Multi-wavelength Surface-Enhanced Raman Scattering from Molecules Adsorbed on Plasmonic Nanowires

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Abstract: Multi-wavelength Raman scattering from benzene-thiol adsorbed on randomly distributed silver-coated plasmonic nanowires was measured in the visible optical range to probe the density of states of the chemical, changed due to adsorption.
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Plasmonics is known for its ability to significantly increase the optical scattering from a substance, whether it is a single molecule or a multilayer film. This is achieved by using nanotextured metals such as Ag and Au which have the property that, when exposed to light, surface plasmons are generated which interact with the laser light to increase the local electromagnetic fields and thus lead to surface enhanced Raman scattering (SERS). These enhancements are electromagnetic in nature and do not account for the chemical properties of adsorbed molecules. Earlier, it has been shown that a molecule such as benzene-thiol (BZT), while is transparent in the visible in its neat state can develop new states due to its interaction with Au or Ag surfaces [1]. Here we demonstrate that this change in density of states can be probed by using multiple-wavelength SERS measurements.

We have used a highly sensitive SERS substrate based on a random distribution of dielectric core/metal shell nanowire geometry [2, 3], which can reliably detect 0.2 pg of Rhodamine 6G (a standard SERS-active dye). In this case, SERS enhancement as high as 10^8 was observed with fluorescence being also increased by 3-5 orders of magnitude [2]. We believe that the random distribution of Ag/dielectric nanowires (NW) is important, because it maximizes the density of hot high electric field regions and allows molecules more access in depth than nanoshell geometries. Such samples exhibit a broad surface plasmonic resonance in the visible range [4], which allows using multi-wavelength Raman as a probe of the density of states of the adsorbed molecule.

An example of multi-wavelength dataset showing SERS response of BZT adsorbed on silver coated plasmonic nanowires acquired over visible spectrum is shown in Fig.1 (a). For comparison, a similar dataset acquired from a sample of neat liquid BZT in liquid is shown in Fig. 1 (b). Significant broadband fluorescence background observed for SERS samples was removed numerically. In order to account for SERS response degradation during the measurement, spectral intensities were recalibrated using 1070 cm^{-1} peak of BZT as a standard. The bright peak at 520 cm^{-1} on Fig. 1 (a) belongs to the silicon substrate, and its wavelength-dependent dependence is disrupted as a result of this recalibration, since silicon Raman response does not change much compared to SERS signal.
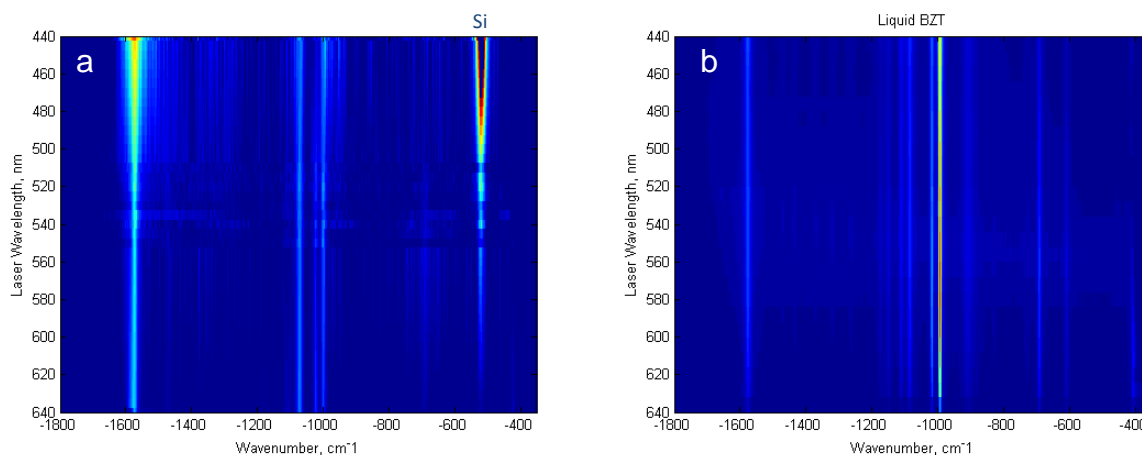

Fig. 1. Multi-wavelength SERS signal of benzene-thiol (BZT) adsorbed on silver-coated nanowires, normalized using 1070 cm^{-1} peak of BZT (a) compared to multi-wavelength Raman response of neat liquid BZT for the same optical range (b).

Dataset shown in Fig. 1 (a) demonstrates that in comparison to BZT peak at 1070 cm^{-1}, the peak at 1019 cm^{-1} increases its intensity at longer wavelengths while the BZT peak at 1570 $^{-1}$ peak intensity increases at shorter

wavelengths. Similar data for liquid neat BZT shown in Fig 1b do not demonstrate this behavior, which is therefore specific to BZT SERS signal.

SERS samples used in these measurements consist of randomly distributed Ga_2O_3 nanowires [5], which are formed by the controlled oxidation of pure Ga metal in a vacuum tube furnace are shown in Fig.2. The source material was placed at one end of a 4" alumina boat, with the substrate at the opposite end. The substrate consisted of a Si wafer with a 20nm Au catalyst thin film for the VLS growth. The metal of choice for SERS is Ag or Au, because their optical constants are well suited for Mie scattering. Thus, the sheath of the nanowires is formed by e-beam evaporation, as well as electroless Ag plating techniques, with optimal 6-7 nm coverage.
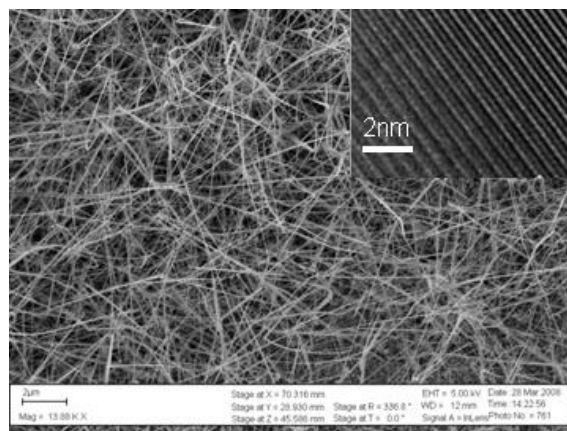

Fig. 2. SEM image of Ga_2O_3 nanowires grown by VLS at 900°C, using an Au catalyst and a Si substrate; HRTEM image of one wire (inset).

Both multi-wavelength Raman datasets were acquired using Swept Wavelength Optical resonance-Raman Device (SWOrRD) designed and used for contactless identification of various chemical and biological samples [6, 7]. SWOrRD employs optical parametric oscillator (OPO) pumped by frequency-tripled Nd:YLF Q-switched laser operating at 1 kHz repetition rate. For these measurements OPO signal output tunable over the range 420 - 700 nm was used. Laser spot size was ~500 micron spot at average powers ~10-50 mW. Light scattered off plasmonic nanowires was collected using fiber-optic probe connected to the two-stage spectrograph model SP-2700i (Princeton Instruments, Inc.) equipped with "Newton" silicon detector (Andor Technology PLC). Synchronized tuning of the OPO, gratings in the spectrograph and data acquisition was accomplished by using "Labview" computer software (National Instruments Corp.).

Presented experimental results demonstrate that for BZT molecules adsorbed on silver coated nanowires, the behavior of the different molecular vibrations is a function of excitation wavelength, which is different from the liquid BZT excitation profile. These measurements demonstrate a possibility to explore the density of states of the adsorbed molecule by using multi-wavelength Raman spectroscopy.

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