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Research paper

SERS polarization dependence of Ag nanorice dimer on metal and dielectric film

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ABSTRACT

The polarization dependence plays a great impact on the SERS intensities for the surface plasmon coupling between nanoparticle aggregating. In this work, the SERS intensities collected from nanorice heterogeneous dimer or homogeneous dimer on Au, ITO and glass substrates exhibit strong polarization dependence. This result is further analyzed by the simulated surface charge distribution and electromagnetic enhancement distribution. Our data illustrate that SERS polarization dependence exhibits in all gaps in whole system, not only the gaps between nanorices but also gaps between nanorices and film, which could be important for the application of SERS as an ultrasensitive sensing technique.

1. Introduction

Owing to their unique optical properties arising from surface plasmon, metal nanostructures have tremendous applications in catalysis [1], optical sensing [2], thermal therapy [3], waveguiding beyond diffraction limit [4], surface enhanced spectroscopy [5], etc. Especially in surface enhanced Raman scattering (SERS) [5–15], the metal nanostructures have been treated as excellent substrate since it was discovered on 1974 [6] . This is because the collective oscillation of free electrons could confine light tightly on metal surface and therefore huge electromagnetic field is generated to greatly enhance Raman signal of nearby molecule [16]. Because the small cross section in traditional Raman is overcome by huge enhanced electromagnetic field in metal nanostructures, SERS as a spectrum analytic technique with high sensitivity even at single molecule level has been widely investigated in recent years [7,8,12,17].

Because the properties of surface plasmon are highly influenced by the shape, size, configuration, component of metal nanostructures, plenty of metal nanostructures have been studied in SERS [2,16,18]. Among them, the sliver nanoparticle is one of the most favorite targets because of its good optical response in visible region and convenient modulation in geometry. For its anisotropy in structure and sharp tips, sliver nanorice as a novel plasmon nanoparticle has been reported in recent years and exhibits interesting surface plasmon properties such as multipole plasmon resonance which has exhibited amazing abilities in optical activity and environment sensor [19–24]. Therefore, the choice of sliver nanorice as enhanced material could be interesting and may exhibit amazing abilities in SERS.

In studies of SERS, the polarization dependence is an important issue in spectrum analytic technique. And the introduction of asymmetric plasmonic nanostructure plays a great impact on Raman intensities in SERS spectrum [25–28]. For example, in nanoparticle-nanowire system the maximum SERS intensity is obtained as the polarization of incident laser is perpendicular to the nanowire's long axis no matter what the nanoparticle is [29]. This fact points out the fluctuation of SERS intensities influenced by polarization should be considered in practical application. Therefore, the polarization dependence of SERS in various metal nanostructures should be investigated for the further development in the application of SERS.

Although substrate performed in all SERS measurement, a lot of previous studies on SERS in metal nanoparticles ignored substrate (e.g. glass or ITO) influence on SERS. In recent years, several groups have found out not only metal films but also dielectric films play great impacts on the SERS measurement of the effective coupling between surface charge on nanoparticle dimer and image charge on film [30–35]. Therefore, in this work, the SERS spectra of Ag nanorice dimer on different substrates (Au, ITO, glass) are investigated. Firstly, the SERS spectra of the homogeneous nanorice dimer

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made of two nanorices of similar size and heterogeneous nanorice dimer of different size are obtained on Au film. And then, the SERS spectra of similar nanorice dimers are collected on glass film and ITO film. Finally, the distributions of surface charge and electric field are simulated through finite element method to analyze the experimental results.

2. Experimental section

2.1. Material and sample preparation

$AgNO_3$, polyvinylpyrrolidone (PVP) and poly ethylene glycol 600 (PEG600) were purchased from Aladdin. 4-Nitrothiophenol (4NBT) was purchased from Aldrich Chemical co. All chemicals were used as received without further purification. Ag nanorices were synthesized according to Ref. [20].

2.2. Surface-enhance Raman scatting analysis and characterization

Raman measurements were performed with a self-build Raman microscope (iHR550, Horiba). A 633 nm laser was irradiated onto the sample with a 100× objective. A half-wave plate for 633 nm was used to modulate the polarization of incident laser. All instruments were standardized by silicon wafer before experiment and the intensities of silicon peak didn't change when the direction of incident laser was changed. A copper grid was attached on film to calibrate the position of dimers.

2.3. Simulation parameters

A commercial simulation tool based on finite element method (COMSOL commercial package) was used to calculate the distributions of electric field and surface charge. The gap between two silver nanorices was set as 2 nm and the nanorice dimers were located 2 nm above the Au, glass and ITO film. A 633 nm incident light was vertical to film surface.

3. Results and discussion

Fig. 1 shows the polarization dependence of SERS spectra in homogeneous and heterogeneous nanorice dimers on Au film. Ag nanorice dimer made of two nanorices of similar size on Au film substrate, as schematically described in Fig. 1a. Fig. 1b presents the polarization diagrams of the SERS intensity at 1067 cm^{-1}. The black and red polarization diagrams represent homogeneous nanorice dimer and heterogeneous nanorice dimer, in which the polarization dependence can be easily observed. The SERS spectra are carried out with various angles of θ, where $\theta = 0°$ means the polarization direction of incident light is vertical direction. The SERS spectra of homogeneous dimer are shown in Fig. 1c, where a maximum SERS intensity at $\theta = 40°$, a minimum SERS intensity at $\theta = 120°$ and a median SERS intensity at $\theta = 80°$ are exhibited. The right inset SEM image shows the corresponding homogeneous nanorice dimer is 400 nm in length and 100 nm in width. According to three SERS spectra, it is obvious that the SERS intensity of 4NBT importantly depends on the polarization direction of incident laser. Besides, the extra Raman peaks at 1143, 1390 and 1432 cm^{-1} demonstrate 4-4′dimercapto-azobenzene (DMAB) produced by 4NBT on Au film where a plasmon driven surface catalysis (PDSC) reaction is performed [36–38]. Comparing the SEM image with the polarization diagram, it can be obtained that maximum SERS intensity is reached when the polarization direction of incident laser is almost perpendicular to the nanorice's long axis. On the contrary, minimum SERS intensity is reached when the polarization direction of incident laser is parallel to the nanorice's long axis. Fig. 1d shows the SERS spectra of the heterogeneous nanorice dimer on Au film. The right inset SEM image shows that heterogeneous nanorices are 400 nm and 200 nm in length and 100 nm in width. There are three spectra given of maximum SERS intensity at $\theta = 40°$, minimum SERS intensity at $\theta = 120°$ and median SERS intensity at $\theta = 80°$. It clearly shows that the SERS intensity of 4NBT is obviously enhanced with an increase of the incident laser angle until the polarization direction of the laser is perpendicular to the nanorice's long axis. Similar to homogeneous dimer, there are three extra Raman peaks at 1143, 1390 and 1432 cm^{-1} demonstrating DMAB produced by 4NBT on Au film. Equally, according to the SEM image and the polarization diagram, similar conclusion can be deduced that the maximum SERS intensity could be achieved when the polarization direction of incident laser is vertical to the long axis of nanorice and minimum SERS intensity could be generated under parallel conditions.

To investigate the influence of substrate on the polarization dependence of nanorice dimer, Fig. 2 presents the SERS polarization dependence of the homogeneous nanorice and heterogeneous nanorice dimers on ITO and glass film. The SERS spectra with maximum intensity are illustrated in Fig. 2a, in which the red, black, pink, blue, orange and navy lines represent heterogeneous nanorice dimer on ITO film, homogeneous nanorice dimer on ITO film, homogeneous nanorice dimer on glass film, heterogeneous nanorice dimer on glass film, homogeneous nanorice dimer on Au film and heterogeneous nanorice dimer on Au film. It is very easy to obtain that the SERS intensity on Au film is the strongest, and the SERS intensity on ITO film is stronger than that on glass film with the same laser intensity, which could be understood due to the more image charge produced on Au film than that on ITO film and glass film according to our recent work [33]. From the date in Fig. 2a, it can be found three extra peaks at 1143, 1390 and 1432 cm^{-1}, which demonstrate DMAB produced by 4NBT on ITO and glass film. The polarization diagrams of four nanorice dimers are presented in Fig. 2b–e. Fig. 2b shows the diagram of homogeneous nanorice dimer on ITO film and the nanorices are 400 nm in length and 100 nm in width; 2c shows the diagram of heterogeneous nanorice dimer on ITO film and the nanorices are 400 nm and 250 nm in length and 100 nm and 80 nm in width; 2d shows the diagram of heterogeneous nanorice dimer on glass film and the nanorices are 400 nm and 250 nm in length and 100 nm and 80 nm in width; 2e shows the diagram of homogeneous nanorice dimer on glass film and the nanorices are 300 nm in length and 100 nm in width. The results of Fig. 2b–e are similar with each other. The maximum SERS intensity is achieved when the polarization direction of incident laser is vertical to the long axis of nanorice and the minimum SERS intensity is achieved under parallel conditions. According to the data in Fig. 2, the conclusion can obtain that the polarization dependence of nanorice dimer has no relationship to the types of film.

To better understand the SERS polarization dependence of nanorice dimer, a detailed simulation about the distribution of surface charge is illustrated in Fig. 3, where $\alpha = 0°$ means the polarization of incident laser is horizontal direction. Here heterogeneous nanorices are 400 nm and 200 nm in length and 100 nm in width, and homogeneous nanorices are 400 nm in length and 100 nm in width, in which the polarization direction of incident laser is vertical to the long axis of nanorice. The color legend value of nanorice dimer is small that cannot make out value clearly, and we only plot the maximum and minimum values in color legend value. Fig. 3a–d shows the 2D distributions of surface image charge on Au film and glass film surface, respectively. The charge distribution on Au film is larger than that on glass film which agrees well with electric field enhancement. The difference of the collection and distribution of surface charge resulted in different electric field distribution of whole nanorice dimer. Fig. 3a′–d′ choose the electric field