NEAR-FIELD RAMAN SPECTROSCOPY USING OPTICAL FIBER AND SILICON CANTILEVER

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Abstract: We report near-field Raman spectroscopy to provide higher spatial resolution beyond diffraction limit with sufficiently high sensitivity using Surface Enhanced Raman Scattering.

We have studied two distinct methods on near-field Raman spectroscopy using a chemically etched optical fiber and an AFM cantilever with /without metal coating. Near-field Raman spectra/images from CuPc (copper phthalocyanine) on Ag island films were obtained under attenuated total reflection condition with using a sharpened optical fiber and a shear force mode[1]. Raman spectra of CuPc were obtained with an accumulation time of 1000 s without using surface plasmon excitation or the electronic resonance effect of the molecules. Optimum conditions for enhancing the Raman signal using localized surface plasmon (LSP) on Ag island films were found to be 5 nm in Ag thickness and an incident angle of 50^o. Under these conditions, Raman signal from CuPc (thickness, t_{CuPc} 1.5 nm) was enhanced by a factor of ca. 300, which gives 36 counts/s for ca. 30,000 molecules, and enables us to obtain the Raman spectra in 2 s. Thus, Raman images were simultaneously observed with topography using CCD detector and/or avalanche photodiode. Interestingly, near-field Raman intensity increases with decreasing thickness of CuPc samples below 3 nm. As predicted by numerical simulation[2], local electric field is maximized at the junction of touching Ag particles under the LSP resonances, while only modest enhancement is obtained at other ordinary sites. Then, the spatial distribution of the LSP field can be detected only for quite small CuPc thicknesses with the fiber probe, while thermal dissipation in CuPc layer makes it ambiguous at much thicker region. This was supported by large dispersion of the signal intensity for $t_{CuPc} < 3$ nm compared to faint dispersion for thicker samples. Without the Ag underlayer, near-field Raman scattering intensity increases linearly with CuPc thickness. Thus, the spatial distribution of the LSP field was directly visualized in near-field Raman or elastic scattering images for metal island films. They can be perturbed by the multiple reflections and interferences of the LSP field on different Ag particles, which do not simply correspond to topographic images of the same samples[3, 4]. This is inevitable to utilize the LSP of underlaid films, but not serious for Raman signal due to much sharper decay of the enhanced field. Potentially, metal (coated) tips with appropriate nanostructures are much useful to provide higher sensitivity and spatial resolution than the bare fiber or cantilever probes. Actually additional enhancement factor of 10-100 was obtained using metal coating to the fiber which increases with decreasing gap sizes (Fig. 2a-b). We also adopted silicon cantilever with an AFM scanner placed on an inverse-type microscope, in which the excitation laser at 532 nm is sharply focused at the sample down to 250-300 nm in diameter using a confocal optics[5]. It enables us to study the effect of cantilever approach to the sample surfaces. We observed ca. 5 times intensity evolution in Raman scattering from microcrystalline diamond only with Au-coated cantilever, while negligible intensity changes observed with bare-silicon cantilever. Enhancement factor by the metal tip-approach was estimated to be ca. 3000 based on geometrical parameters used here. Numerical simulation with finite difference time domain (FDTD) method gives good agreement to the observations.

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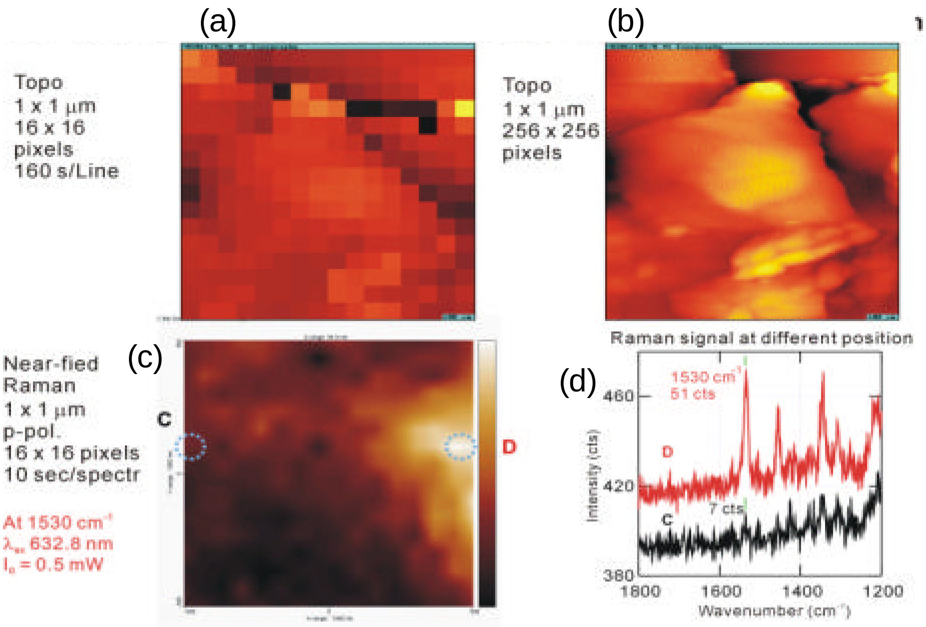

Fig. 1 Topography (a, b), near-field Raman image (c) and spectra (d) from CuPc(1.5nm)/Ag(5 nm) /prism using an etched optical fiber probe. The topography (b) with sufficiently high resolution (256×256) was obtained at first, then with lower resolution (16×16 pixels) topography and SERS spectra (d) were observed with 10 s for accumulation. After the measurement, Raman peak intensity at 1530 cm^{-1} was evaluated at each position to reconstruct the near-fielad Raman image as in (c).

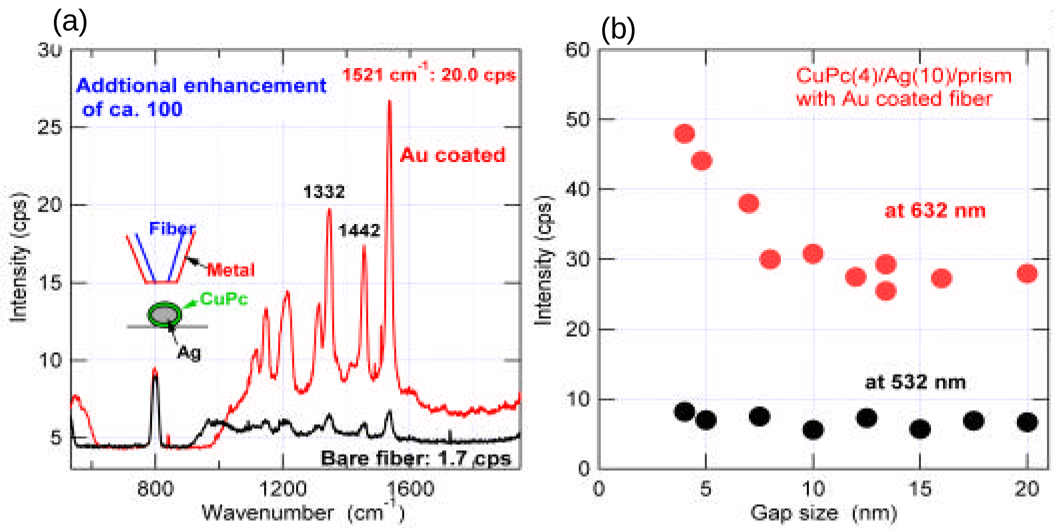

Fig. 2 Tip enhanced near-field Raman spectra from CuPc(1.5nm)/Ag(5 nm)/prism:
(a) effect of metal coating to the fiber, (b) gap size depepndence of the signal intensity. Metal coating to the fiber probe increases the Raman signal by ca.100 at smaller gap sizes (b).