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Calculated shape dependence of electromagnetic field in tip-enhanced Raman scattering by using a monopole antenna model

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ABSTRACT

To evaluate the shape of an Ag tip with regard to tip-enhanced Raman scattering (TERS) signal, the enhanced electromagnetic (EM) field and scattering spectrum, arising from surface plasmon resonance at the apex of the tip, were calculated using a finite-difference time domain (FDTD) method. In the calculated forward scattering spectra from the smooth Ag tip, the band appeared within the visible region, similar to the experimental results and calculation for a corrugated Ag cone. In the FDTD calculation of TERS, the Ag tip acting as a monopole antenna was adopted by insertion of a perfect electric conductor between the root of the tip and a top boundary surface of the calculation space. As a result, the EM field was only enhanced at the apex. The shape dependence i.e. the EM field calculated at the apex with various curvatures on the different tapered tips, obtained using the monopole antenna model, was different from that simulated using a conventional dipole antenna model.
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1. Introduction

The tip-enhanced Raman scattering (TERS) instrument is a kind of scanning probe microscope (SPM). A sharp noble metal tip serves as the probe. With TERS, morphological and highly sensitive Raman spectral images are observed from the sample [1–5]. These originate from the enhanced electromagnetic (EM) field at the apex of the metal tip from excitation light via resonant dipole oscillation of conduction-band electrons (or surface plasmon resonance: SPR) [1–4]. The highly spatially resolved imaging arises from the small curvature of the tip apex. The curvature affects the enhanced EM field via SPR and consequently, the TERS is strongly dependent on the tip because of its optical properties related to the material used, the curvature of the apex, the taper of the tip, and so on. Unfortunately, reproducibility of the spectra is poor because of difference and/or change in the optical properties related to the shape of the tip.

In surface-enhanced Raman scattering (SERS), which originates from the enhanced EM field at the gap between noble metal nanoparticles arising from excitation light via localized SPR, the spectra are consistent with the localized SPR scattering bands of the metal nanoparticles with sample molecules, in terms of excitation polarization and wavelength dependence [6–10]. Subsequently, the localized SPR scattering band can be calculated from the shape of the nanoparticles, which are observed with a scanning electron microscope (SEM), through a finite-difference time-domain (FDTD) method [10,11]. For TERS, on the other hand, the polarization and wavelength dependencies of the SPR at the apex of the tip have been measured through application of an evanescent field [12–15]. Recently, we measured the SPR band at the apex of the tip by conventional dark field illumination [16,17] and confirmed that the x-, y-, and z-polarization dependencies of the SPR is consistent with those of TERS [17], in a similar way to SERS. Subsequently, the SPR spectra and EM field at the apex of the tip were calculated using various models [18–21], although the tip is regarded as a semi-infinite system. In previous calculations of Ag long cones, which were regarded as tips, the SPR scattering intensities and enhancement factors from the apex showed periodicity and tended to increase at longer wavelengths [19,20]. For the cone adhered by Ag hemispheres, the SPR band appeared within the visible region [19]. In the experimental spectra, however, the SPR band was observed within the visible region despite the smoothness of the Ag tip [16,17]. Recently, the EM field and SPR spectra for several micrometer-long Ag nanowires were calculated [22], which is similar to the system for TERS.

In the present paper, the SPR scattering spectra and enhancement factors of a smooth Ag tip, which easily reproduced the original tip, were calculated using an FDTD method. The smooth Ag tip with a perfect electric conductor (PEC), i.e. a monopole antenna model was adopted, because the EM field was only enhanced at the apex. While

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the calculated back scattering signal tended to be more intense at longer wavelengths, as shown in previous calculations [19,20], the band appeared within the visible region in the calculated forward scattering spectra, as also seen in previous experimental results [16,17]. The dependence of the EM field at the apex on the length, taper, and curvature of the tip, as obtained from the monopole antenna model, was compared with the calculated results from the Ag tip without the PEC, i.e. from a dipole antenna model. If the TERS spectra could be estimated by FDTD calculation for a smooth tip through the SPR spectrum in a similar way to that with SERS, the same nanostructures as the optimum tip, which can reproduce the TERS spectra stably, could be fabricated in large quantities.

2. Methods

The scattering cross-sections at various wavelengths and the EM field from Ag tips with various shapes were calculated using the software EEM-FDM (EEM Inc., Saitama, Japan) with a FDTD method. In the calculation, the tip consisted of an Ag hemisphere, cylinder, and/or truncated cone. The calculation space covered the tip, and the perfectly matched layer was adopted as the absorbing boundary condition. Firstly, the model tip consisted of a truncated Ag cone (99 nm in length, 75 nm in diameter) and hemisphere (40 nm in diameter), the calculation space was 150 nm^3, and the mesh size was 1 nm. Secondly, the tip consisted of an Ag rod and hemisphere (50 nm in diameter), the

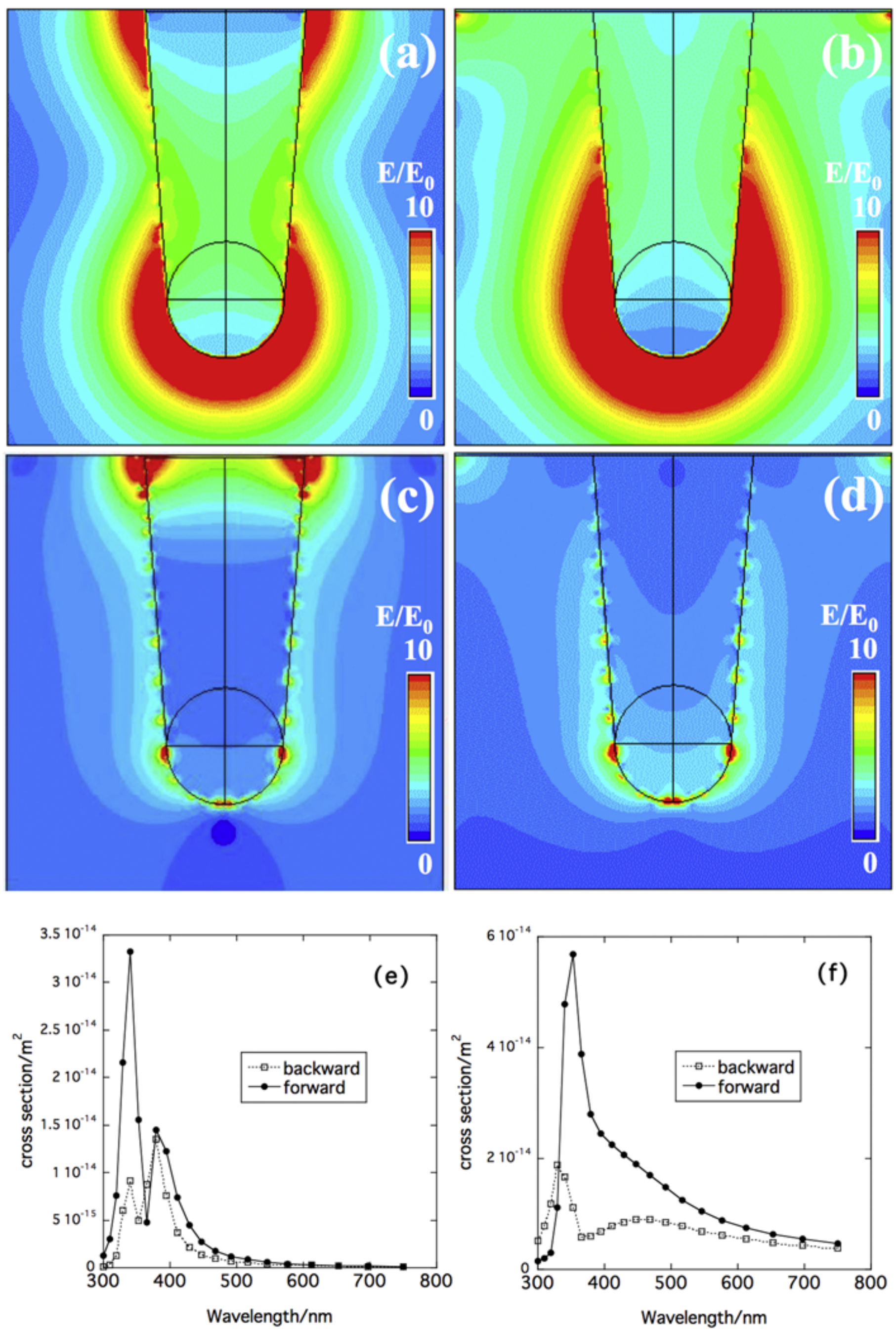

Fig. 1. Calculated distribution of the EM field around the Ag cone (a) without and (b) with the PEC by excitation with parallel polarized light at 577 and 698 nm, respectively. The distribution around the cone (c) without and (d) with the PEC by excitation with perpendicular polarized light at 380 nm. Scattering cross-sections from the cone (e) without or (f) with the PEC by excitation with perpendicularly polarized light at various wavelengths.

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