Preparation of Self-Assembled Monolayer (SAM) Modified Silver Substrates for Surface Enhanced Raman Scattering (SERS)

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Self-assembled thiolate and sulfinate monolayers on smooth silver substrates were successfully characterized with SERS by applying for a selective etchant. The enhancement effect (EF) observed was comparable with those achieved by other techniques. The reusability of the resulted substrate was provided by UV photooxidation of the monolayer in air.

The richness of the spectroscopic information, surface selectivity, and sensitivity of SERS makes it appropriate to solve problems in interfacial chemistry.[1-3] Tremendous research has been directed towards fundamental studies responsible for the enhancement and development of new architectures for SERS substrates.[4-8] Examples of SER-active surfaces include aggregates of colloidal noble metal particles, electrochemically roughened electrodes, evaporated thin films, silver doped polycarbonate films and HNO_3 etched silver foils, etc. All these methods provide surface roughness allowing strong local enhancement of the electric field of both incoming and scattered radiation. However, these surface modification procedures are 'destructive'. In fact, no technique is known to be capable of characterizing monolayers or submonolayers on silver with SERS, where smooth surface is desired during adsorption, without destroying the admolecules or changing their original molecular packing.

It is well known that a monolayer be spontaneously formed when a clean silver surface is exposed to a dilute thiol-ethanol solution or an aqueous sulfinate solution.[9] Our monolayers were prepared by immersing a silver plate with freshly polished surface in 1 mM 1-butanethiol or 4-aminothiophenol or 5 mM aqueous benzenesulfinate solutions. The resulted SAMs, to a great extent, resist foreign species (e.g. etching anions) from penetration, as evidenced from the comparison of the current-potential (i-E) responses of typical bare silver substrate (Figure 1a) and 1-butanethiolate SAM modified silver substrate (Figure 1b). The cyclic voltammograms were collected at 0.1 V/s in 0.2 M Na_2SO_4 vs Ag/AgCl reference eletrode.

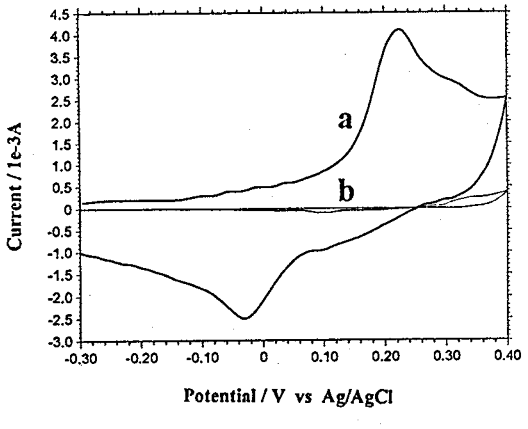


Figure 1. Cyclic voltammograms of (a) bare Ag and (b) 1-butanethiolate monolayer on Ag, in 0.2 M Na_2SO_4 with scan rate of 100 mV/s, referenced versus Ag/AgCl and electrode area 1 cm^2.

Next we attempted to develop an etchant which could effectively remove the unoccupied sites on the underlying silver substrate without affecting the confined molecular assembly. The combination of 0.5 mM $K_3Fe(CN)_6$ and 0.1M KSCN, among various of reagents reacting with silver, was found to be the most desirable solution in this application. To study the etching mechanism, a slow static etching scheme was used, in which a silver substrate was emersed for SERS experiment after being immersed in an etching solution from several hours to several days, mainly depending on the structures of the adsorbed species. Our dynamic experiment was implemented in glassware with N_2 bubbling through the solution constantly. The circulation of the solution facilitated the mass transfer of the etched Ag so that fresh surface was ready to be reached by the intruding etching anions, thus a few hours were generally enough for this process. In both cases, SER spectra of 1-butanethiolate, 4-aminothiophenol, and benzenesulfinate monolayers with high signal/noise ratio and good reproducibility were obtained with Spex model 1403 Raman spectrometer operated at 514.5 nm. Figure 2 shows the spectra of 1-butanethiolate monolayer before etching (a) and after etching (b). For simplicity, only the most enhanced ν(C-C) region was displayed, and the peak assignment will be presented separately.

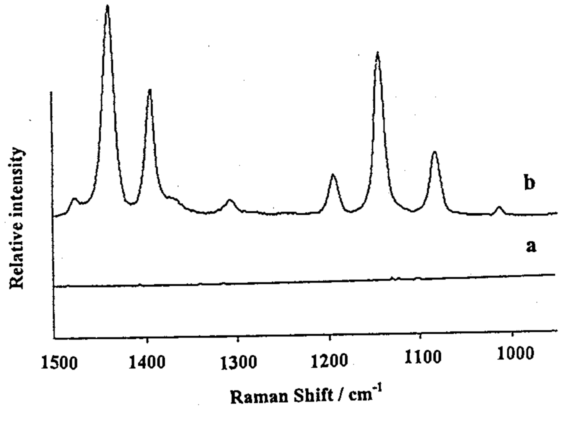


Figure 2. SER spectra of 1-butanethiolate monolayer on silver (a) before etching, (b) after etching.

The surface morphology of the etched substrate was examined with a scanning electron microscope (SEM). The image in Figure 3 shows that silver features have a homogeneous size distribution with the particle diameter in the order of 150 nm, as believed to be responsible for the observed SERS. These particles rooted on the surface and thus were considered very stable. Finer structure in each of the features is yet to be investigated.

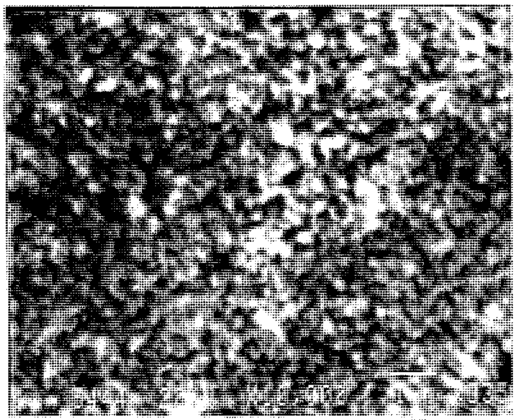
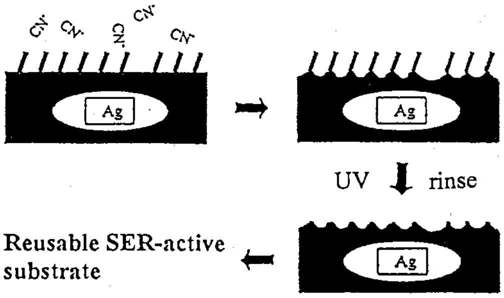


Figure 3. SEM image showing the topography of silver substrates after etching.

Apart from the strong enhancement, another essential criterion that also defines a practically useful SERS substrate is the reusability. To get rid of the adlayer without modifying surface morphology, several schemes were designed and tested, including thermal desorption in water, thermal desorption in absolute ethanol, and sonication in ultrasonic cleaner. Unfortunately, all of them could remove only a small portion of the admolecules due to strong SO_2-Ag or even stronger S-Ag bondings and were found very inefficient for this purpose. Satisfactory results were obtained by applying ultraviolet radiation from a mercury lamp on the entire film with an overall power density of 3 W/cm^2. The photooxidation in air converted the thiolate or sulfinate monolayers into their corresponding sulfonates,[10] which could be either removed by rinsing with water or replaced by exposure to other thiol or sulfinate solutions to be analyzed. SER spectra for the new monolayers were collected with commensurable enhancement.

In summary, we have introduced a new method to prepare SER-active substrate from a monolayer modified silver plate.



Scheme 1.

Scheme 1 outlines this procedure schematically. The utility of this method involves monolayer characterization, substrate preparation for SERS and catalytical application, and other interfacial phenomena study. The resulted substrate meets almost all of the criteria for a really useful substrate: highly enhanced, reproducible, reusable, simple and stable. In addition, considering the chemistry for etching on silver is also applicable for that on gold, we expect that this technique should also be useful for the preparation of SER-active gold substrate. Further investigation of the feature size control by using different etching time and using molecules with different structure is proceeding.

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