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## Electronic Supporting Information

### Adsorbate Enrichment on Zeolite Surface and Assembly of A SERS Sensor: A Case Study with Silver Nanoparticles and The Flavonoid Catechin

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## Material and Methods

### *Materials*

Deionized ultrapure water with a conductivity of 18.2 M $\Omega$ -cm was used in all experiments. Silver nitrate (AgNO<sub>3</sub>), trisodium citrate dihydrate, sodium chloride (NaCl), (+)-catechin hydrate, reagent grade acetone, HPLC grade methanol and trifluoroacetic acid (TFA) were obtained from Sigma-Aldrich Co. (USA). Ethanol (95%) was purchased from Taiwan Tobacco & Liquor Corporation (Taiwan). Zeolite (diameter  $\approx$  0.27cm) was purchased from Hayashi Pure Chemical Ind., Ltd. (Japan).

### *Preparation and quantification of AgNPs solution*

Glasswares were soaked in diluted HNO<sub>3</sub> solution, rinsed with deionized ultrapure water, and dried in the oven. Citrate-capped AgNPs solution was prepared immediately before use by a modified Lee-Meisel protocol<sup>1</sup>. Specifically, silver nitrate (18 mg) was dissolved in 100 mL of deionized water in a reflux system. After boiling, 2 mL of 1% trisodium citrate solution was added to the silver ion solution. The reflux system was isolated from light and kept at approximately 85°C for 1.5 h. The resultant solution of citrate-capped AgNPs was stored in a dark glass bottle at 16°C. UV-vis spectrum and TEM images of a typical preparation are shown in **Figure S2**.

A calibration curve based on UV-vis absorbance was constructed for each individual preparation as follows: Five samples were prepared by diluting a freshly prepared AgNPs solution 2, 4, 8, 16, and 32 folds with water. UV-vis absorbance of each sample was measured against water reference in triplicate. The average peak absorbance of each dilution between 432-442nm was plotted using Microsoft Excel against the logarithm of the respective fold of dilution with respect to base 2. Linear regression of the plot was carried out to give the interpolation equation. For each adsorption experiment (see below), a sample of the beginning and remnant AgNPs solutions were diluted with water equal times prior to UV-vis measurement so their absorbance value fell within

the range of the calibration plot. UV-vis measurement were made and the corresponding fold of dilution was calculated using the interpolation equation.

### ***Preparation and quantification of catechin solution***

A stock solution of catechin (0.01M) was prepared by dissolving catechin hydrate in water immediately before use. Four dilution samples were made by diluting this stock solution to  $7.5 \times 10^{-3}$ ,  $7.5 \times 10^{-4}$ ,  $7.5 \times 10^{-5}$ , and  $7.5 \times 10^{-6}$ M. Each of these five samples was injected into a Mightysil RP-18 GP 250-4.6 (5 $\mu$ m) HPLC column and eluted in triplicate as follows - injection volume: 20  $\mu$ L; eluent: 75% A/25% B (A = 0.1% TFA, B = methanol); flow rate: 0.8mL/min for 30 minutes; detection: 280nm. The average peak area of each dilution at retention time around 9.5 min was plotted using Microsoft Excel against the respective concentration. Linear regression of the plot was carried out to give the interpolation equation. For each adsorption experiment (detail below), a sample of the beginning and remnant catechin solutions was analyzed by HPLC in the above manner. The concentration was calculated using the interpolation equation.

### ***Preparation of zeolite beads***

Commercial zeolite beads were cleansed before use, following a multiple-wash-and-soak procedure in an ultrasonic cleaner (Branson 2510). Zeolite beads were first washed with running water, then soaked in ethanol and acetone, each for 10 minutes. The resultant zeolite beads were drained and dried at 100°C in the oven overnight. After cooling down in a dried box, the beads were covered with plastic wrap and stored.

### ***Preparation of SERS samples on glass and mica***

Glass or mica slides were cleaned thoroughly with detergent and water, rinsed with ethanol and acetone, and dried in the oven. Using the volume ratios (catechin:AgNPs:NaCl) determined in a previous study<sup>2</sup>, glass or mica slides were first incubated with AgNP solution in a Petri dish, covered

with aluminum foil, under shaking at 16°C for 24 hrs. Catechin solution and NaCl solution were then added, and shaking was continued at 16°C for 3 hrs. All the liquid was removed from the Petri dish, and the slides were characterized with a confocal Raman spectrometer.

***Preparation of SERS samples on zeolite for adsorption studies and routine analysis***

A pair of stainless steel tweezers was cleaned thoroughly with ethanol and used to pick up zeolite beads in all steps to minimize contamination. Ten zeolite beads were randomly taken from the pool of zeolite prepared in the above and placed in an Eppendorf centrifuge tube.

(a) Adsorption of AgNPs - AgNPs solution (300µL) was added to the tube. The mixture was covered and incubated at rt for 24 hours. The beads were transferred to a glass vial to dry for one hour before characterization or next soaking step. The volume of the remains in the tube was measured using a set of pipettes of decreasing volume. Samples were then taken from the remains and analyzed by UV-vis spectroscopy.

(b) Adsorption of catechin - catechin solution (diluted to  $2.0 \times 10^{-3}$  M from the stock, 500µL) was added to the tube. The mixture was covered and incubated at rt for 3 hours. The beads were transferred to a glass vial to dry for one hour before characterization or next soaking step. The volume of the remains in the tube was measured using a set of pipettes of decreasing volume. Samples were then taken from the remains and analyzed by HPLC. For cumulative adsorption studies, this step was repeated using the beads that had been dried for one hour.

(c) Adsorption of AgNPs and catechin – Step (a) and (b) were performed in sequence.

(d) Sample preparation for routine SERS protocol - AgNPs solution (300µL) was added to the tube. The mixture was covered and incubated at rt for 24 hrs. Catechin solution (0.01M, 100µL) and NaCl solution (1M, 100µL) were then added, and incubation was continued at rt for 3 hrs. The liquid was removed with a set of pipettes of decreasing volume and its volume measured. For each set of experiment, five samples were prepared this way and the volume removed was

averaged at 370 $\mu$ L. Four of the 50 beads prepared accidentally fell off the grip of the tweezers at one point or another during the procedure and were excluded from the subsequent characterization process by confocal Raman.

### ***Characterizations***

Absorption spectra of the AgNPs solution were recorded on a U-1800 spectrophotometer (HITACHI, Japan). Transmission electron microscopy (TEM) images of AgNPs were recorded using a JEOL JEM2010 HRTEM system with an accelerating voltage of 200 KV (JEOL, Ltd., Japan). Field Emission Scanning Electron Microscope (FE-SEM) images of zeolite and AgNPs@zeolite were recorded using a JSM-6700F system with an accelerating voltage of 200 KV (JEOL, Ltd., Japan).

A microRaman system equipped with a 532nm laser (Shanghai DreamLasers Technology, SDL-532-1000T) at 63.2 mW output was employed for study of zeolite treated sequentially with AgNPs and catechin.

A confocal microRaman system (Horiba Jobin–Yvon, France) equipped with a 20mW/514.5nm Ar<sup>+</sup> laser (Lexel Laser, Fremont, Canada), a 50 $\times$  objective lens (Olympus, Japan), and TRIAX 550 Jobin Yvon monochromator (1200 gr/mm grating) coupled with a CCD detector was employed in the final Raman/SERS protocol. The Raman scattering light was routed through a 0.2 mm entrance slit and a 0.2 mm exit slit. The instrument was calibrated against a silicon wafer (peak position: 520 cm<sup>-1</sup>) prior to spectrum collections. Data acquisition conditions for all SERS measurements are as follows: spectral resolution 3.0 cm<sup>-1</sup>; integral times of 3 seconds and 10X accumulations. All SERS measurements involving zeolite were carried out in solid phase. Room temperature was controlled at 16 $^{\circ}$ C.

### **Figure Legends**

**Figure S1:** A picture of the 46 zeolite SERS sensors.

**Figure S2:** UV-vis spectrum and morphology of AgNPs used in this study.

**Figure S3:** SEM photography of a zeolite bead before and after treatment with AgNPs: (a) whole-bead view, (b) areal view of the bead, (c) whole-bead view post treatment, and (d) areal view of the bead post treatment.

**Figure S4:** Comparison of confocal SERS spectra of catechin co-deposited with AgNPs on various substrates: (a) glass, (b) mica, and (c) zeolite.

**Figure S5:** Randomly-picked SERS spectra of catechin on ten AgNPs@zeolite sensors.

Figure S1



Figure S2

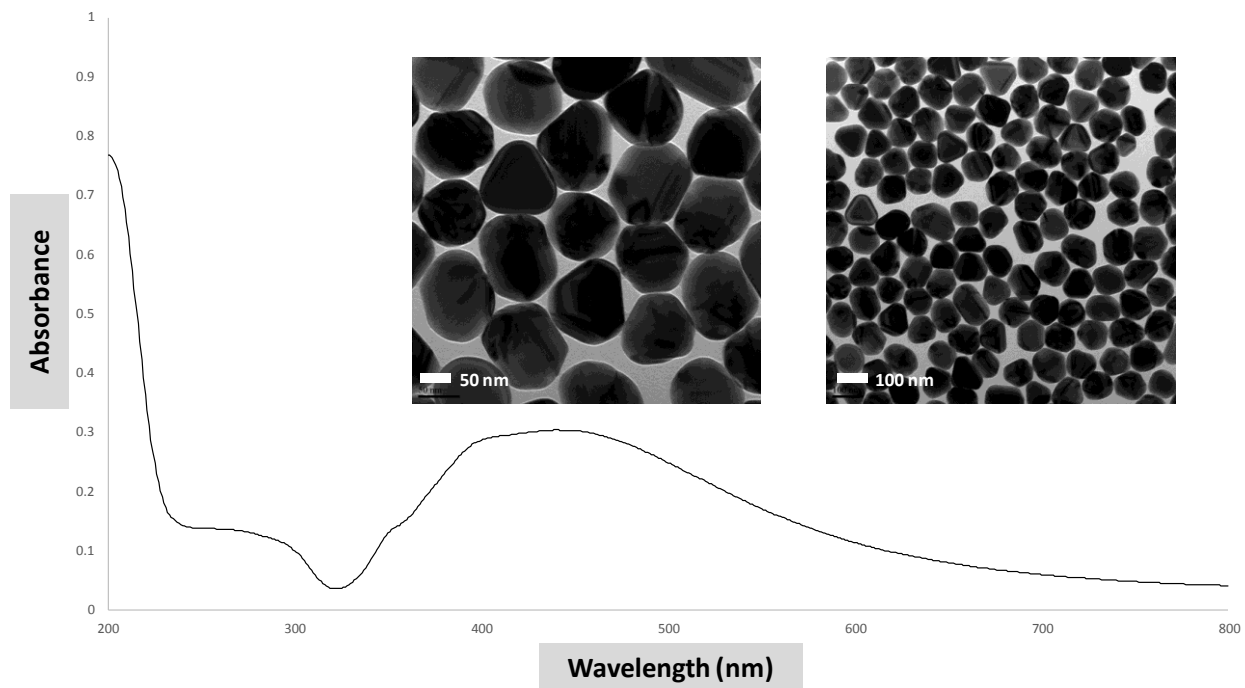




Figure S3

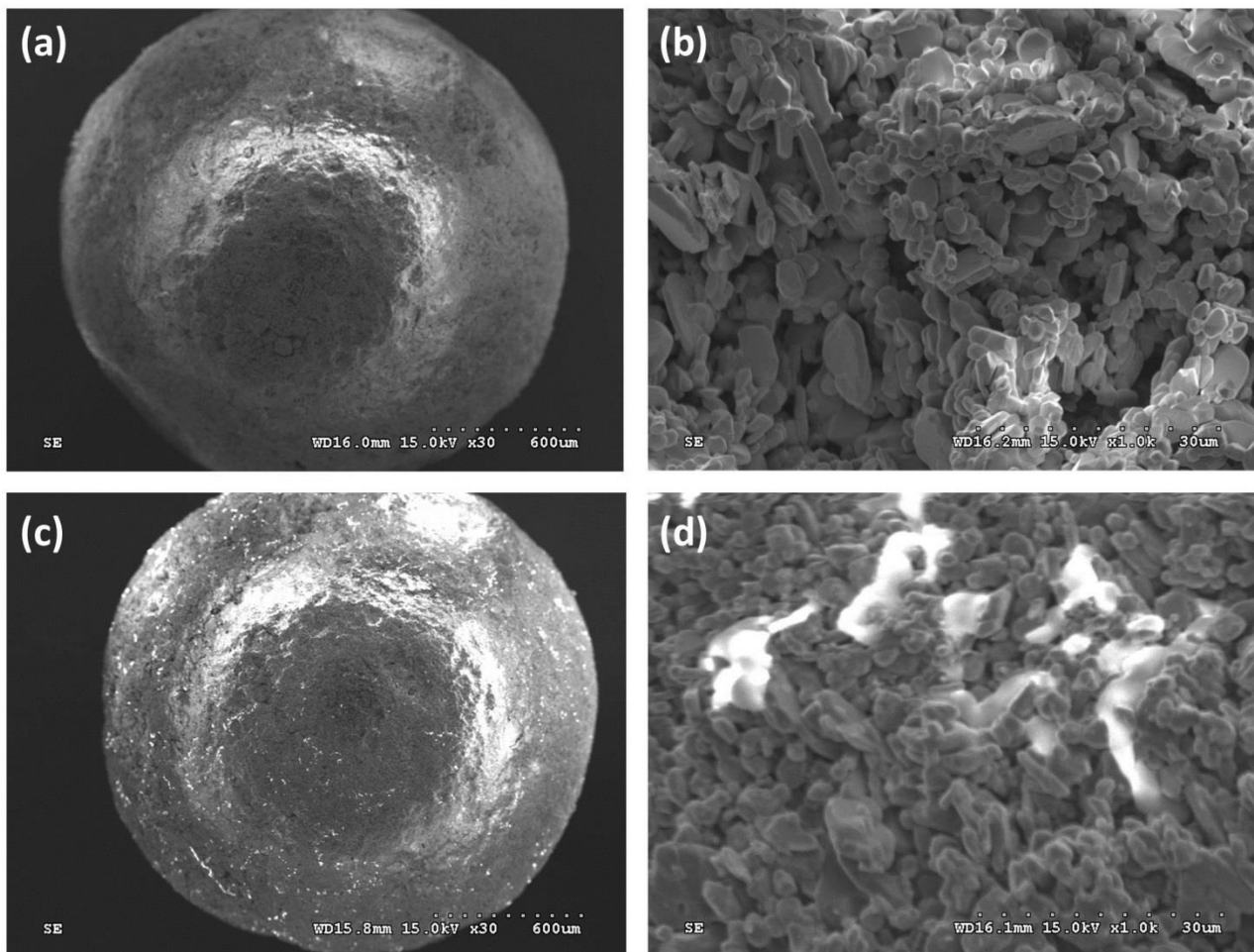


Figure S4

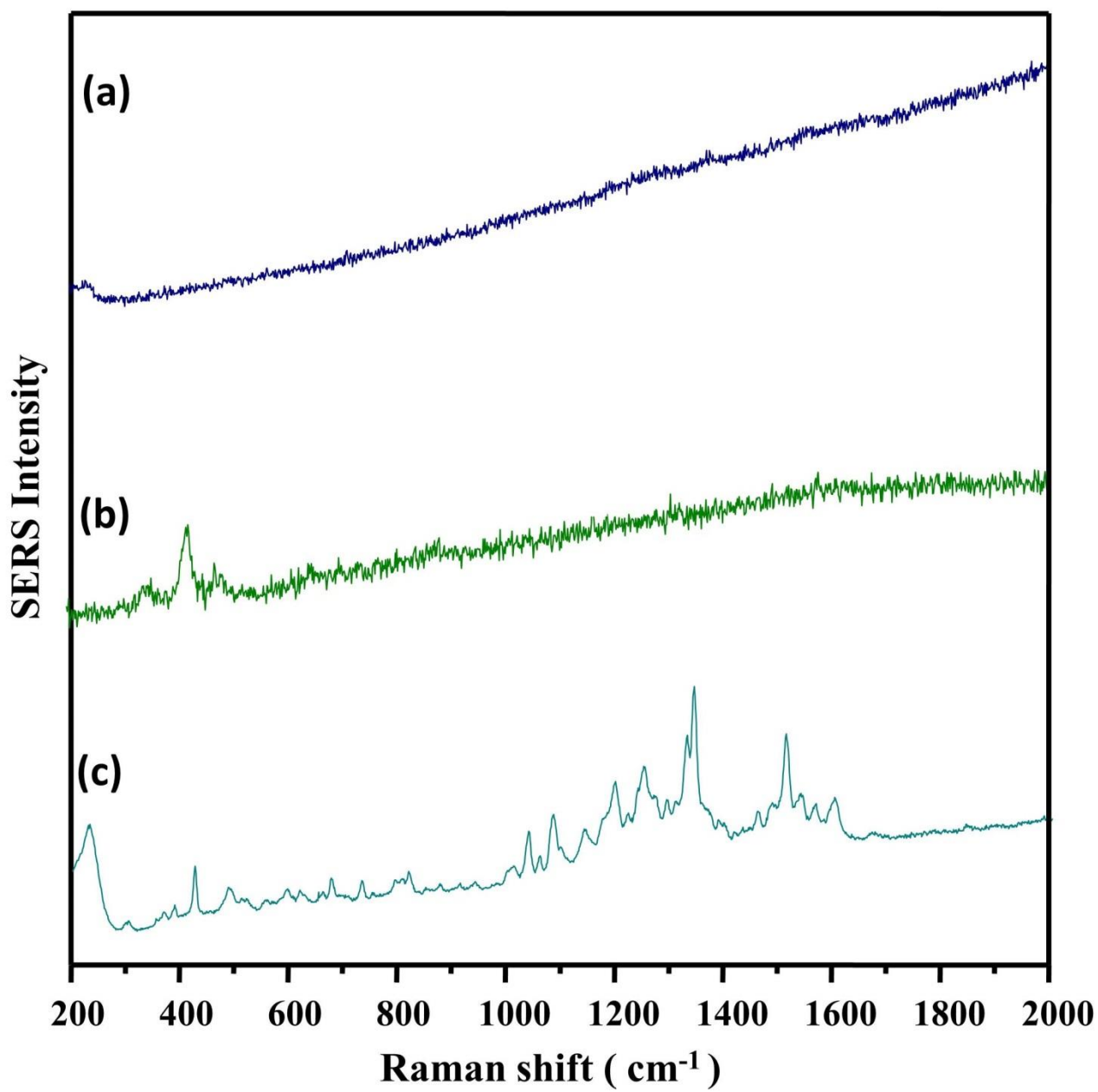
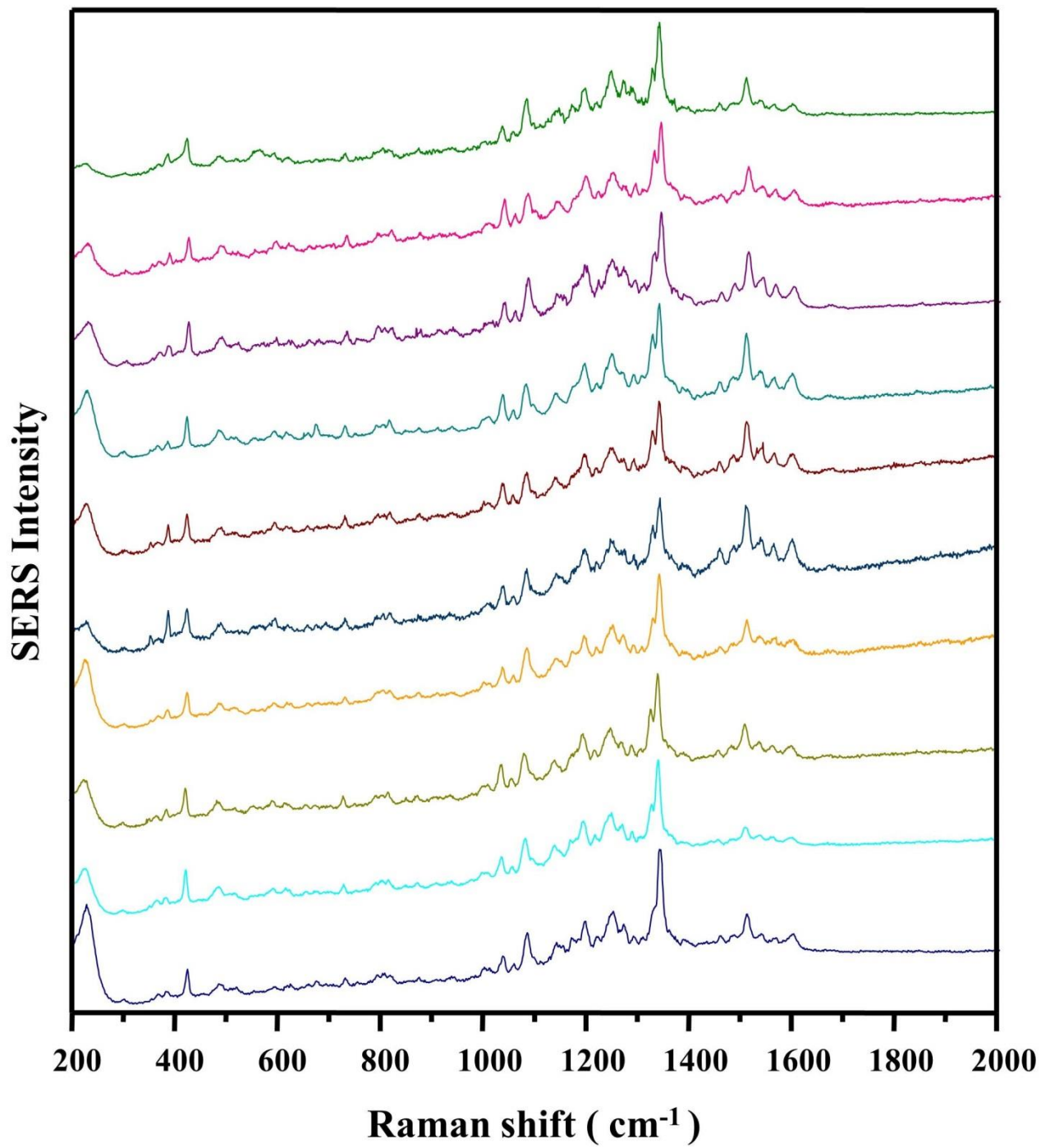


Figure S5



**References:**

1. P. Lee and D. Meisel, *J. Chem. Phys.*, 1982, **86**, 3391-3395.
2. C.-C. Huang and W. Chen, *Microchimica Acta*, 2018, **185**, 120.