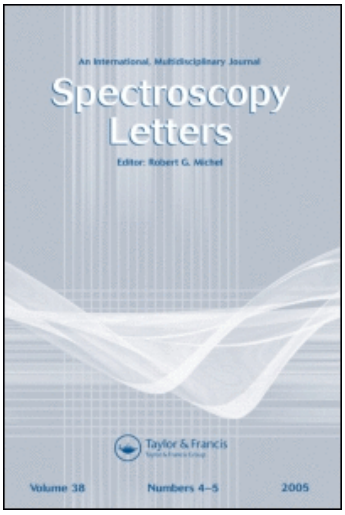

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A Direct Experimental Evidence of Collective Electron Resonance Mechanism of Surface Enhanced Infrared Spectroscopy (Seirs)

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A DIRECT EXPERIMENTAL EVIDENCE OF COLLECTIVE ELECTRON RESONANCE MECHANISM OF SURFACE ENHANCED INFRARED SPECTROSCOPY (SEIRS)

Key words: Silver Island Films, Langmuir-Blodgett, Surface Enhanced Infrared Spectroscopy (SEIRS)

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Abstract

We report here the preliminary results of the surface enhanced transmission infrared spectra of $CH_3(CH_2)_7Azo(CH_2)_3COOH$ monolayers on CaF_2 substrate which was coated by silver island films with different size and distribution. The larger enhancement of absorbance of ν(C=O) in COOH residing between silver island gap and small enhancement of absorbance of vibration mode of COO^- located on the silver islands are observed. It give us a direct experimental evidence of the collective electron resonance mechanism of surface enhance infrared spectroscopy (SEIRS), i.e. the decrease of the electromagnetic (EM) coupling reduces the enhancement factor of SEIRS.

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Introduction

Surface enhanced infrared spectroscopy (SEIRS) on small nanometric scale metal particles or rough metal surface at a nanometric scale have been reported in recent years[1,2]. Many efforts have been made to elucidate the possible mechanism of SEIRS. Most of the studies suggested that the collective electron resonance was responsible for the SEIRS, especially the coupling of the local surface electromagnetic (EM) field between the metal particles, which has been verified by indirect experimental evidence, for example, the red-shift of absorption peak of the collective electron resonance into IR region as the metal islands aggregate[2-9].

In this letter, we reported a new strategy which reveals the collective coupling between the particles of the thin silver island films play an important role in SEIRS. The procedure of this strategy involves fabrication and characterization of SEIRS-active substrate, which contains the different size and distribution of silver islands on CaF_2 substrate. Afterwards, the transmission infrared spectra of $CH_3(CH_2)_7Azo(CH_2)_3COOH$ (referred as ABD) LB monolayer on this kind of silver island films are investigated.

Experimental

Plates of CaF_2 (30×10 mm), mica wafers (10×10 mm) were used as supporting substrates for spectroscopy and Atomic Force Microscopy (AFM) studies. Prior to evaporation of silver island film, these substrates are carefully cleaning[10]. Thin silver films were deposited on the substrates by vacuum evaporator at a pressure of 4×10^{-5} torr. The thickness was measured by a quartz thickness gauge, and the deposition rate was kept at 0.1 nm/s.

For thermal annealing of the silver film, a Rapid Thermal Processor was used (Model KST-2, Beijing Instrument Factory, China). These silver coated substrates

were annealed for 20 second at 100°C, 200°C, 250°C, 300°C, 350°C, 400°C, 500°C, and 600°C, respectively. The whole system is protected by dry N_2 during the process of annealing to prevent silver oxidation.

The AFM used in this study was a Nanoscope III (Digital Instruments, USA). UV-Visible spectra of silver coated CaF_2 substrates were recorded on a Shimadzu UV-3100 UV-Visible spectrophotometer with a resolution of 2 nm. In the measurement, the bare CaF_2 plate was used as the reference. The LB monolayers of ABD were deposited onto the silver coated CaF_2 substrate by a commercialized Langmuir trough (FACE, Japan)[10].

Infrared spectra were obtained with a Perkin-Elmer System 2000 FT-IR spectrometer, equipped with a liquid nitrigen cooled MCT detector. All the spectra were obtained by referencing 100 sample (LB monolayer on silver-coated CaF_2) scans to 100 silver-coated CaF_2 without LB monolayers background scan at 4 cm^{-1} resolution with strong apodization. The sample chamber was purged with dry N_2 to eliminate the spectral interference from water vapor in air.

Results and Discussion

In order to get the silver island with different size and distribution on CaF_2 substrate, a series of same thickness silver island films on CaF_2 are prepared firstly by thermal evaporation, and then treated by annealing at different temperature[11]. As an example, the atomic force microscopy (AFM) images of as-prepared silver island film, silver films annealed at 250 and 600°C are displayed in Fig. 1a, b, and c, respectively. The results of the morphological studies show that the size of silver island films particles increases with the annealing temperature, in which the average diameter of silver particles are measured to be around 10-55nm, along with the increase of the gaps between silver islands. The

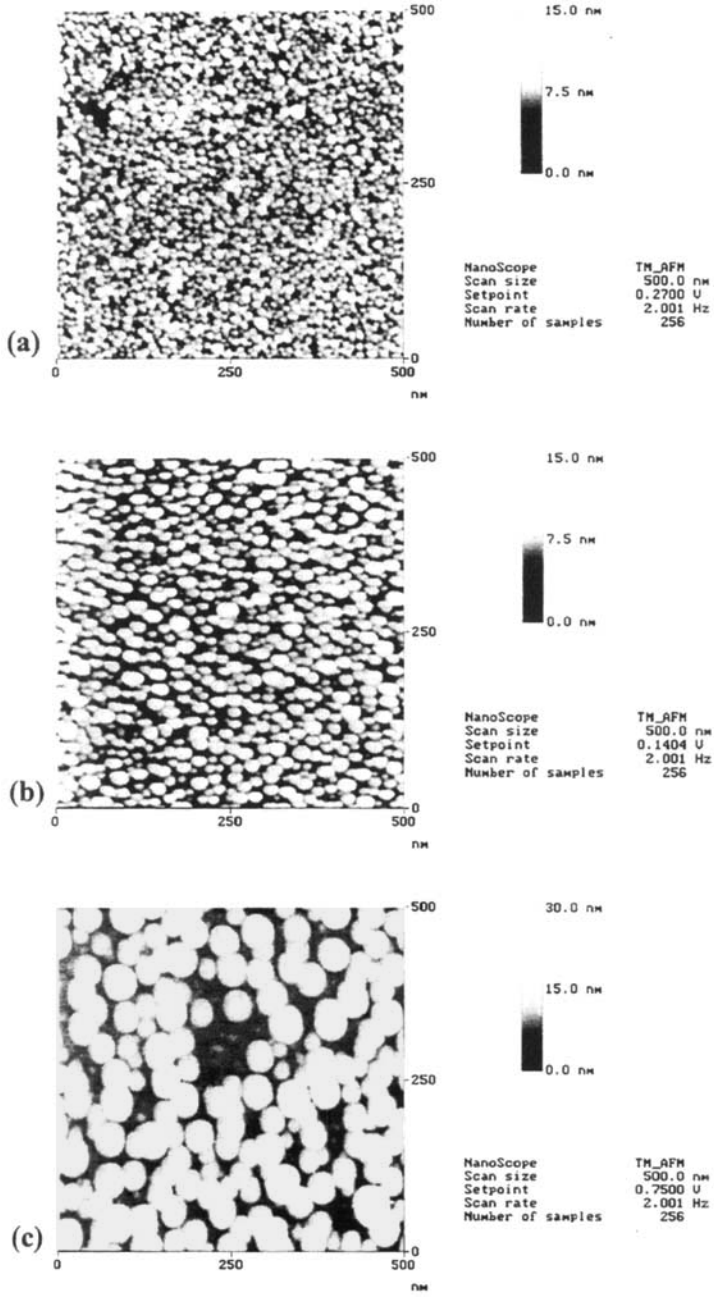

Fig. 1 The AFM images of silver island films on CaF_2 substrate: As-prepared (a), 250°C (b) and 600°C (c).

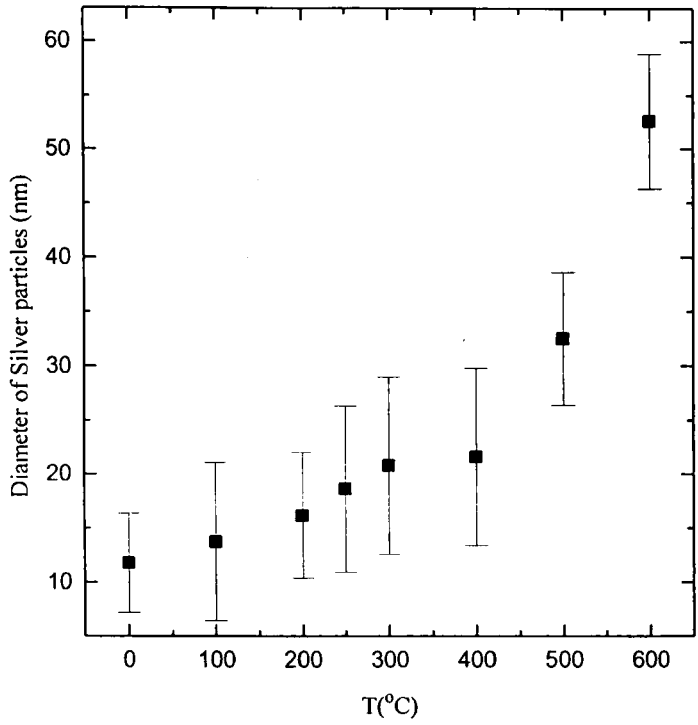

Fig. 2 The average height of the silver particles versus the annealing temperature.

height of the particles is adopted as the parameter to describe the size of the particles, obtained by manual measurement particle by particle through the section analysis of the AFM instrument. Figure 2 shows the average height of the silver particles versus the annealing temperature, in which the increase in the silver particles by annealing is clearly demonstrated.

As we know, the excitation of surface plasma oscillation is essential for surface enhanced spectroscopy (including Raman, Infrared, and Luminescence) [11-12]. Therefore, it is important to have an investigation into the optical absorption of these silver island films. Figure 3 shows the peak position of surface

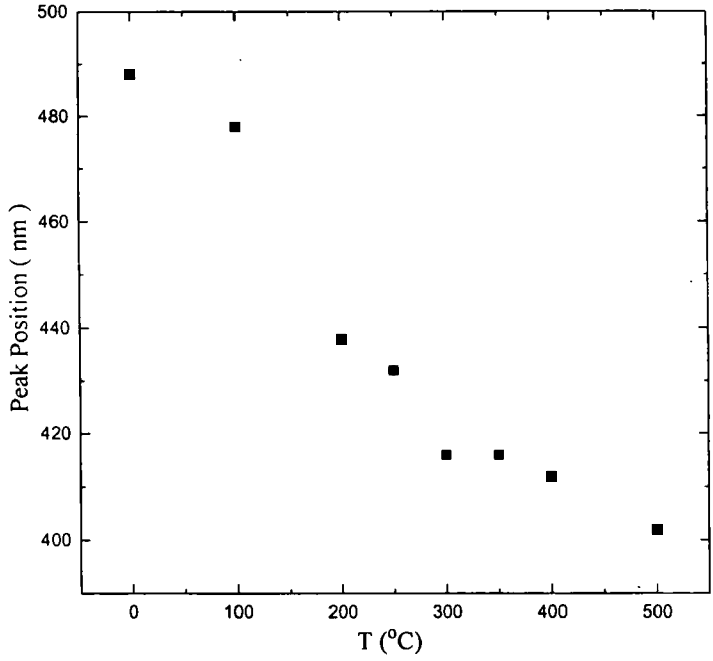

Fig. 3 The peak position of surface plasma resonance absorption of silver island films versus the annealing temperature.

plasma resonance absorption versus the annealing temperature, in which the absorption peak is found to be around 400~500nm, and a blue-shift of ~90nm is found as the temperature increase from 0°C to 600°C ('0°C' represents 'without annealing' or 'as-prepared'). The blue shift of the absorption peak of surface plasma resonance in the UV-visible spectra of these silver films is in contradiction of the principles of dependence of electron resonance on metal particle size. Previous studies on the optical absorption of metal island films show that the absorption peak of surface plasma resonance will be red-shift if the metal particles grow larger or it will remain unchanged peak if the diameter of the particles are

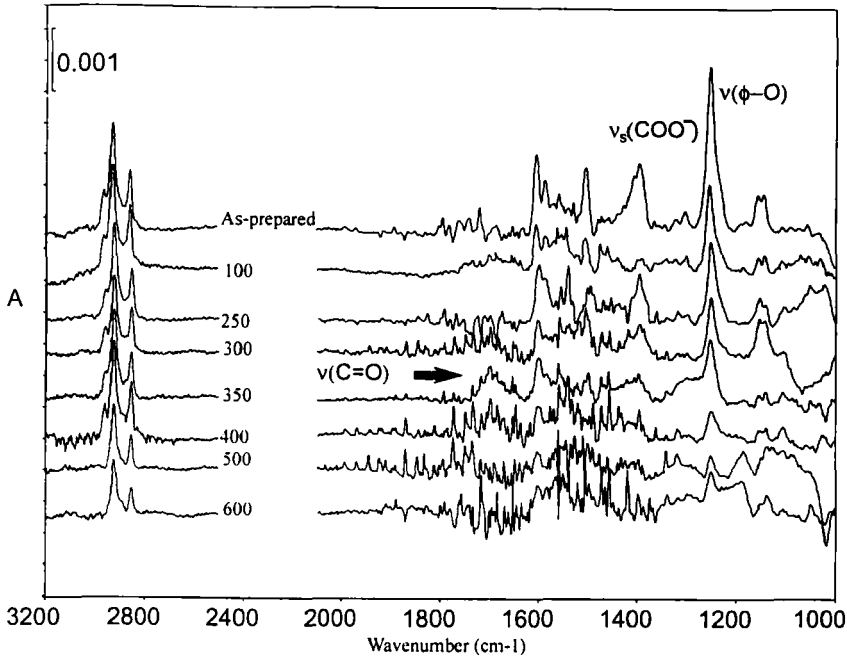

Fig. 4 The infrared spectra of ABD LB monolayers on different silver island coated CaF_2 substrate.

less than 1/10 of the wavelength of the incidence radiation[11-12]. We believe this blue shift of the absorption peak of surface plasma resonance is attributed to the less aggregation of the silver particles, i.e., the less coupling of surface plasma between neighbor particles. In other words, the only factor that affects the absorption peak position is the state of distribution of the silver particles, i.e., the distance between different particles in this study.

Langmuir-Blodgett (LB) monolayers of ABD are deposited onto these silver films. The transmission infrared spectra of the LB monolayers on these silver island-coated substrates are shown in Fig. 4. It is seen that the IR spectra are

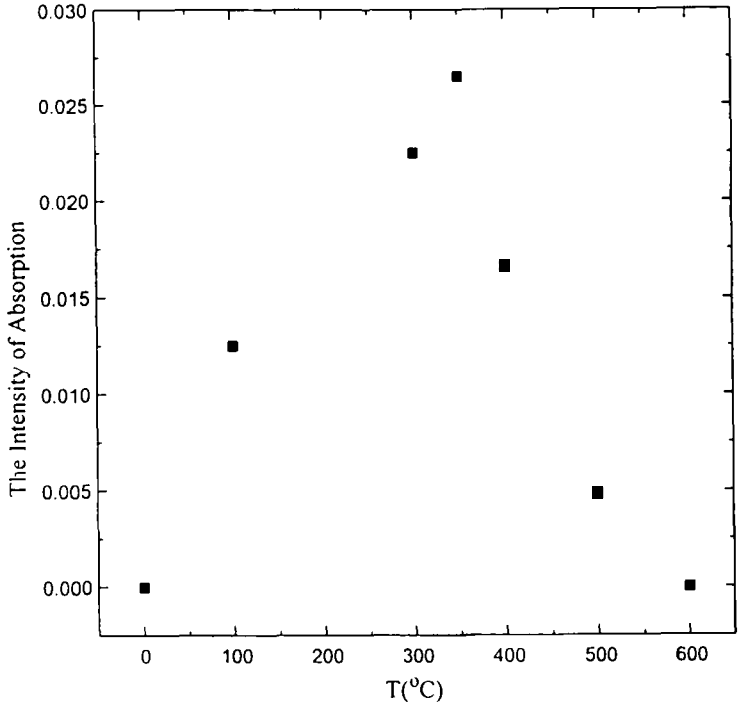

Fig. 5 The variation of the intensity absorbance of ν(C=O) in COOH with the annealing temperature.

considerably enhanced due to the presence of silver island films. One of the feature should be noticed that the carboxyl group (COOH) and carboxylate group (COO^-) are found to co-exist on the substrate, and the sensitive distinguishing ability to these two groups by infrared spectroscopy allow us to make a direct comparison between the enhancement effect on the particles and in the gap between the particles. Most importantly, the enhancement of absorption of most vibration modes decrease on the silver film which have been annealed at higher temperature, except for υ(C=O) in COOH, whose intensity increases at first and

then decrease as the annealing temperature get higher (shown in Fig.5). This phenomena of the variation of the intensity of υ(C=O) absorption can be understood as that: the increase in the gap between the island results in the increase in the amount of the COOH group, and consequently, brings about the increase in the absorbance of the υ(C=O) groups. As the distance between the island increase further, the decrease in the enhancement factor begins to take effect, resulting in the fall in the absorbance. In other words, if the silver particles are more separated, the coupling of their surface EM field will be reduced, and the absorption of infrared radiation will be decrease.

In a conclusion, mutual coupling of electromagnetic field between silver islands are directly evidenced to have its predominant effect on the SEIRS.

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