. 5 and are shown in Table 1.

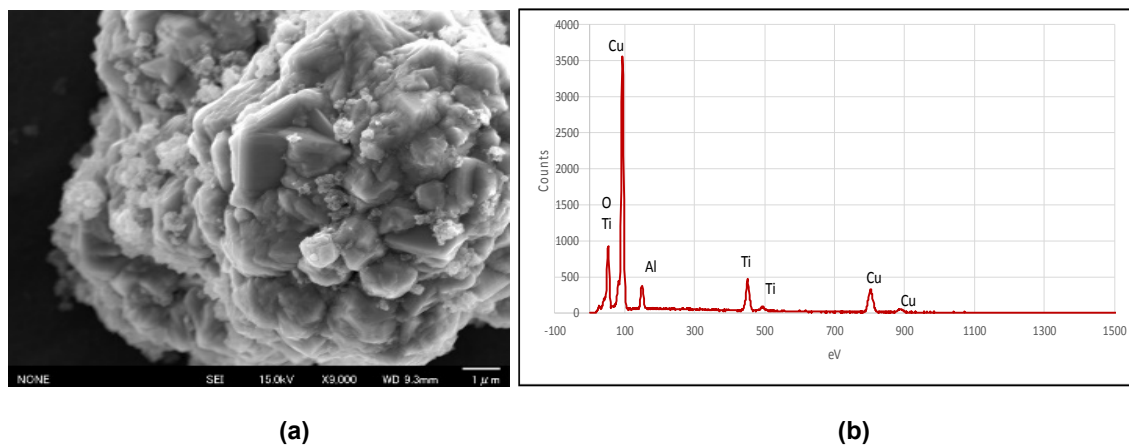


Fig. 1. SEM image of the substrates and point EDS pattern of the substrate. SEM image of the substrates. ($\times 9000$) (a) Point EDS pattern of the substrate. (b)

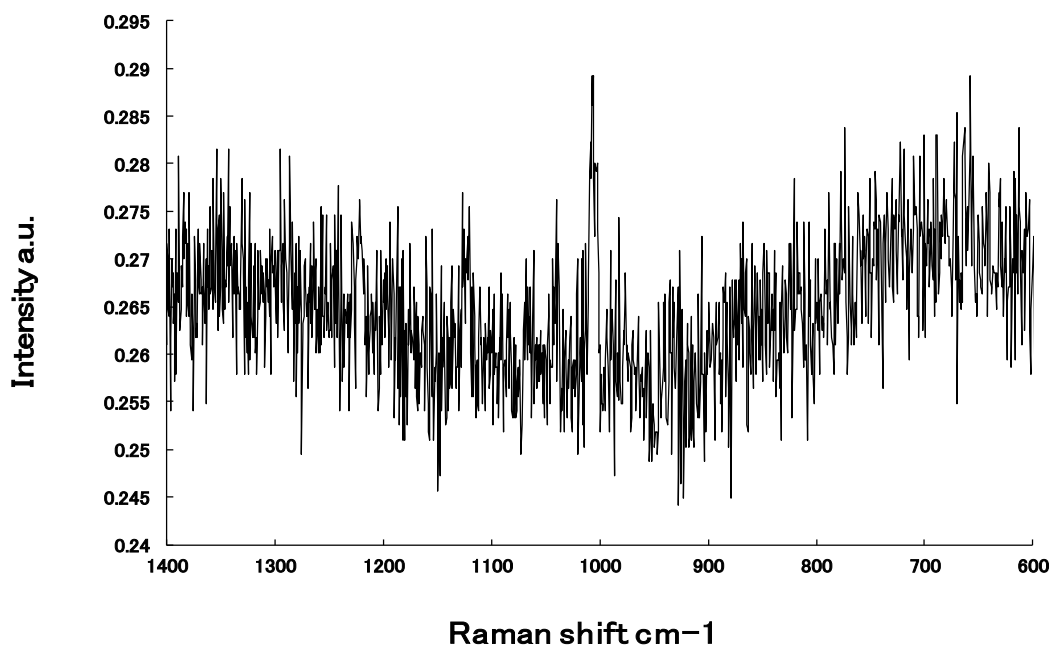


Fig. 2. SERS of pyridine
SERS spectra obtained from the "Cu, TiO_2/Al substrates" using pyridine as the probe molecule. The collection time was 20 s

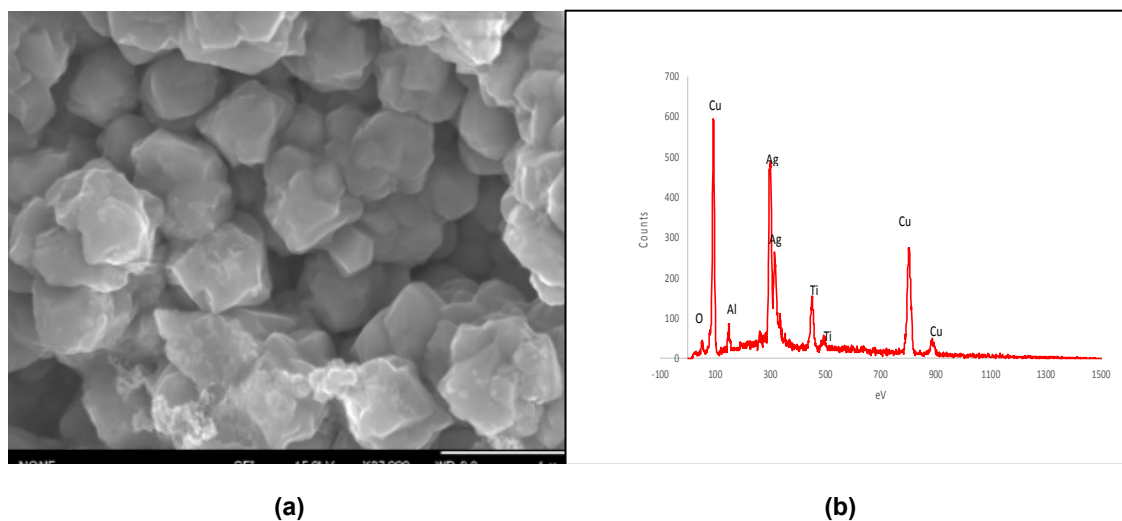


Fig. 3. SEM image of the substrates and Point EDS pattern of the substrate. SEM image of the substrates. ($\times 27000$) (a) Point EDS pattern of the substrate. (b)

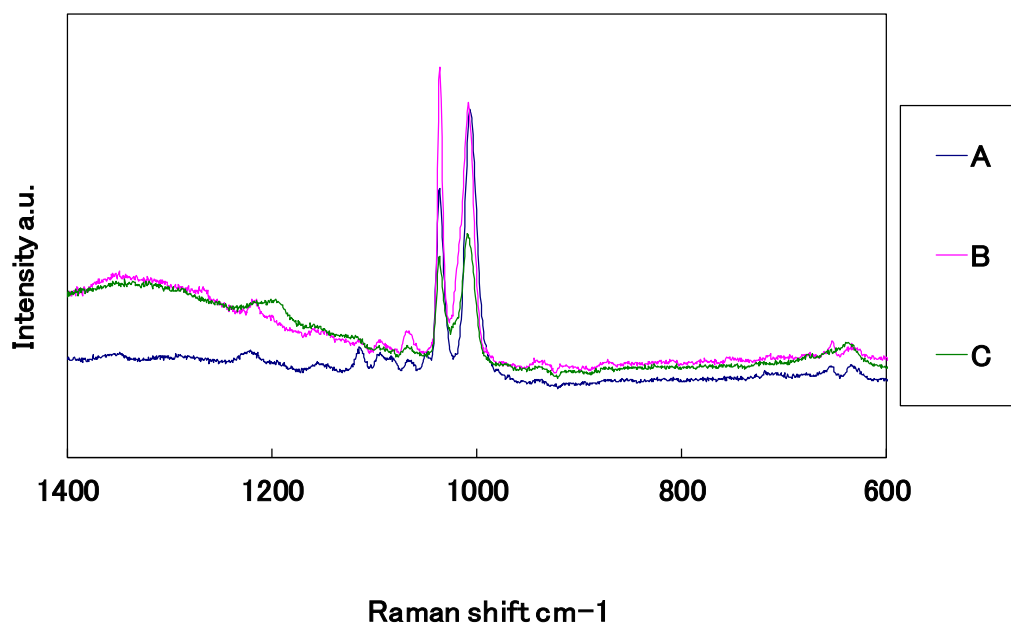


Fig. 4. SERS of pyridine
SERS spectra obtained from the “Ag, Cu, TiO_2/Al substrates” using pyridine as the probe molecule after (A) 2 hours, (B) 68 days and (C) 93 days. The collection times were 20 s

It was also possible to coat a glass substrate with an Ag/Cu/ TiO_2 film. Fig. 6 shows an SEM image and the EDS pattern of the modified glass substrate. Some of the NPs aggregates deposited on the surface of the Ag NPs are anatase TiO_2 NPs. In addition, the Cu NPs were not adsorbed onto the glass substrate, which can be attributed to the Cu making an inorganic

complex, and that Cu complex decomposed between a pH of 2 and 3. Then, the Cu adsorbed onto the Al surface owing of its ionization tendency but it couldn't get adsorbed onto the glass surface.

Fig. 7 shows the intensity of the Raman signals from the “Ag, $\text{TiO}_2/\text{glass}$ substrates.”

Having established that the TiO₂ nanoparticles and Ag nanoparticles adsorb onto the Cu particles, a further experiment was conducted where the anatase TiO₂ and Ag NPs were adsorbed onto an Al surface without APTMS following a similar procedure. We considered the possibility that the process of making Ag, TiO₂, Cu/Al substrates did not require APTMS. SEM

was again used to characterize the SERS substrate, and Fig. 8 shows the image and the EDS result. It appears that the Ag and anatase TiO₂ NPs are both assembled on the Cu particles. Fig. 9 shows the intensity of the Raman signals from the Ag, TiO₂/Al substrates without using APTMS after 68 days. It can be used as a material for biosensors.

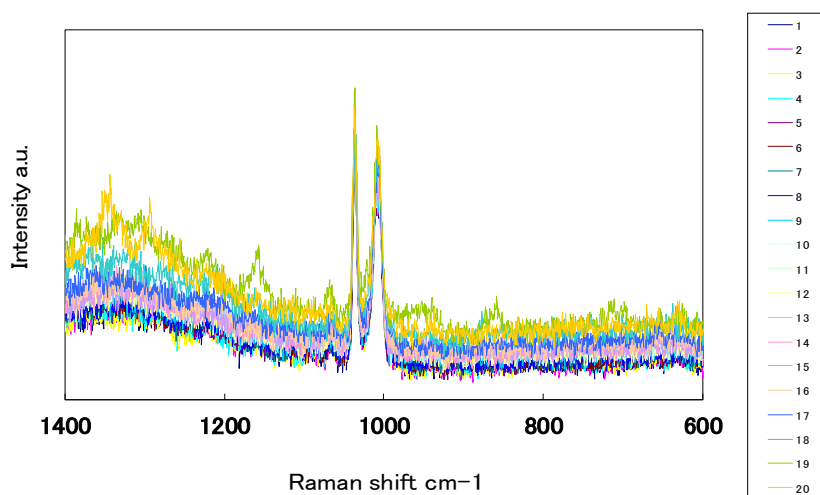
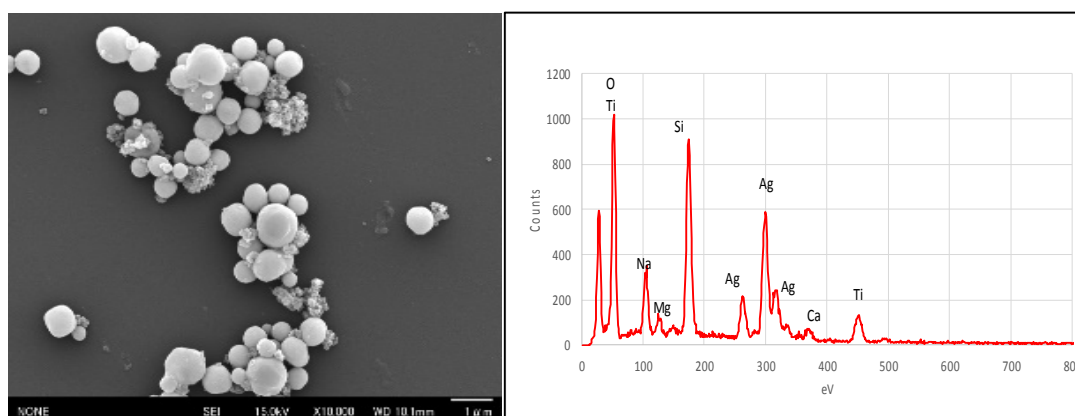


Fig. 5. Reproducibility of SERRS spectra

SERS spectra obtained from the “Ag, Cu, TiO₂/Al substrates” using pyridine as the probe molecule after 68 days. The collection times were 1 s

Table 1. Details of the SERS spectra obtained from the Ag, Cu, TiO₂/Al substrate after 68 days

SERS spectra obtained from the Ag, Cu, TiO ₂ /Al substrate after 68 days.		
Raman shift of the peak (cm ⁻¹)	1008	1036
Mean intensity	0.5708	0.6309
SD	0.02262	0.0285



(a)

(b)

Fig. 6. SEM image of the substrates and point EDS pattern of the substrate. SEM image of the substrates. (×9000) (a) Point EDS pattern of the substrate. (b)

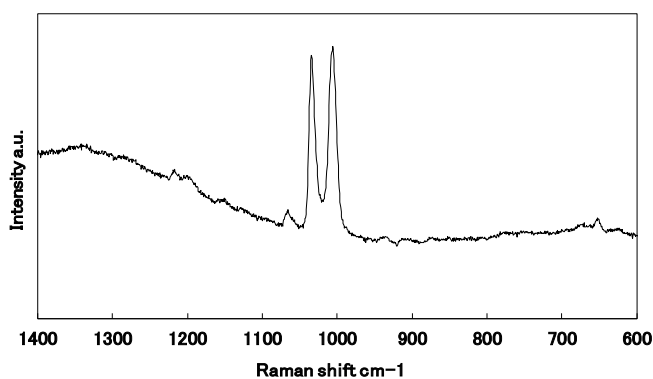


Fig. 7. SERS of pyridine

SERS spectra obtained from the "Ag, TiO₂/Glass substrates" using pyridine as the probe molecule. The collection time was 20 s

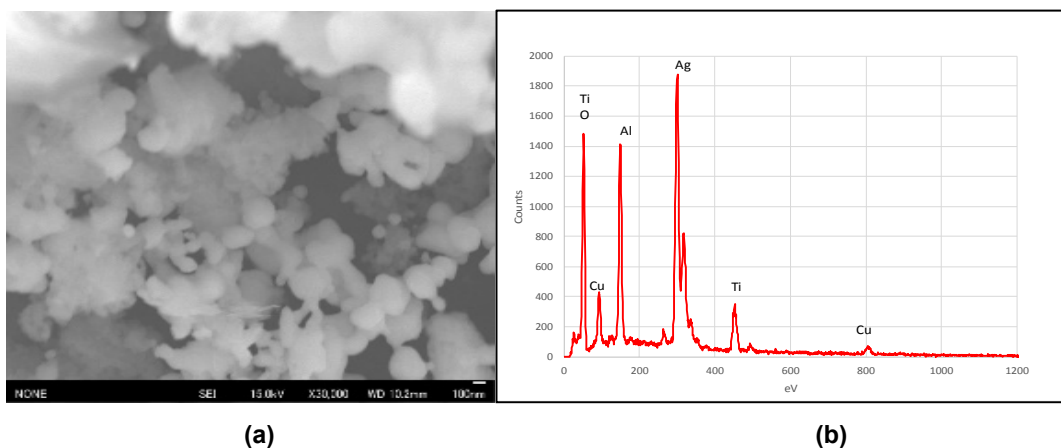


Fig. 8. SEM image of the substrates and point EDS pattern of the substrate
SEM image of the substrates. ($\times 30000$) (a) Point EDS pattern of the substrate. (b)

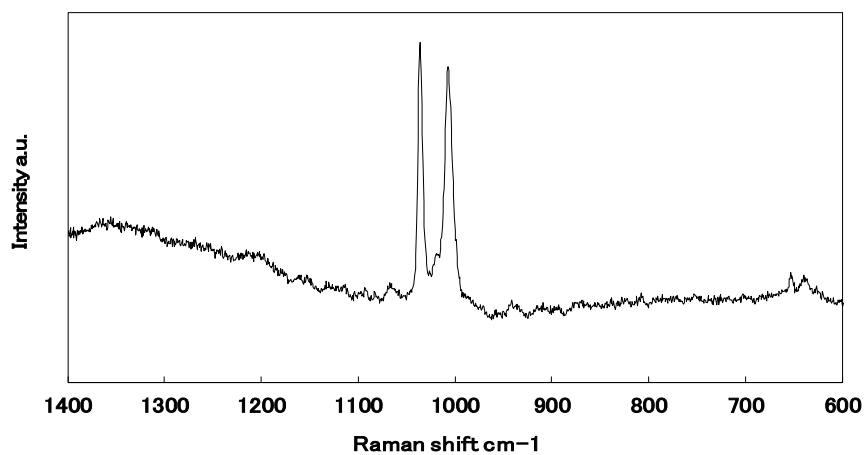


Fig. 9. SERS of pyridine

SERS spectra obtained from the "Ag, Cu, TiO₂/Al substrates" using pyridine as the probe molecule. The collection time was 20 s

4. CONCLUSION

A fine particle solution was obtained using aqueous anatase TiO₂ solution (500 mL, 0.02%) by boiling under vigorous stirring for about 20 min. HCl was then added to stabilize the dispersion of TiO₂. Since Al surfaces dissolve below a pH of 2 and anatase particles cohere at higher pH values, a pH of 3 was chosen for the synthesis of the various substrates. The zeta potential is an important factor because, if 2 approaching particles are sufficiently repelled by their surface charges, they will remain in a state of dispersion. Anatase TiO₂ can be dispersed in a strongly acidic medium with a pH of 2 or less, and the particles do not cohere [19,20]. However, an Al surface dissolves at a pH of 2 or less, and as a result, it was found that pH 3 was the optimum pH to adsorb anatase on an Al surface without particle coherence.

Raman shifts in the vicinity of 1036 and 1008 cm⁻¹ can be seen when pyridine is adsorbed onto the modified surface [11]. Since the Ag NPs and anatase TiO₂ NPs were assembled on the Cu Ps, the Raman intensity was measured from the mixture of Ag NPs, anatase TiO₂ NPs, and Cu Ps. Stable Raman intensities were obtained when a mixture of Ag NPs, anatase TiO₂ NPs, and Cu Ps were immobilized by Cu particles on the Al substrate. The possible redox reactions of the Ag NPs were stabilized through the localized presence of the anatase TiO₂ NPs and Cu Ps. Based on these results, using Cu and TiO₂, a long-term stable Ag NPs substrate has been fabricated. Moreover, it was possible to coat a glass substrate with both Ag NPs and anatase TiO₂ NPs at the same place on the substrate.

ACKNOWLEDGEMENTS

I am grateful to all the following people for rendering their valuable comments and allowing me to use the experimental facilities and equipments required for my experiments: Dr. Kazue Tani and Mr. Satoki Sinozuka. (University of Yamanashi). In particular, I am grateful to my teacher for his valuable advice. Moreover, I would like to sincerely thank Professor Emeritus and Dr. Nobutoshi Kiba (University of Yamanashi).

COMPETING INTERESTS

Author has declared that no competing interests exist.

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