

Adsorption characteristics of 4,4'-bipyridine molecules on gold nanosphere films studied by surface-enhanced Raman scattering

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Abstract

We have measured and compared the surface-enhanced Raman scattering (SERS) spectra of 4,4'-bipyridine (bpy) molecules deposited (adsorbed) on the films of gold nanospheres (NSs, mean diameter 35 ± 5 nm), as prepared by the salting-out method using NaClO_4 and NaOH . The bpy-deposited (adsorbed) films were prepared by casting an aliquot of the bpy–ethanol solutions in different concentrations (less and above the monolayer converge on the gold surface), or on immersion of the NS films into the concentrated bpy solution. The enhancement of the SERS spectra of bpy was larger for the NS film prepared from NaClO_4 than that from NaOH . But, the SERS intensity was independent of the concentration of the bpy solution. The changes in the intensities and the shapes of the SERS spectra were distinctly observed on immersion of the bpy-deposited (adsorbed) NS films into pure ethanol, and these spectral changes were prominent for the NS film prepared from NaClO_4 . This must be attributed to considerably coalesced structures of the NS film prepared from NaClO_4 . From the comparison of the intensity changes before and after immersion into ethanol, it is suggested that the vertical orientation of the bpy molecules adsorbed on the NS films changes into the flat orientation with respect to the surface of the gold nanoparticles at the solid–liquid interface, on immersion of the film into pure ethanol.

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1. Introduction

Recently, the adsorption of organic molecules on metal surfaces, including the surfaces of metal nanoparticles, has attracted tremendous research interests from the viewpoints of the development of electronic and optical thin films [1], catalysis [2,3], functional nanostructured arrays, and so on [4]. In addition to those practical considerations and ultra sensitive chemical analysis [5], the fundamental interests in the metal adsorbate systems have increased in the viewpoint of the elucidation of the adsorption mechanism [6,7]. The most widely studied and well-characterized systems are adsorption of molecules on gold and silver nanoparticles. The gold and silver nanoparticles have unique characteristics, namely surface plasmon resonance, fluorescence enhancement, and the effect

of enormously enhanced electromagnetic field, which depend on the size, shape, and morphology of the nanoparticles and their assemblies [5–9].

One of the most interesting tools for analyzing adsorption systems on the gold and silver nanoparticles is surface-enhanced Raman scattering (SERS), which occurs on roughened substrates [6,10] and nanoparticles [5,7–9,11] of noble metals such as silver and gold. The studies on SERS using gold and silver nanoparticles have been intensively done for the purpose of the improvement of the enhancement factor in SERS [12], the detection of the biomolecules such as deoxyribonucleic acid, ribonucleic acid, and proteins [11,13,14], and the elucidation of the SERS mechanism [15–19]. The mechanisms of SERS enhancement are considered to be divided into electromagnetic effect and a chemical effect. It is well-known that the former effect induces the intensities of the SERS spectra and the latter induces the changes of the peak positions, the relative intensities, and the bandwidths of SERS spectra. Therefore, SERS makes it possible to obtain vibrational informations of molecules adsorbed on the surfaces of

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the metal substrates and to evaluate their environmental and adsorption conditions.

For example, adsorption characteristics of 1,4-phenylene diisocyanide (1,4-PDI) on gold nanoparticles have been investigated by means of SERS and surface-enhanced infrared absorption spectroscopy in the colloidal solution system [20,21]. The 1,4-PDI molecule has two NC groups and Au–C bonds are formed via the carbon lone-pair electrons. It has also been suggested that the adsorption mechanism is dependent on the concentration of 1,4-PDI. Namely at lower concentrations, one 1,4-PDI molecule is bound to two gold nanoparticles as the binder, while at higher concentrations, the newly adsorbing 1,4-PDI molecules are bound to Au via only one of the two NC groups, due to the limited space available to cross-link the different nanoparticles.

Although the adsorption characteristics of molecules on gold and silver nanoparticles have been extensively evaluated by SERS spectroscopy [5,6,20–22], the measurements have mostly been carried out under the conditions of colloidal solution systems. Therefore, it is quite difficult to directly examine the adsorption characteristics of molecules on the gold and silver nanoparticle substrate. Recently, we found that the three-dimensional assemblies of the gold nanoparticles were easily formed only by the addition of electrolytes into the colloidal aqueous solutions of gold nanoparticles [23–25]. This method has great advantages of controlling the size and the morphology of the nanoparticle aggregates, only by changing the electrolytes for sedimentation of the gold nanoparticles. Moreover, we have found that the SERS enhancement is profoundly dependent on the morphology of gold nanoparticle films. From these viewpoints, we have measured, in this work, Raman spectra of 4,4'-bipyridine (bpy) and rhodamine 6G (R6G) using the gold nanosphere (NS) films in order to investigate the adsorption characteristics of bpy molecules on the NS film substrates, in comparison with R6G molecules.

2. Experimental details

The colloidal solution of gold NSs for SERS measurements was prepared by using the seed/growth method [26]. At first, a seed solution, the aqueous solution of small gold NSs (2.5×10^{-4} M), was synthesized by the reduction of HAuCl_4 with citric acid as described in the literature (mean diameter 15 ± 1 nm) [27]. In the meantime, an aqueous solution containing 2.5×10^{-4} M HAuCl_4 and 0.1 M hexadecyltrimethylammonium bromide (CTAB) was prepared as the growth solution. In a vial, 40 mL of the growth solution was mixed with 0.1 mL of 0.1 M ascorbic acid solution while stirring. As a result, the yellow color changed into colorless. Next, 4.0 mL of the as-described seed solution was added to the above solution, and then stirred for 10 min until the solution turned to wine red. Particles prepared by this method were mostly spherical with the mean diameter of 35 ± 5 nm.

The NS film was prepared by the addition of a saturated aqueous NaClO_4 or NaOH (3 M) solution, as described elsewhere [23–25]. Namely, the glass slides (1×1 cm) were

set on the bottom of the vial ($\phi = 32$ mm) with 10 mL of the gold NS colloidal solution. Subsequent addition of 0.2 mL of the aqueous NaClO_4 or NaOH solution induced the precipitation of the gold NSs. After being left overnight, sedimentation of the gold NSs on the glass slides was completed, when the supernatant solution became colorless. Then the supernatant solution was removed and the sample substrates were dried in air, followed by immersion into water and ethanol for rinsing, and finally drying in air. The sample substrate was cut into almost equivalent 4 pieces and used as the SERS substrates. The NS films prepared from NaClO_4 and NaOH are denoted as NS (NaClO_4) and NS (NaOH), respectively.

R6G and bpy (Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. In the case of cast deposition (adsorption) condition, an ethanol solution of bpy ($10 \mu\text{L}$: 1.0×10^{-5} or 1.0×10^{-3} M) was dropped on the gold NS film so as to spread uniformly, followed by drying in air. In the case of immersed adsorption condition, the gold NS film was dipped into an ethanol solution of bpy (0.1 M, 3 mL) for 2 h or R6G (4.7×10^{-4} M, 3 mL) for 1 day. The subsequent changes in the adsorption phenomenon of bpy or R6G after as-described immersed adsorption procedure was carried out by soaking the adsorbed NS film in 3 mL of pure ethanol. The Raman spectra were excluded from the scattering light coming from the glass substrate.

SERS spectra were measured by a hand-made microscopic Raman spectrometer [28]. The excitation source is a diode laser (785 nm, LVL/RLT78500G, Lambda Vision) through a band pass filter. It was focused to the sample by an objective lens ($\times 10$, N.A. 0.25) through a half mirror. The power of the laser light was 30 mW before the objective lens. The backscattering light was collected by the same objective lens and passed through the half mirror, and the Rayleigh scattering was blocked by a sharp cut filter. The spectrometer (YKM0300-01, YUJI KIKAKU Ltd.) has a single diffraction grating, and the spectra were detected by a cooled charge-coupled device (LVCCD-2000, Lambda Vision). The spectral resolution of the system was about 15 cm^{-1} .

A scanning electron microscope (SEM, Hitachi S-5000) was used to investigate the shape and distribution of the gold NS films on the glass substrates.

3. Results and discussion

Fig. 1(a) shows the Raman spectrum of bpy powder, which represents the typical peaks at 659, 755, 997, 1219, 1293, 1508, and 1607 cm^{-1} , respectively. From the earlier vibrational assignments [29–31], the Raman spectrum is analyzed and listed in Table 1. Fig. 1(b) shows the Raman spectrum of the NS (NaClO_4) without bpy. However, the spectrum had weak peaks around 765, 1445, and 1620 cm^{-1} . The bands at 765 and 1445 cm^{-1} are assignable to CTAB [32,33]. This indicates that the CTAB molecules used in the preparation of NS (see Experimental section) are still adsorbed on the surface of NS film. The band at 1620 cm^{-1} is not clear at this time. However, taking into consideration of the sublimation property of bpy, some contamination of bpy molecules is not completely

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