



Polarization-dependent hotspots formed in crossed silver nanowires for surface-enhanced Raman spectroscopy



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ABSTRACT

Well-defined metal nanostructures with highly tunable optical properties are promising substrates for surface-enhanced Raman scattering (SERS) research and applications. In this paper, we present a crossed junction to create plasmonic hotspot, which was fabricated by the micromanipulation of chemically synthesized silver nanowires. The field enhancements were evaluated via the detection of Raman spectra by the means of local and remote excitation, respectively. The experimental investigation and numerical simulation of dependence on polarization direction were performed. The nature of the polarization dependent enhancement is further discussed. This work would be valuable for studying properties of more complex regular nanostructure, such as 3-dimensional structures consisting of nanogaps and vertical stacking, for ultrahigh-enhancement SERS.

1. Introduction

Interaction of light with metallic nanostructures leads to the excitation of surface plasmons (SPs), a collective oscillation of conduction electrons, which can greatly enhance electromagnetic (EM) fields by several orders of magnitude when light is localized in the gaps or junctions of the nanostructures [1–3]. This effect of the enhanced EM fields that are usually called “hotspots” have been successfully used in surface-enhanced Raman scattering (SERS) with ultra-high and even down to single molecule sensitivity for extensive applications in the field of chemical [4,5], biological [6,7] and material sciences [8], etc.

Majority of previous work on SERS in general were conducted on metallic rough surfaces [9,10], islands/fractal films [11] and complex nanoparticle aggregates [12], etc., drawbacks of which are extreme inhomogeneity and random polarization orientation of the hotspots in them. It is important and challenging to fabricate regular-shaped nanostructures to study optical properties of the hotspots for SERS fundamental research and wide applications. As an important kind of foundation elements in the nanostructures, metallic nanowires have been extensively used in plasmonic science and technology at the nanoscale [13,14]. Though the distal ends of the single nanowire are able to excite SPs when incident light is polarized along the nanowire axis, the ends are rarely used for SERS due to relatively weak enhancement [15]. This limitation can be broken when a single nanoparticle

is in close proximity to the individual nanowire. The nanoparticle can function as an antenna that provides a means of coupling light into nanowire plasmons and generating the hotspot [16]. Wei et al. investigated the optical properties of the hotspots in gold nanoparticle–nanowire systems, and found that the SERS intensity is maximal when the incident light is polarized across the particle and the wire [17]. In addition, nanowire–nanowire systems can also produce the SERS hotspots. Tao and Yang fabricated aligned films of silver nanowires and studied SERS signal with respect to polarization and structural ordering [18]. Their results show that the hotspots are localized in the interstitials between adjacent nanowires with very sensitivity to the polarization of the incident light. Since then many studies on the optical properties of the hotspots have been conducted on various well-defined nanostructures, such as single silver nanowire–nanoparticle array [19], nano-gap between adjacent nanostructure [20], grating-like arrays of nanoparticles [21], silver nanowire dimers [22,23] and silver nanowire bundles [24,25], etc.

Silver nanowires have attracted much attention due to their incomparable advantages, such as easy preparation, regular and uniform geometry, ability to transfer light energy with relatively low-absorption loss due to the propagation of SPs [26–28]. For instance, a single silver nanowire of ~100 nm in diameter can be used as efficient plasmonic waveguides over many microns distance, providing a route to separate

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the point of the light excitation from the point of SERS detection. This remote excitation methodology (RE-SERS) affords low background spectra with greatly reduced sample photo-degradation [29,30]. Moreover, the coupling of light into SPs makes it possible to reduce the dimensions of light-based devices to nanoscale [31]. In recent years, Song et al. studied remote-excitation surface catalysis reaction via the junction of crossed nanowires [32].

In this work, we present a crossed junction to create plasmonic hotspot, which was fabricated via micromanipulation of chemically synthesized silver nanowires on a glass substrate. SERS spectra in the local and remote excitation conditions were detected, respectively. In order to verify the SPs induced field enhancement, Raman spectra at the cross junction of the Cu₂O nanowires excited and detected in the same way were also measured. The polarization behaviors of the SERS scattering in the silver cross junction were investigated systematically. Furthermore, the numerical simulation of EM field enhancement was also performed, the results of which have explained these behaviors and revealed the nature of the polarization dependence enhancement.

2. Method details

2.1. Material synthesis

The silver nanowires used in the experiments were synthesized by the polyol method [33,34]. The synthesis process is described as follows. Firstly, 50.94 mg AgNO₃ was dissolved into 3 ml Ethylene Glycol (EG) and 199.8 mg PVP was dissolved into another 3 ml EG solution, respectively. The PVP/EG solution was preheated at 70 °C for 40 min to ensure the PVP fully dissolved. Meanwhile, another 5 ml EG was preheated at 160 °C for 40 min in an oil bath pot. Next, the AgNO₃/EG and PVP/EG solution were dropped into the prepared 5 ml EG solution at the same time and the dropping rate should be controlled at 0.3 ml/min. After the dropping process was finished, the mixture solution was still stirred and heated at 160 °C for another hour. The stir rate was controlled no more than 260 rpm. When the color of reaction solution became light gray, the silver nanowires had been produced. In the end, the reaction solution was centrifuged and rinsed. The completed solution of Ag nanowires was diluted 10 times. The diluted solution was then dropped onto a clean glass substrate. The average diameter of the silver nanowires was measured to be 100–150 nm from SEM images, and typical SEM images of the nanowire are shown in Fig. 1(a) and (b). The inset in Fig. 1(b) displays the corresponding EDS spectrum of the nanowire, which indicates that the nanowire structure only consists of Ag element, while the peak in 2.17 keV is ascribed to Au which was sputtered on the Ag nanowire–glass surface in order to get the SEM picture.

2.2. Experimental setup

The experimental setup for silver nanowire manipulation and SERS detection is schematically shown in Fig. 1(c). The micromanipulator (MMO-202ND, Narishige, not shown in the figure) was applied to manipulate the silver nanowires and construct the cross structures through an optical fiber probe under the inspection of an optical microscope. The fiber probes were prepared by pulling a heated optical fiber, whose diameter of the probe tip apex was several tens of nanometers. After the cross structures were ready, the ethanol solution of the malachite green (MG) molecules (10⁻⁵ M) as probe molecules was added and left to dry in air, as shown in the zoom diagram in Fig. 1(c).

For SERS detection, the laser light with wavelength of 632.8 nm, passing through a neutral density filter and polarizer, is reflected by the mirrors and then focused on the sample with spot size of ~1 μm through the objective lens (100×, N.A. = 0.85). The neutral density filter and polarizer are used to control the excitation light power and polarization state of the incident light, respectively. Scattering light from the sample is collected by the same objective lens and guided into the confocal

Raman spectrometer (Renishaw, Invia), which basically consists of a dichroic mirror, pinhole, spectro-grating and CCD, etc. Since the pinhole used in the spectrometer is 50 μm and the objective is 100×, the detection region is consequently ~500 nm.

3. Results and discussion

3.1. Raman scattering enhancement

A typical optical image of the manipulated structures consisting of two almost orthogonal silver nanowires is shown in Fig. 2(a) and corresponding Raman spectra of the MG molecules detected from the cross junction at different excitation positions are given in Fig. 2(b). In this figure, the letters L, D and M represent the different excitation positions corresponding to local junction, distal end and middle of the nanowire, respectively. And the red and blue arrows represent polarization direction of the excitation light at local junction and distal end, respectively. The power of the excitation light was 4.2 mW and the collection time was 10 s. From the spectrum (red curve) excited at the local junction, the characteristic peaks of the MG molecules can be clearly resolved. As we know, peaks at 1615, 1590, 1486 and 1291 cm⁻¹ are assigned to the ring C–C stretching vibration, peaks at 1392 and 1365 cm⁻¹ are assigned to N–ph + ring vibration and N–ph vibration, peaks at 1215, 1176, 913 and 798 cm⁻¹ are assigned to the in-plane C–H bond bending, respectively. The enhancement factor (EF) can be calculated by using the following formula [35]

$$EF = \left[\frac{I_{sers}}{N_{sers}} \right] / \left[\frac{I_{ref}}{N_{ref}} \right] \quad (1)$$

where I_{sers} is the surface enhanced Raman intensity of the MG molecules on the SERS-active substrate (crossed silver nanowires) and I_{ref} is the intensity of the same Raman band under non-SERS conditions used as reference. A 10⁻³ M MG solution was employed as the reference and the corresponding Raman spectrum is shown in the inset of Fig. 2(b). N_{sers} is the number of MG molecules adsorbed on the SERS-active substrate under the laser spot area and N_{ref} is the number of molecules illuminated within the volume of the laser waist for the 10⁻³ M MG solution. The solid nature of the silver nanowires prevents the vertical incidence laser from penetrating, thus the MG molecules adsorbed on the back of top nanowire do not contribute to the Raman scattering. With laser directly irradiation onto the junction, the irradiation area of the bottom wire was ~6 × 10³ nm². For estimating the N_{sers} value, the MG molecules were assumed to be adsorbed on the SERS-active substrate as a monolayer (one MG molecule occupies 1.3 nm² [36]), yielding an estimated N_{sers} of 4.6 × 10³. N_{ref} was calculated as

$$N_{ref} = (VcN_A/A_{sub}) A_{laser} \quad (2)$$

where V is the volume of the droplet, c is the molar concentration of the analyte on the reference region, N_A is Avogadro's number, A_{sub} is the size of the substrate, and A_{laser} is the size of the laser spot. In the experiment, 10 μL MG ethanol solution (1.0 × 10⁻³ mol/L) was dried onto the glass substrate (1 × 1 cm²). The probe molecules are assumed to distribute uniformly on the substrates, and the diameter of the light spot is about 0.5 μm, leading to $N_{ref} = 1.18 × 10^7$. Based on $I_{sers} = 4.5 × 10^4$ and $I_{ref} = 710$ at 1615 cm⁻¹ Raman peak signal, the enhancement factors were estimated to be 1.6 × 10⁵ for the junctions.

In order to confirm the SPs induced field enhancement, the Cu₂O nanowires were applied since Cu₂O materials are usually acted as SERS substrates due to their chemical enhancement (CE) effect, where charge transfer (CT) plays a crucial role at the semiconductor–molecule interface [37]. More specifically, amplification of the molecular polarization tensor occurs and thus the Raman scattering of molecules is enhanced. In the present experiment, the Raman spectra at cross junction of the Cu₂O nanowires shown in Fig. 2(c), excited and detected in the same methods as above, were measured and given in Fig. 2(d). From the result obtained with local excitation and detection, it is easy to find that the

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