

Ag NANOPARTICLE-COATED ZEOLITE AS SURFACE ENHANCED RAMAN SCATTERING SUBSTRATE FOR 2-ACETYL-2-THIAZOLINE DETECTION

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Received: August 03, 2020; Revised: November 09, 2020; Accepted: November 17, 2020

Abstract

Surface enhanced Raman scattering or spectroscopy (SERS) is one of the techniques that have a high potential to enhance the Raman signal used to identify a low concentration of organic chemicals. In this work, zeolite was used as an adsorbent and the Ag nanoparticles were created on top of the zeolite surface for SERS spectroscopy. The morphology of the zeolite and the SERS chip was characterized by scanning electron microscopy (SEM). The Ag element on the zeolite surface was confirmed by energy dispersive X-ray spectroscopy (EDX) spectrum and powder X-ray diffraction (XRD). The average size of Ag nanoparticle was around 14 nm suggested by SEM. Oxidizing agents were eliminated from the SERS chip by a burning process, and the charge on the SERS chips surface was cleared by plasma surface treatment, using 2-acetyl-2-thiazoline (2AT), as an organic chemical. Raman enhancement of SERS was analyzed using Fourier transform Raman spectroscopy (FT Raman). The results demonstrated the potential ability of SERS with burning process to enhance the Raman signal of 2AT at 792 and 1,637 cm^{-1} of Raman vibrational bands.

Keywords: Y-type zeolite, Ag nanoparticle, SERS, Raman spectroscopy

Introduction

Surface enhanced Raman scattering or spectroscopy (SERS) is an analytical technique for detection and identification of chemicals at low concentration (Han *et al.*, 2011), as well as being one of the techniques for enhancing Raman spectroscopy (Kahraman *et al.*, 2017). The technique was discovered by Fleischmann *et al.* (1974). They did experiments about the Raman band intensity of

pyridine adsorbed onto a silver electrode (Fleischmann *et al.*, 1974). Raman spectroscopy was not widely used because of the low scattering cross-section, about $10^{-30} \text{ cm}^2 \text{ molecule}^{-1}$, resulting in the weak intensity of the Raman signal (Sur, 2013) and the low chemical concentration was also a problem attenuating the weak intensity of the Raman signal, which might not even appear such as

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the volatile compound of rice aroma. Especially, agricultural product of Thailand such as KaoHom Mali and KaoHomPrathumtani has an identity volatile compounds that indicate the quality of rice product. The identified volatile of rice is a 2-Acetyl-2-thiazoline (2AT) and it is also important volatile compound identified in beef flavor and another food flavor (Plancken *et al.*, 1971; Buttery *et al.*, 1983; Fang and Cadwallader, 2014). Therefore, adsorbent materials are interesting to research for use as a SERS substrate.

Zeolites are a natural mineral which is based on three-dimensional frameworks of aluminosilicate minerals, which are mainly composed of silicon, aluminum, and oxygen elements. Their structure is a microporous material and they were discovered by a Dutch scientist A.F. Cronstedt in 1756 (Auerbach *et al.*, 2003). The one of properties of zeolite can be an adsorbent material (Osakoo *et al.*, 2017). Zeolites have been used extensively for many purposes such as water and gas purification, catalysis in agriculture, and aquaculture (Sprynskyy *et al.*, 2005), especially being used as an adsorbent (Widiastuti *et al.*, 2011; Alshameri *et al.*, 2014; Mazloomi and Jalali, 2016; Gil *et al.*, 2019; Sun *et al.*, 2019).

The properties of zeolite in the nature were not needed to use for some application. The scientists have synthesized them to increase certain properties such as a good absorbent, acid resistant and heat resistance, etc. The type of zeolite has been synthesized, such as ZSM-5, Y type, L type, Mordenite, and BETA, etc. The adsorption properties of synthetic zeolites are different, which can be indicated from the Brunauer-Emmett-Teller (BET) surface area value, according to the literature report that the Y-type zeolite is $630 \text{ m}^2 \text{ g}^{-1}$ (Osakoo *et al.*, 2017; Budtri *et al.*, 2019) reports that the adsorbed volume of NaY zeolite type, was analyzed by N_2 adsorption-desorption isotherms, increased rapidly at low-pressure to produce a monolayer. Furthermore, temperature and pressure were affected on the zeolite Y type structure. Greaves *et al.* (2003) reported that the collapse of zeolite depended on temperature and pressure increasing. Therefore, the type of zeolite is synthesized that effect affects the properties of zeolite.

The interaction between incident light and SERS structure in nanoscale analysis is successful when the chemical is close to or on the surface of the nanoparticle metal structure. The enhancement of the Raman signal is caused by the electric field of SERS which is attributed to the interaction between metal nanoparticles and the optical intensity (Hardiansyah *et al.*, 2015) due to localized surface plasmon resonance (LSPR) which was created by metal nanoparticles such as gold, platinum, or silver on a substrate's surface (Abdelsalam *et al.*, 2007).

The SERS potential was evaluated in terms of its enhancement factor (EF). EF is explained as the ratio of normal Raman intensity and SER scattering intensity. The range of the EF was normally reported to be about 10^6 - 10^{16} (Hardiansyah *et al.*, 2015). SERS was pervasively used and built into a variety of different techniques. Zhang *et al.* (2014) studied the enhancement of the Raman signal of 2,4,6-Trinitrotoluene (TNT) with SERS which was performed in a colloidal solution of Ag nanoparticles. The results showed that the particle size of the Ag nanoparticles dispersed in the solution was in the range of 50 to 80 nm. In addition, other researchers have prepared colloidal nanoparticle solutions with nanoparticles ranging in size from 14 to 1,500 nm (Kim *et al.*, 2009; Lin *et al.*, 2011; Prucek *et al.*, 2014; Zhang *et al.*, 2016). Besides, the colloidal nanoparticle solution technique, Ag coated on a glass surface was another technique for making a SERS substrate (Fang *et al.*, 2008). The Ag nanoparticles were ordered on the surface of the glass as a 150 nm thin film. Electrochemical deposition of Ag nanoparticles coated on an Indium tin oxide film was also reported by Yang *et al.* (2014). An important step in the preparation of the SERS chip was elimination of the oxidation of Ag nanoparticles on the SERS sample's substrate surface because the oxidation could decrease the SERS activity (Han *et al.*, 2011). The most two thermodynamically stable oxides of the silver element are silver (II) oxide (AgO), and silver (I) oxide (Ag_2O). The decomposition of AgO can be used during thermal processing to decrease the oxygen element from the oxide of silver (Waterhouse *et al.*, 2001). Thermal processing treatment of the SERS sample's substrate surface may be used in the SERS process.

In this work, the weak intensity of the Raman signal was improved by SERS substrate development. The SERS substrate was prepared from Y type zeolite as an adsorbent material base. The Ag element is a lustrous transition metal, with high electrical conductivity and thermal conductivity, which was used to induce the localized surface plasmon (Schlücker, 2014). The zeolite was coated with Ag onto its surface according to the literature (Taylor *et al.*, 2010). The phase and functional groups of the silver nanoparticle coating were characterized by XRD and Fourier transform infrared spectroscopy (FTIR). Morphology of the nanoparticle silver coated onto the zeolite surface was analyzed by SEM and the Ag element on the zeolite surface was confirmed by EDX mode. 2AT is a volatile organic chemical compound that was used in this work. The enhancement of Raman signal was analyzed by FT Raman.

Materials and Methods

Chemicals

Zeolite was used for the experiment: Y-type zeolite (390HUA) was provided by Tosoh Asia Pte. Ltd. Silver nitrate (99.88%, AgNO_3), Ammonia (30%, NH_3), Ethanolamine (99%, $\text{NH}_2\text{C}_2\text{H}_4\text{OH}$), and Formaldehyde (37% w/v, HCHO) were provided by Carlo Erba. 2-acetyl-2-thiazoline ($\text{C}_5\text{H}_7\text{NOS}$, 2AT) was provided by Sigma Aldrich. All of the chemicals were analytical grade. DI water type II was used for the experiment.

Preparation of the Silver Coating on Zeolite

The silver coating on each chip of zeolite substrate was applied according to the literature (Taylor *et al.*, 2010). As a pretreatment step, the zeolite surface was cleaned in deionized water by washing them in an ultrasonic bath for 30 min. The suspension was prepared by directly adding 8.3 M ethanolamine and 1.4 M silver nitrate at room temperature for one h. Then the suspension was centrifuged and washed with deionized water for three times. The pretreated zeolite was coated with silver in a silver coating step: the zeolite was coated in a 0.1 mM silver nitrate solution; formaldehyde (37% aq. solution) was added immediately and the solution stirred as ammonium hydroxide (8%) was dropped at one drop every 2-3 sec. The sample was centrifuged and washed with deionized water three times to remove any unreacted treatment chemicals and dried at 65°C.

Preparation of SERS Substrates and Volatile Samples

Silver-zeolite and pure zeolite were mixed together. The ratio of the sample mixture was 15% of silver-zeolite with 85% pure zeolite. The mixture was made into a cylindrical shape and compressed into a thin layer of pellets under a high pressure, of 10 tons, for 2 min. Then the sample was burnt with a gas burner using propane gas mixed with argon gas at $500 \pm 10^\circ\text{C}$ for 15 sec. Some of the sample was spattered onto the SERS substrate treated surface by Leica EM ACE600 sputter coater using plasma treatment mode.

2AT was used as a volatile organic chemical sample for SERS testing. A 2AT solution was prepared by adding in ethanol as 5% of the total volume and 95% as DI water. The concentration of the 2AT solution was 100 ppm. The SERS substrate was put in the head space of the solution container and incubated at 60°C for one hour. Five samples (pure zeolite, pure zeolite with 100 ppm of 2AT, 15% silver-zeolite, 15% silver-zeolite with 100 ppm of 2AT, and 100 ppm of 2AT) were determined by

Fourier transform Raman spectroscopy with 128 scan time and resolution of 4.

SERS Characterization

The structure of the zeolite was studied by SEM on a JEOL JSM-6400 under secondary and backscatter modes, and by EDX. The samples of both the zeolite and the Ag-zeolite composite were studied by XRD on a Bruker D8 ADVANCE diffractometer using $\text{Cu K}\alpha$ X-ray ($\lambda = 1.5406 \text{ \AA}$), generated with a current of 40 mA and a potential of 40 kV within a range 2θ of 5 to 80° with 0.02° as the increment. The interaction between the zeolite and silver was determined by FTIR on a Bruker TENSOR 27 FTIR spectrometer, using ATR, and FT Raman on a Bruker SENTERRA Raman II imaging microscope using 1,064 nm excited Nd:YAG infra-red laser and 128 scan times.

Results and Discussion

Characterization of Nano Ag on Zeolite

Figure 1 shows the SEM micrograph and EDX spectrum of Y-type zeolite before and after coating with silver as a precursor. The morphology and surface structure of zeolite particles is shown in Figures 1(a) and 1(b), they are orthorhombic, and single crystals are cubical, the structure of Y type zeolite similar to the literature (Kaduk and Faber, 1995; Seo *et al.*, 2006; Sung-Man *et al.*, 2007). Figure 1(b) shows that the silver was coated onto the zeolite surface as white spots. The average size of the silver nanoparticles was 14 nm. The distribution of silver nanoparticles did not cover all of the zeolite surface and the coverage area of the silver nanoparticle was about 4.54% of a total imaging area. The literature research (Budtri *et al.*, 2019) reported the ZEM-5, mordenite, and Y-type of zeolites were coated with silver solution on the zeolite surface using silver nanoparticle in the range of 4.09-14.76 nm as a plasmonic material (Li *et al.*, 2012; Sharma *et al.*, 2012). In the Figure 1(b), the presented spectrum was obviously showed three peaks located between 0.5-3.0 keV. The maximum located at 0.5 keV was indicated as an oxygen characteristic (Puchalski *et al.*, 2007; Budtri *et al.*, 2019) and the peak at 1.75 keV was indicated as a silica element (Sankar *et al.*, 2018). To confirm the Ag element on zeolite surface, the peak was presented in the EDX spectrum at 2.9 keV of energy (Puchalski *et al.*, 2007; Budtri *et al.*, 2019).

The elucidation of the nanoparticle silver coating on the crystal structure of the zeolite was indicated by XRD pattern. The reflection of X-ray light on any crystal of zeolite formed many

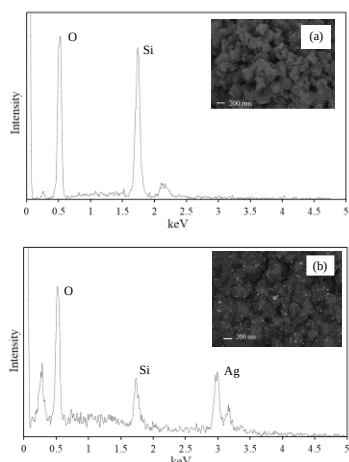


Figure 1. EDX spectra and SEM micrograph of (a) Ag nanoparticle uncoated and (b) coated on zeolite

diffraction patterns and the physico-chemical characteristics of the crystal structures were also reflected by the diffraction patterns (Zhang *et al.*, 2016). Figure 2 shows the peak of pure and Ag coated Y-Type zeolite which was referenced against the standard pattern published by the International Zeolite Association (IZA). The XRD pattern of zeolite after reaction showed a broad band at angle $2\theta = 24^\circ$ indicating the changing of crystalline form to amorphous form (Rida and Harb, 2014). Since, the reaction during the coating process was basic hydrolysis. The hydrolytic reaction of Al_2O_3 made the pH of the solution culminate at a pH of about 10, and consequently the zeolite crystalline structure was destroyed. The nano Ag coated on zeolite was confirmed by the diffraction line at 2θ of $\sim 38^\circ$ and 65° (Dag *et al.*, 2011).

SERS Characterization and Surface Enhancement Raman Spectroscopy

The dark brown color of the SERS chip fades after burning as in Figure 3(a), but the color was not changed by plasma mode. Normally the black material absorbed this wavelength band (Agnihotri *et al.*, 2018) therefore the reflectance of light could not scatter to the detector. For reducing light absorption, the color of the sample was faded from dark brown color. The nano Ag was evenly distributed onto the zeolite surface after compression as a cylindrical shape (Figures 3(b) and 3(c)) and the appearance of nano Ag particle was unchanged after burning.

The results of FTIR in Figure 4 shows the spectrum of pure zeolites and nano Ag-zeolites. A 3D silica phase of zeolite was usually suggested in vibration bands at $460\text{--}970\text{ cm}^{-1}$ which were assigned to Si-O (Shameli *et al.*, 2011). The

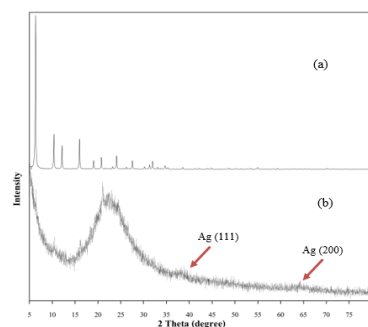


Figure 2. XRD pattern of (a) pure zeolite and (b) Ag nanoparticle coated on zeolite.

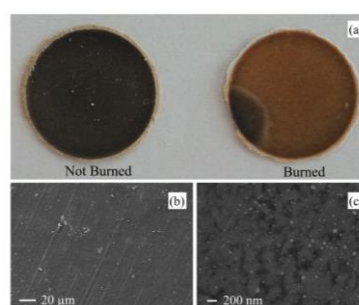


Figure 3. The image of SERS chips (a) before and after burning process condition. SEM micrograph of (b)10k-X and (c) 30k-X of SERS chip

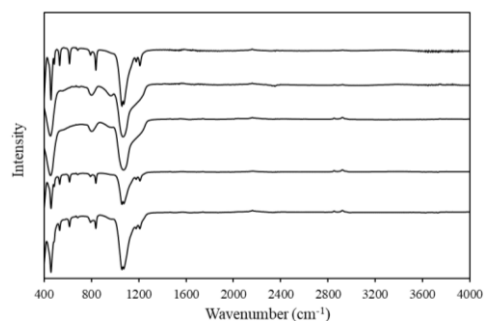


Figure 4. FTIR spectrum between (a) pure zeolite, (b) Ag nanoparticle coated on zeolite, (c) Ag nanoparticle coated on zeolite with burning process, (d) 15% silver-zeolite and (e) 15% silver-zeolite with burning process

vibration bands at $460\text{--}546$ and $1,000\text{--}1,100\text{ cm}^{-1}$ were assigned to Si-O-Si antisymmetric stretching vibration (Lambert *et al.*, 1987). The vibration of Ag-Ag metallic bonds showed no peak because the vibration frequency of metal-metal bonds would respond in the mid-infrared range ($400\text{--}4,000\text{ cm}^{-1}$) (Gharibshahi *et al.*, 2017). The FTIR spectrum of nano Ag-zeolite was not significantly changed after burning and plasma treatment. The absorption characteristic of nano Ag-zeolite was still

unimpaired because the effect of nano Ag had no interference on the zeolite surface (Budtri *et al.*, 2019). Zeolite structure was changed in the chemical coating process because the FT-IR spectrum of Ag nanoparticle coated on zeolite in Figure 4(b) was unappeared the peak at wavenumber 532, 613, and 837 cm^{-1} . The thermal effect on zeolite structure and collapse at the burning process was not affected at 450-500°C because the FT-IR spectrum of the sample in Figures 4(c) and 4(e) were not changed after burning.

To confirm of enhancement of the Raman signal from development of SER. The Raman spectrum of pure zeolite of all types (Figures 5 and 6) showed vibration bands at 298, 302, 492, and 510 cm^{-1} . The strong bands at 492 and 510 cm^{-1} and weak bands at 298 and 302 cm^{-1} are assigned to the six-member ring of Y type zeolite (Yu *et al.*, 2001). Figure 5(a) shows the spectrum of a SERS chips which did not have the burning process and plasma surface treatment. The results showed that the 15% silver-zeolite SERS chip did not enhance the Raman signal but the intensity was higher than for the pure zeolite SERS chip. The effect of plasma surface treatment was the cause of the enhanced intensity as show in Figures 5(b) and 6(b). Nevertheless, the Raman signal was not enhanced by SERS. The charge on the surface was not completely clean because the charge-transfer process could not encourage up to several orders of amplitude

to surface enhancement value (Han *et al.*, 2011). Figure 6(a) shows the spectrum of SER chips following the burning process. The spectrum of 15% silver-zeolite of the SERS chip can enhance the Raman signal of 2AT in the vibration bands at 792 and 1,637 cm^{-1} assigned to deformation of CH in the benzenes ring and N-H or NH_2 in primary amides (Lambert *et al.*, 1987). According to the electromagnetic enhancement mechanism for SERS, the interaction of Ag nanoparticles and incident light enhances the incident field to generate a local field (Alonso-González *et al.*, 2012).

Conclusions

The SERS chip was fabricated on Y type zeolite as an adsorbent material base and the SERS chip was coated with silver nanoparticles using a chemical reaction. The size of particle was average 14 nm and well distributed on the zeolite surface. The EXD spectrum and XRD pattern of Ag nanoparticles at 2.9 keV of energy and the existence of Ag nanoparticles, respectively. The SERS chips were treated in a burning process and plasma treatment for elimination of oxidation reactions. The SERS chip with burning process absorbed 100 ppm of 2AT which enhanced the Raman signal of 2AT. Raman bands at 792 and 1,637 cm^{-1} are assigned to deformation of CH in

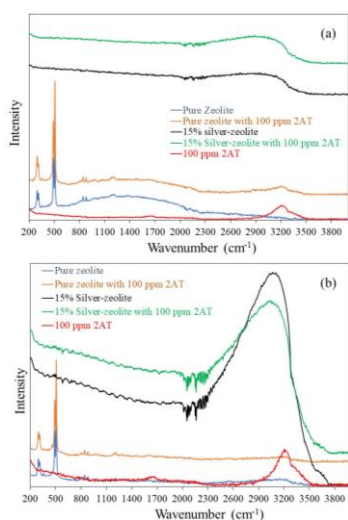


Figure 5. Raman spectra of 2AT and SERS effect of pure zeolite, pure zeolite with 100 ppm of 2AT, 15% silver-zeolite, and 15% silver-zeolite with 100 ppm of 2AT. The experimental condition has no burning process with (a) no plasma surface treatment and (b) plasma surface treatment

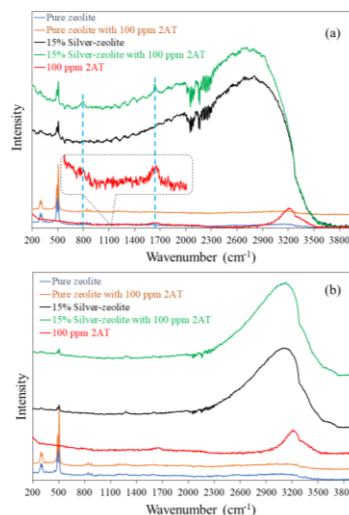


Figure 6. Raman spectra of 2AT and SERS effect of pure zeolite, pure zeolite with 100 ppm of 2AT, 15% silver-zeolite, and 15% silver-zeolite with 100 ppm of 2AT. The experimental condition has burning process with (a) no plasma surface treatment and (b) plasma surface treatment

benzenes rings and N-H or NH₂ in primary amides. The assignments are a part of 2AT.

Acknowledgments

We would like to thank the National Research Council of Thailand (NRCT) and Suranaree University of Technology (SUT) for their support. This work was carried out in the Packaging and Food Innovation Research Unit, Suranaree University of Technology.

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