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Remote-Excitation Surface-Enhanced Raman Scattering Using Propagating Ag Nanowire Plasmons

Yurui Fang,[†,‡] Hong Wei,[†,‡] Feng Hao,[§] Peter Nordlander,[§] and Hongxing Xu[‡,||,*]

Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Box 603-146, 100190, Beijing, China, Department of Physics and Astronomy, Department of Electrical and Computer Engineering, Laboratory for Nanophotonics, Rice University, Houston, Texas 77005, USA, Division of Solid State Physics/The Nanometer Consortium, Lund University, Box 118, S-22100, Lund, Sweden

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ABSTRACT

Using propagating plasmons on silver nanowires as an excitation source we perform surface-enhanced Raman scattering (SERS) at a nanoparticle/wire junction located remotely from the laser illumination spot with sensitivities in a few molecules range. Simultaneous multisite remote-excitation SERS sensing can also be achieved.

The study of the propagation of plasmons in metallic nanostructures has recently been the subject of intensive focus due to their potential applications in new types of devices for nanoelectronics and nanophotonics.[1−4] The coupling of light into surface plasmons (SPs) in nanostructures and the subsequent emission after finite propagation distances has been studied in a variety of different nanostructures, for example, nanoparticle arrays,[5] metal strips,[6,7] and nanoholes[8,9] and grooves[10] in metal films. Recently it was demonstrated that silver nanowires can serve as plasmonic waveguides.[11,12] A nearby nanoparticle or wire defect can serve as an efficient nanoantenna, directing both the input and output coupling of light for the propagating nanowire plasmons.[13,14]

The excitation of SPs in metal nanostructures can generate sizable electromagnetic field enhancements due to the large transient surface dipoles induced by the plasmons. Such field enhancements are the underlying physical basis for surface enhancement Raman scattering (SERS), an analytical chemical sensing technique growing in importance since it was first reported three decades ago.[15−17] The extremely large enhancements of the Raman cross sections provided by the SPs make the detection of analytes possible at extremely low concentrations, even at the single molecules level.[18−22] Since SERS can provide spectroscopic fingerprints of molecules and can also permit measurements of samples with minimal invasiveness, it is playing an increasingly important role in biophysics, biochemistry, and biomedical research.[23,24]

In a conventional SERS experiment, the incident laser light is focused onto the SERS active spot on the nanostructure and the emitted Raman light is detected from the same spot. While this geometry is easy to accomplish on a substrate, such an approach would not be feasible in numerous applications, especially in living systems, where the higher power incident laser light might cause cell destruction or induce a chemical modification of the analyte. In a recent study, we showed that the junction between a nanowire and an adjacent nanoparticle can provide large SERS enhancements similar in magnitude to what is obtained for resonant excitation of nanoparticle dimer "hot-spots".[20,25−27]

In this work, we demonstrate that a large SERS signal can be detected from a location that is remote from the illumination point. By generating propagating plasmons at one end of a silver nanowire, a clear Raman signal can be obtained at a distant location on the wire, where an adjacent nanoparticle is present.[28] The remote-excitation SERS of probe molecules is obtained only from the locations of the nanoscale junctions formed between silver nanoparticles and the nanowire.

Ag nanowires and nanoparticles were synthesized following a standard protocol.[29] The colloidal solution containing Ag nanowires and nanoparticles was then mixed with a solution

* Corresponding authors. E-mail: hxxu@aphy.iphy.ac.cn
† These authors contributed equally to this work.
‡ Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Box 603-146, 100190, Beijing, China
§ Department of Physics and Astronomy, Department of Electrical and Computer Engineering, Laboratory for Nanophotonics, Rice University, Houston, Texas 77005, USA
|| Division of Solid State Physics/The Nanometer Consortium, Lund University, Box 118, S-22100, Lund, Sweden.

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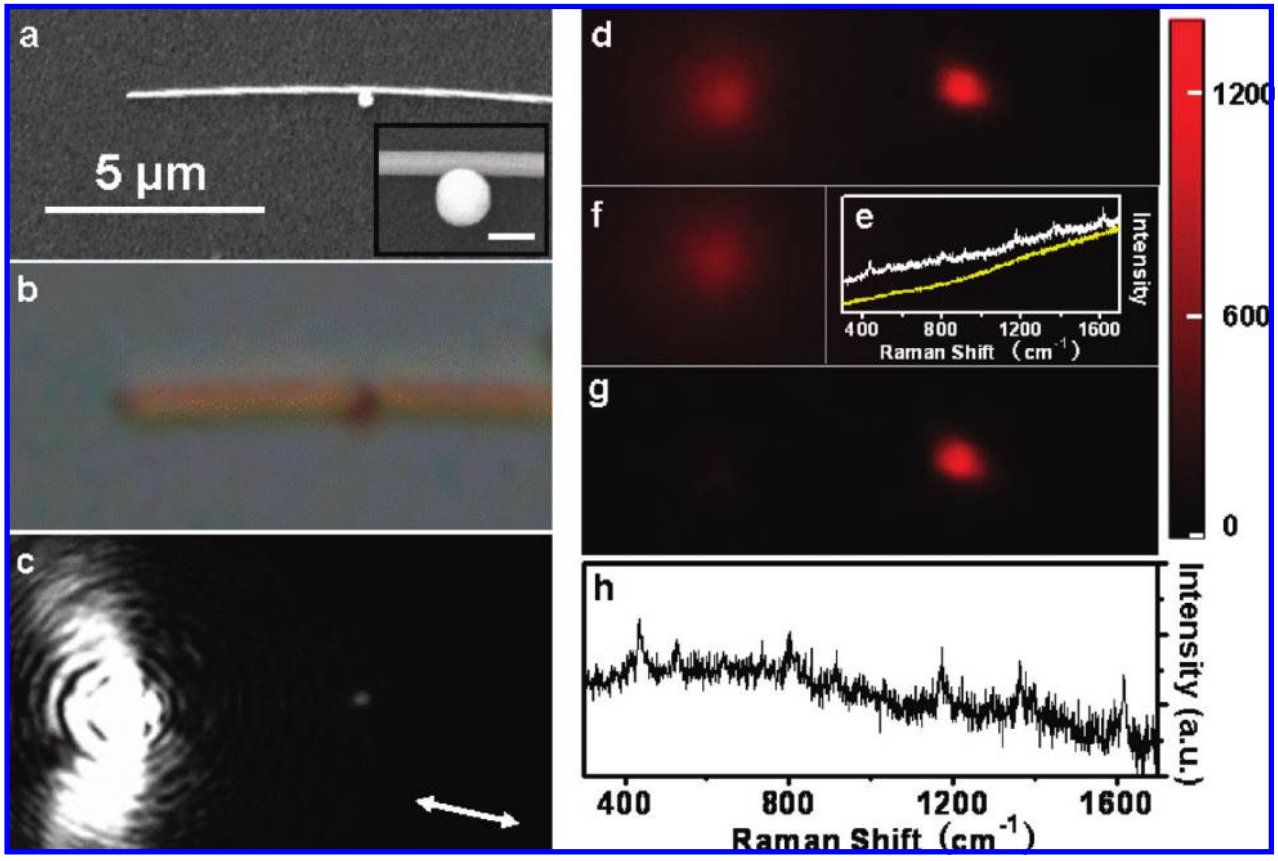

Figure 1. Remote-excitation SERS of MGITC molecules excited through propagating plasmons. (a) SEM image of a nanowire−nanoparticle system. (b) The corresponding bright field optical image. (c) The optical image of the same system collected with a TE cooled 1392 × 1040 CCD detector and 0.1 s integration time. The size of the laser spot is smaller than 1 μm. This image is taken after the Raman measurements. (d) The corresponding Raman image at the Raman peak of 436 cm^{-1}. The integration time is 10 s, the size of the laser spot is about 2 μm, and the laser power is about 3 mW at the left end of the nanowire. (e) Raman spectra from the laser spot at the left end of the nanowire and the remote site of the wire/particle junction, respectively. The remote-excitation SERS spectrum is obtained by separating the Raman collection spot from the laser spot. The laser intensity is 0.7 mW at the left end of the nanowire, and the integration time is 10 s. (f) The fluorescence background image of smooth ITO glass only. (g) The Raman image after background subtraction of panel d from panel f. (H) The remote-excitation SERS spectrum after fluorescence background correction with the spectra taken from panel e.

of malachite green isothiocyanate (MGITC) molecules in the order of 10^{-11} M at the same volume ratio. We believe that the number of MGITC molecules in the nanoparticle/wire junctions is on average less than one molecule based on the general estimation means of many previous single molecules SERS studies.[18−22] After incubating for 3 h, 10 μL of the mixture was spin-coated on a clean ITO glass and dried. The structures formed contained both individual nanowires and nanowires with adjacent nanoparticles and were found to be well separated on the glass surface.

The bright field image is obtained in a Leica microscope equipped in a confocal Raman spectroscopic system (Renishaw, Invia) through an objective 50× with the numerical aperture (NA) of 0.75, which is the same objective used for all Raman measurements. The Raman image is detected by the TE air-cooled 576 × 400 CCD array in the confocal Raman system with a band-pass ±20 cm^{-1} at the Raman shift of 436 cm^{-1}, while the laser light was blocked by two notch filters (OD > 12). The integration time is 10 s, the size of the laser spot is about 2 μm, and the laser power is about 3 mW at the left end of the nanowire. The remote-excitation SERS spectrum is obtained by separating the Raman collection spot from the laser spot. The laser intensity is 0.7 mW at the left end of the nanowire, and the integration time is 10 s. After the Raman measurements, the optical image illuminated with focused laser beam through an oil immersion objective (NA = 1.35) with the incident wavelength of 632.8 nm is collected with a TE cooled 1392 × 1040 CCD detector and 0.1 s integration time. The size of the laser spot is smaller than 1 μm.

Figure 1a shows a scanning electron microscopy (SEM) image of a typical nanowire−nanoparticle system. The inset shows a high magnification image of the Ag nanoparticle near the Ag nanowire with a scale bar of 300 nm. The corresponding bright field optical microscopy image is shown in Figure 1b, where the dark spot on the nanowire is caused by the different scattering characteristics from a nanoparticle/wire junction. When a He−Ne laser beam of wavelength 632.8 nm through an oil immersion objective (NA = 1.35) is focused on one end of the nanowire, as shown in Figure 1c with the incident polarization as the white arrow (same polarization as in the Raman measurements), the light coupled out from the nanowire−nanoparticle junction can be clearly seen as a bright spot. The propagation distance

from the laser spot is about 6 μm. For convenience, the oil immersion optical image is obtained after the Raman measurements.

Figure 1d shows the Raman image of the nanowire−nanoparticle system at the Raman peak of 436 cm^{-1}. Surprisingly, strong SERS signals from the nanowire−nanoparticle junction are obtained. The extremely low molecule density resulting from our preparation method suggests that these signals may originate from only a few MGITC molecules at the resonant frequency. The luminescence from the ITO glass substrate contributes a significant background to the signal that constitutes the Raman image. An analysis of the spectrum from the laser spot shows that no Raman modes are present while the remote-excitation spectrum at the nanowire−nanoparticle junctions clearly displays the relevant MCITC Raman modes (Figure 1e). To directly show the intensity of the Raman signal, we subtract the fluorescence background taken elsewhere from a bare ITO glass surface without metal nanostructures shown in Figure 1f. The corresponding Raman image, which now is directly proportional to the Raman signal, is shown in Figure 1g. The Raman spectrum after the fluorescence background subtraction is shown in Figure 1h, which clearly shows the vibrational features of MCITC,[26,30] similar to the normal SERS spectrum (Supporting Information). Approximately 10% of the particle/wire systems investigated show such behavior in the experimental conditions used here. Since there are no detectable Raman signals from the laser focus spot, it is unlikely that the Raman signal emitted from the junction is a directly excited Raman signal that has propagated from the illumination point to the nanowire/particle junction. No detectable remote-excitation SERS was observed for bare Ag nanowires, although a weak fluorescence background could sometimes be observed at the other end of some of the shorter nanowires investigated. The picture clearly reveals that the nanowire−nanoparticle junction serves as a hot-spot for remote-excitation Raman spectroscopy. Keeping the same remote distance, if the laser focus spot is not on the left end of the wire in Figure 1, there are no remote-excitation SERS signals. This fact can rule out any possible experimental artifacts due to the background scattering and demonstrate a true remote-excitation SERS sensing here.

Efficient remote-excitation SERS sensing can be also realized by other strongly coupled systems. In Supporting Information, we show that nanowire-nanowire junctions can also serve as remote-excitation Raman scattering hot spots.

To provide more insight and an understanding of the remote-excitation Raman scattering observed in the present experiment, we have performed electromagnetic calculations using a finite element method using the commercial COMSOL multiphysics software package. For simplicity, we model the system as a solid nanosphere next to a cylindrical wire. This idealized geometry will result in underestimates of the actual field enhancements in the junction, since local imperfections in the junction can drastically enhance the local fields.[31] The plasmonic SERS enhancement in a nanostructure is a product of two enhancement factors, the local electromagnetic (EM) enhancement factor and the Raman emission (RE) factor.[32] The EM factor originates from the large electromagnetic field enhancements caused by the excitation of plasmons and is proportional to the square of the actual induced local electromagnetic fields in the nanoparticle/wire junction. The RE enhancement factor in a junction is proportional to the square of the maximum obtainable electromagnetic field enhancement and is independent of the excitation mechanism. In Figure 2, we plot the EM, RE, and the total SERS enhancement factors along a typical nanowire−nanoparticle system. Panel a shows the calculated electromagnetic field enhancements along the wire following a localized excitation at the left end of the wire. A coupling of the incident electromagnetic light into the wire is apparent. The field enhancement in the hot spot in the nanowire−nanoparticle junction located at a distance of 6 μm from the wire end is around 20 giving an EM enhancement factor of 400. A calculation of the field enhancement at an individual nanowire following end-wire excitation shows that the decay of the local field enhancement with plasmon propagation distance along the wire is essentially exponential with a $1/e$ length of 4.35 μm at the laser wavelength used in the experiment. For a junction located at x micrometers from the excitation point, the actual field enhancement can thus be parametrized as $80e^{-x/4.35}$. Panel b shows the RE enhancement, that is, the square of maximum obtainable field enhancement along the wire for a plane wave excitation with polarization across the nanowire−nanoparticle junction. Panel c shows the mapping of the remote-excitation SERS enhancement, which is obtained by averaging the product of the EM and RE factors with a weight function proportional to $\exp(-r^2/r_0^2)$ in order to simulate the remote-excitation Raman image in Figure 1g. A value of $r_0 = 150$ nm was used in order to reproduce the spatial extent of the image of the Raman hotspot detected in the experiment. The calculated remote-excitation SERS enhancement is found to be only weakly dependent on the polarization of the excitation light. The calculated remote-excitation SERS enhancement at the hotspot is found to be around 10^7-10^8, which may be sufficient for detection of a few molecules at the resonant frequency of the molecule.[33]

Interestingly, simultaneous multisite remote-excitation SERS sensing can also be achieved. Figure 3 shows three examples where propagating wire plasmons coupled out at nanoparticles or crossed nanowire junctions can function as remote-excitation SERS sites. Figure 3a,d shows a case of two nearby remote sites. These two positions are too close to be clearly distinguished by the present Raman imaging system. Figure 3d shows an asymmetric dumbbell-like Raman spot that appears to be a combination of possible two Raman spots with different Raman intensities. As shown in Figure 3a, these two sites are formed from a small cluster of two spherical, one cubic, and one rodlike nanoparticle. Figure 3b,e shows the case of two well-separated remote sites. The site closest to the laser illumination spot is quite weak, probably due to the weak plasmon coupling between the cubic Ag nanoparticle and the Ag nanowire. A much stronger remote-excitation SERS site is located about 7 μm away from the illumination spot. The strong coupling

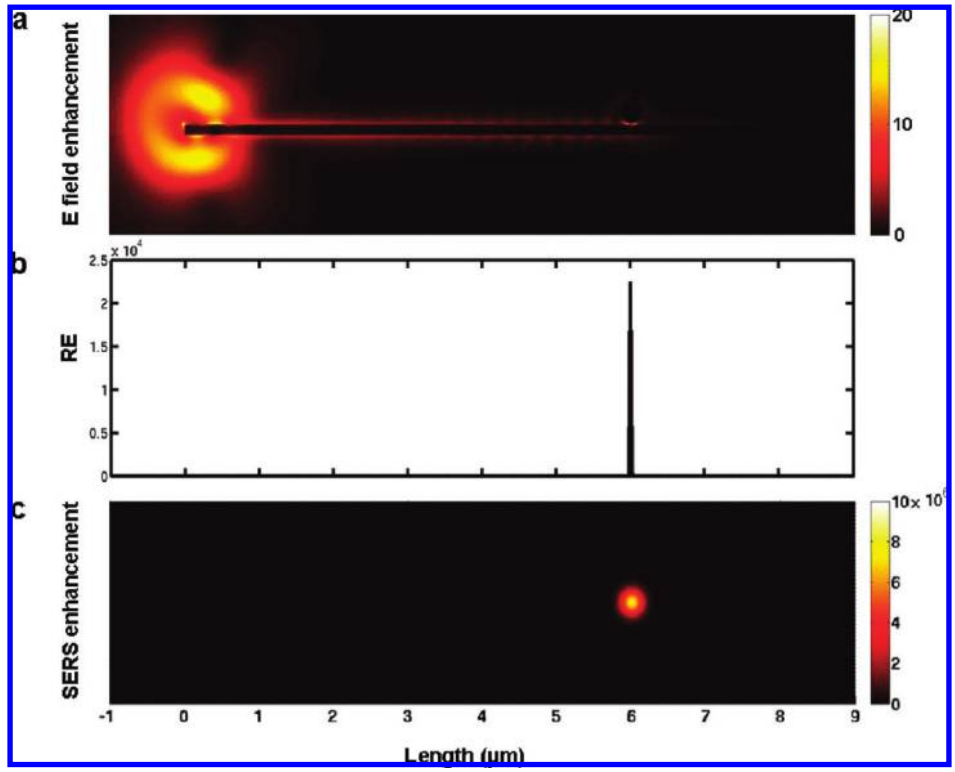

Figure 2. Calculated electromagnetic field enhancement in the nanowire/nanoparticle system. (a) The field enhancements along the wire following a local excitation at the left end of the wire. (b) The RE enhancement factors, calculated as the square of the field enhancements in the system following a plane wave excitation of the system with polarization across the nanoparticle-wire junction. (c) The mapping of the Raman signal, calculated as the product of the EM and RE enhancement factors, and then averaged with weight function $\exp(-r^2/r_0^2)$, where r_0 is 150 nm. The nanoparticles are modeled using dielectric data from Johnson and Christy. The length of the nanowire is 18 μm and its diameter is 120 nm. The nanoparticle is assumed spherical with a diameter of 300 nm placed 1 nm away from the wire.

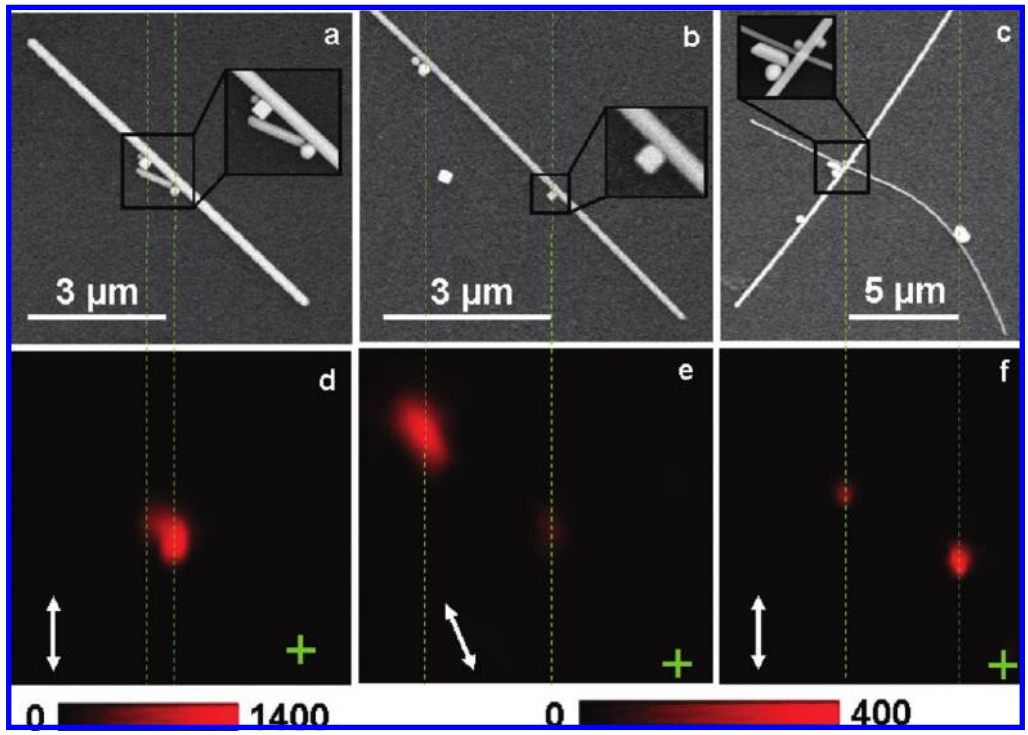

Figure 3. Systems showing two remote sites for SERS; the experimental conditions are same in Figure 1d. (a−c) SEM images. (d−f) Corresponding Raman images with the fluorescence background corrections same as in Figure 1f. The white arrow shows the incident polarization, and the green cross is the position of the laser spot.

between the spherical Ag nanoparticle and the Ag nanowire still enables long distance remote-excitation SERS sensing at a few molecules level, although the intensity of propagating plasmons should decrease as the distance from the excitation source increases.[12] In the Supporting Information, we show that remote-excitation Raman sensing is possible even at distances beyond 10 μm. For the system shown in Figure 3c, the thin Ag nanowire was illuminated by the laser at the right end. A strong Raman signal is observed both at the large Ag nanoparticle near the Ag nanowire and at the junction crossing between the thin and thick wires. This multisite sensing capability could be very useful in a variety of contexts from probing complex molecular processes in intracellular environments to studying the propagation characteristics of plasmon waves themselves on nanowires or other nanoscale structures. It may even be useful for constructing complex plasmonic networks, where the junction between nanowire and nanoparticle would serve as a node. Such possibilities could greatly expand the use of surface plasmons for local communications and information transfer at submicrometer length scales.

Our finding of long propagation lengths and weak damping of Ag nanowire plasmons, leads us to believe that it may also be possible to detect the Raman signal at a remote location. The strong coupling of the molecules to the nanoparticle-wire junction should in principle allow the Raman scattered light to couple into propagating wire plasmon which then could be detected at the remote site. Such a remote Raman excitation and detection would represent a major new SERS modality and is presently being investigated.

In summary, we present a novel technique for performing SERS using propagating plasmons as a remote excitation source rather than direct optical excitation. This approach allows for remote-excitation SERS sensing. This new geometry has great potential to expand ultrasensitive chemical detection to new systems. For example, it may become an even more powerful tool if combined with advanced micromanipulation techniques. Recently developed femtoinjection devices that can introduce colloidal particles to specifically selected intracellular regions[34] could be used to assemble an intracellular "chemical communications network" of sensor sites, all monitored by the insertion of a minimally invasive nanowire excitation source. This type of nanoscale optical network, based on the capabilities we have shown in these initial experiments, could be used to probe the greater complexity of intracellular responses at the molecular level in situ, such as an immunological challenge, neural cell signal generation, or the onset of mitosis or aptosis at its earliest stages.

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Supporting Information Available: Typical SEM images of Ag nanowires and nanoparticles, experimental setup, normal SERS spectrum of MGITC measured at the Ag nanowire−nanoparticle junction, estimation of the number of molecules in the junctions, a nanowire−nanoparticle system showing longer propagating distance, and two examples showing that coupled nanowires can make remote-excitation SERS possible. This material is available free of charge via the Internet at http://pubs.acs.org.

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