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Study of Molecular Junctions with a Combined Surface-Enhanced Raman and Mechanically Controllable Break Junction Method

Jing-Hua Tian,† Bo Liu,† Xiulan Li,§ Zhi-Lin Yang,† Bin Ren,† Sun-Tao Wu,‡ Nongjian Tao,*,§ and Zhong-Qun Tian*,†

Department of Chemistry, State Key Laboratory of Physical Chemistry of Solid Surfaces and Pen-Tung Sah Micro-Electro-Mechanical Systems Research Center, Xiamen University, Xiamen, China, and Department of Electrical Engineering and Center for Solid State Electronic Research, Arizona State University, Tempe, Arizona 85287

Received July 15, 2006; E-mail: zqtian@xmu.edu.cn; nongjian.tao@asu.edu

Surface-enhanced Raman scattering (SERS) has been the subject of renewed interest since the late 1990s, which was mainly motivated by the observation of SERS from single molecules.[1] It has been found that the single-molecular SERS signals from a few molecules trapped between two silver or gold nanoparticles are many orders of magnitude stronger than those on other surfaces.[2] In order to reach a better understanding of SERS mechanism and develop SERS applications in sensors, the surface enhancement dependence on the size and shape of the nanoparticle dimer and incident light polarization have been investigated.[3,4] However, the dependence on the separation between two nanoparticles, as the most effective factor predicted by the electromagnetic enhancement theory,[5] has not been realized experimentally, because there has not been any method capable of precisely and flexibly adjusting the separation during the SERS measurement.

Here we report a combined SERS and mechanically controllable break-junction (MCBJ)[6] method to measure SERS signals of molecules located inside the nanogap between two electrodes on a Si chip. This approach allows us to reach two goals: First, the MCBJ allows us to precisely and stably adjust the separation among the electrodes on a chip over a range from a few angstroms to about nanometers with a resolution of one angstrom.[7] The apexes of the electrode pairs could be simulated as a nanoparticle dimer with a controllable gap width for the SERS study. Second, building molecular devices also highly demands an ultrasensitive spectroscopic method that can directly characterize single molecules connected to two electrodes at room temperature.

Our MCBJ was fabricated by first preparing microfabricated gold electrodes on a Si substrate using optical lithography and then reducing the gap between the electrodes from about 1 μm to 1 nm or less electrochemically.[8] The gap is controlled mechanically using a piezoelectric transducer with sub-Å resolution.[7] Incident laser was focused onto the molecular junction via a lens from the top of the MCBJ chip, and the scattered light was collected with the same lens and directed to a spectrometer (LabRam 1, Jobin-Yvon) as shown in Figure 1. We choose a well characterized molecular system, 1,4-benzenedithiol (BDT) on gold, for this study because (1) the molecule is terminated with two thiol groups that bind strongly to gold electrodes, (2) it is fairly conducting owing to its conjugated structure, and (3) its symmetric structure gives strong SERS signal.

We started the SERS measurement by setting the gap at 1∼2 nm. A droplet of BDT solution (0.1 mM in ethanol) was placed over the gap to allow the molecules to adsorb on the electrodes.[6]

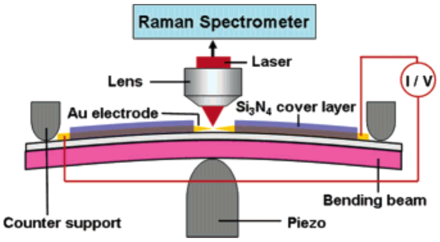

Figure 1. Schematic drawing of the experimental setup of combined Raman and MCBJ.

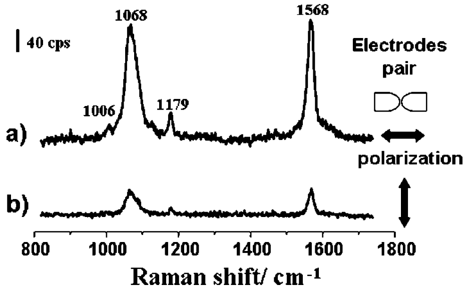

Figure 2. SERS of 1,4-benzendithiol. The gold electrodes pair has its axis (a) parallel and (b) perpendicular to the incident polarization. Laser: 632.8 nm.

Before carrying out a detailed SERS study on the molecular junction, we first analyzed the SERS activity of different parts of the electrodes, such as the smooth surface, edge, and gap. Since the electrodeposited layer is smooth on the nanoscale (see Figure 1S, Supporting Information), the SERS signals of probe molecules from the surfaces and edges are weak (Figure 2S). In contrast, the signal from the gap is much higher than from other areas. This indicates that SERS signals of molecules trapped between two electrode apexes are many orders of magnitude stronger than those on flat surfaces.[2]

We used a 3-dimensional finite difference time domain method[9] to calculate the distribution of the electromagnetic field of the junction with 1 nm separation (see Figure 3S). It shows that when the incident laser polarization is along the two electrodes, the field in the nanogap is the strongest because of the coupling of the localized surface plasmon resonance of two gold electrodes.[4] As a consequence, the SERS enhancement factor reaches the maximum. To confirm that the molecular junction gives pronounced SERS signal, we examined the polarization dependence of incident light. When the electrodes are rotated to be perpendicular to the polarization direction, the SERS intensity decreases dramatically (Figure 2). Since SERS from molecules on surfaces other than the gap region should be depolarized, the observed polarization

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† Department of Chemistry, State Key Lab, Xiamen University.
‡ MEMS Center, Xiamen University.
§ Arizona State University.

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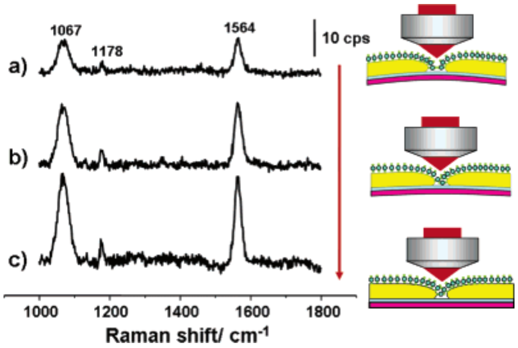

Figure 3. SERS of 1,4-benzenedithiol in the nanogap with the process of bending the metallic electrodes pair. The gap width is reduced, from (a) 8 Å, (b) 6 Å, (c) 4 Å. Laser: 632.8 nm.

dependence provides strong evidence that molecules inside the nanogap are responsible for the SERS signal.

After characterizing the molecules in the gap, we studied systematically the SERS intensity dependence on the gap width by controlling the voltage applied to the piezoelectric transducer. During the change of the gap width, current between the two electrodes was monitored (Figure 1), and the optics was also carefully monitored and adjusted to ensure that the SERS intensity change is solely due to the gap change.

Figure 3 shows three typical SERS spectra of BDT inside the gap at the different separation. The SERS intensity was increased considerably when the gap width was changed from about 8 Å to 4 Å. This change in SERS intensity is not unexpected because the electromagnetic field increases dramatically as one reduces the gap width.[5] Similar results were obtained from other probe molecules, such as 4-aminothiophenol (see Figure 4S). It should be noted that at the present stage, the success rate in observing the gap width dependent SERS is about 20%, which will be improved by optimizing the surface morphology and gap configuration. Nevertheless, these preliminary results illustrate that the combined SERS and MCBJ can be further developed as a new method to study the enhancement mechanism in detail on the molecular junction between a pair of microelectrodes.

Regarding the second goal of this work, we are interested in probing single molecules wired to two electrodes for molecular electronics applications. Vibrational spectroscopy can determine the chemical identity of a sample molecule and provide valuable structural information of the molecule. Inelastic tunneling spectroscopy (IETS),[10] Fourier transform infrared (FTIR),[11] and SERS[12] have been used to measure vibration modes of molecules self-assembled on metal surfaces. The IETS measures electron tunneling which is powerful but requires cryogenic temperatures. The FTIR studies rely on multiple reflections with limited sensitivity. Very recently, SERS and surface-enhanced infrared spectroscopy (SEIRS) have been employed to characterize molecules within two metal plates at room temperature, which have been so far limited to large electrodes and fix separation. Because MCBJ can continuously adjust the gap between two electrodes, one can maximize the SERS activity by tuning the gap width in order to probe the molecules wired to electrodes during electrical measurement. We believe that SERS is a useful tool to characterize molecules in molecular junctions and thus contribute to a better understanding of electron transport in molecules. However, like other spectroscopy tools, it cannot easily distinguish if the signal comes from the particular molecules that are responsible for the current between the electrodes.

In summary, we have described a combined SERS and MCBJ method that can detect and characterize molecules in the nanogap of two electrodes with a gap width continuously adjustable from several Å to nanometers on a silicon chip. The SERS intensity of sample molecules depends critically on the gap width and the incident light polarization, indicating that the signals came from the molecules inside the gap. This kind of measurement, together with the theoretical modeling, will provide us with a better understanding of the mechanism of single-molecule-SERS. Furthermore, the SERS−MCBJ method shows potential as a powerful characterization tool for molecular electronics studies and to answer questions, such as if and how a molecule is present between two probing electrodes. Finally, we point out that the ability of detecting a single or a small number of molecules in nanoparticle/aqueous solution interfaces may open the door to the analysis and study of single biomolecules.

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Supporting Information Available: Experimental details, including electrodeposition, SEM and SERS results, and FDTD calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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