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An investigation of the surface-enhanced Raman scattering (SERS) effect from a new substrate of silver-modified silver electrode

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Abstract

A roughened silver electrode modified with silver nanoparticles is used as a substrate, on which high-quality surface-enhanced Raman spectroscopy (SERS) of isonicotinic acid (INA) are obtained, indicating that the silver-modified silver electrode is a highly SERS-active substrate. It is difficult to separate the contributions of the electromagnetic and chemical mechanisms to the great enhancement of the Raman signal. The shift by 5–20 cm^{-1} of the surface-enhanced Raman spectroscopy (SERS) bands and the change in their relative intensity compared with the ordinary Raman spectrum indicate the chemisorption of the sample molecules on the silver-modified silver surface. Furthermore, the silver nanoparticles modified on the roughened silver surface play the important role of magnifying the surface local electric field near the silver surface through resonant surface plasmon excitation. From the rich information on the silver-modified silver electrode obtained from high-quality potential-dependent SERS, we may deduce the adsorption behavior of INA and the probable SERS mechanism in the process. The probable reasons are given.

Keywords: Surface-enhanced Raman spectroscopy (SERS); Isonicotinic acid (INA); Silver nanoparticles; Silver electrode; Silver-modified silver electrode; Adsorption behavior

1. Introduction

Since the discovery of surface-enhanced Raman spectroscopy (SERS) by Fleischmann et al. [1] in 1974, this technology has shown the great advantages of high sensitivity and high quenching of the fluorescence. Now, SERS technology has been well established for obtaining detailed information of molecules adsorbed on the surface of silver, gold, or other noble metals, such as the adsorption configuration of molecules and the mechanism of interaction of the molecules with the surfaces of substrates [2–7]. Currently, there are many kinds of SERS-active substrates used in the wide range of SERS applications. Some examples are electrochemically roughened electrodes [8–12], negatively or positively charged silver colloidal solutions [13–15], acid-etching silver foil [16], metal island films formed through thermal evaporation [17,18], and laser-ablated silver plate [19,20]. However, electrochemically roughened electrodes offer many advantages in comparison to other substrates. These advantages include the potential control possibility with an electrode, the availability of a clean and reproducible surface for each analysis, and the possibility of fabricating the area of the working electrode to be comparable to the beam from the Raman microprobe. We know that the sensitivity for the roughened electrode is not high enough compared to the other SERS substrates due to the instinctive limitation of the electrochemical oxidation–reduction method. Therefore a large number of investigations [21–25] of surface enhancements from various modified electrodes have been carried out in order to optimize the SERS effect and extend the applied region of electrochemically roughened systems.

In the present work, silver nanoparticles are modified successfully on a roughened silver electrode surface and are characterized by surface-enhanced Raman spectroscopy

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(SERS) and scanning electron microscopy (SEM). High-quality SERS of isonicotinic acid (INA) is obtained, indicating that the silver-modified silver electrode is a highly SERS-active substrate. The great enhancement of the SERS on the silver-modified silver electrode surface can be contributed by two main mechanisms together: the electromagnetic mechanism and the chemical mechanism. The strong enhancement of 1608 cm^{-1} (8a; υ_{ring}), which is an essential feature of a SERS-CT spectrum [26–29], shows that the CT mechanism contributes to this case. Moreover, the uniform silver nanoparticles may magnify the local electric field (E_1) formed by the roughened silver surface. The second localized surface plasmon (LSP) resonance may induce an additional electric field (E_2) at the surface of the modified silver nanoparticles. Due to the superposed fields E_1 and E_2, the enhanced local electric field may lead to a giant electromagnetic effect on the silver-modified surface.

On the other hand, the high-quality potential-dependent SERS show that most bands' relative intensities change obviously and some frequencies shift 5–20 cm^{-1}. With the potential shifting from 0 to -0.6 V the adsorbed INA may gradually change the adsorbed orientation from perpendicular to the surface with carboxyl to parallel to the surface with aromatic ring. Additionally, it is conjectured that the variation of SERS intensity as the applied potential changes is a reflection of the electronic behavior, which, in turn, is related to the charge transfer mechanism. The adsorption behavior of INA molecules on the silver-modified silver electrode, as well as the approach of charge transferring, might change with the negative shifting of electrode potential. The probable reasons are given.

2. Experimental

2.1. Preparation of silver colloid

Silver colloid was prepared according to Lee and Meisel's method [30]. In 500 ml of deionized water, 90 mg of silver nitrate was dissolved and the solution was heated to boiling. Then 10 ml of a 1% trisodium citrate aqueous solution was added to the boiling silver nitrate solution dropwise, accompanied by vigorous stirring. The mixed solution was kept boiling for a further 10 min. Finally, a green-gray silver colloid was obtained, which was stable for several days or weeks.

2.2. Preparation of roughened silver electrode

The three-electrode spectroelectrochemical cell has been described elsewhere [10]. The counter electrode was a platinum ring (99.9%). An Ag/AgCl electrode was used as reference. The working electrode was made from a 99.9% polycrystalline silver rod. A silver disk of diameter ca. 3.5 mm was mounted in a Teflon holder. The silver electrode was first mechanically polished with 1.0-, 0.3-, and 0.05-µm alumina powder in turn to a mirror finish, followed by ultrasonic cleaning with Milli-Q water, before it was mounted in the cell filled with 0.1 M KC1 solution. Two or three ORCs were performed with a double potential step: -0.35 to 0.25 V, kept for 8 s at $+0.25$ V, and then back to -0.35 V.

2.3. Preparation of samples of silver-modified silver electrode for SERS measurement

A drop of aqueous solution mixed with 1 ml 0.01 M INA and 6 ml silver aqueous colloid solution was uniformly added onto rough dried silver electrode; then the electrode was dried for about 5 min. By repeating the procedure three times, the modified silver electrode for SERS measurement with certain proportion of silver nanoparticles and INA molecules was obtained.

2.4. Instrumentation

The Raman spectra were recorded by a microprobe Raman system (RENISHAW H13325 spectrophotometer), and the excitation line was at 514.5 nm from an Ar ion laser. With a holographic notch filter and a CCD detector, it has an extremely high detecting sensitivity. The head laser power was 1.1 mW in the case of the modified electrode and 4.5 mW in the case of the colloidal solution and the roughened silver electrode. A CHI440A electrochemical instrument was used to control the applied potential of the working electrode. All the potentials are quoted versus Ag/AgCl electrode. All the chemicals used were analytical reagent grade and the solutions were prepared using Milli-Q water.

3. Results and discussion

Fig. 1 shows the SERS spectra of (a) 0.01 M INA on silver-modified silver electrode, (b) 0.01 M INA on roughened silver electrode, and (c) 0.01 M INA in silver colloidal solution, as well as (d) the normal Raman spectrum of solid INA. In these spectra, Fig. 1a is the original spectrum, while Figs. 1b and 1c are three times the original spectrum. Interestingly, although the laser power in Fig. 1a is only a quarter of that in Figs. 1b, 1c, and 1d, the SERS activity of the silver-modified silver electrode (Fig. 1a) is much superior to that of the silver aqueous colloid (Fig. 1c) and the roughened silver electrode (Fig. 1b). Moreover, the information reflected by Fig. 1a is also greater than that reflected by Figs. 1b and 1c. These notable results indicate that the silver-modified silver electrode is a highly SERS-active substrate.

Moreover, the significant differences between the ordinary Raman spectrum and the SERS spectrum on the silver-modified silver electrode with respect to the relative intensities, bandwidths, and peak positions indicate a strong interaction between the metal and adsorbate, causing quite a different derivative of the molecule's polarizability tensor [31].