

# Highly sensitive Raman spectroscopy using a gap mode plasmon under an attenuated total reflection geometry<sup>☆</sup>

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## ARTICLE INFO

### Article history:

Received 27 January 2014

Received in revised form 7 March 2014

Accepted 16 March 2014

Available online 26 March 2014

### Keywords:

Surface enhanced Raman scattering

Propagating surface plasmon

Gap mode

Coupling of plasmons

P-aminothiophenol

Adsorbed state

## ABSTRACT

We investigated a gap mode plasmon under an attenuated total reflection (ATR) configuration toward realization of near-field Raman spectroscopy with a single molecule sensitivity and spatial resolution. Additional enhancement in Raman scattering at a nanogap was obtained by a coupling of a propagating surface plasmon (PSP) of Ag films on a prism, and a gap mode between Ag films and Ag nanoparticles (AgNPs). Immobilization of AgNPs on Ag films through thiol-SAM slightly up-shifted the resonance angle of a PSP, which broadened the reflectivity dip owing to an increased out-coupling of a PSP. Raman enhancement factor at a nanogap increased with decreasing surface coverage of AgNPs, albeit the enhancement factor averaged over illuminated area in Ag films decreased, ensuring the largest enhancement factor in tip-enhanced Raman scattering. This is due to increased efficiency for a PSP excitation at lower coverage of AgNPs in consistent with that in theoretical evaluation using finite difference time domain calculations. A gap mode under an ATR configuration was applied to elucidate a plausible photochemical reaction of p-amino thiophenol (PATP) adsorbed on Ag films on a prism. Spectral changes in Raman scattering under laser illumination were observed for PATP with a deuterated amino group, but suppressed by a dimethyl amino group owing to steric hindrance, supporting the photochemical dimerization.

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## 1. Introduction

Enormous enhancement with high reproducibility is critical to the utilization of Surface Enhanced Raman Scattering (SERS) in quantitative analysis of target molecules. Single molecule detection by Raman scattering has been achieved using a coupled localized surface plasmon (LSP) of closely adjacent metal nanostructures [1,2]. We have formed a few closely adjacent silver and gold nanoparticles, flocculates of AgNPs and AuNPs, showing enormous SERS enhancement favored by controlling the interaction between metal nanoparticles (MNPs) and target molecules in solutions [3–5]. Theoretical calculations suggest that one of AgNPs or AuNPs in flocculates can be replaced with metal substrates [6], such as Pt [7–9], Rh and Fe having large damping factors of a surface plasmon, while providing enormous enhancement factors in SERS equivalent to those obtained in flocculates of AgNPs and AuNPs. Furthermore, an MNP can be attached to the tip of cantilevers or

sharpened optical fiber probes for tip-enhanced Raman scattering (TERS). Such fabrication is expected to provide Raman images in a single molecule sensitivity and spatial resolution of a few nanometers [7,10]. Also, higher enhancement in Raman scattering at a nanogap is expected by a coupling of a propagating surface plasmon (PSP) of Ag films [11], and a gap mode between Ag films and AgNPs. A PSP is excited at a resonance angle of incidence, at which the wave vector and the energy of excitation light accord with those of a PSP at an interface between adsorbed molecules and Ag films on a prism. This configuration is a promising strategy for TERS to suppress a substantial background signal from the sample illuminated by a laser spot (1–10 μm) much larger than the tip size (10–30 nm). Indeed, an evanescent wave is transferred to propagating light at sample surfaces, only where the tip probe approaches in TERS ensuring inherently subtle background intensity. However, the coupling between a PSP and a gap mode has not been evaluated in detail, for instance the effect of AgNPs on resonance conditions of a PSP, and on the enhancement in electric field at a nanogap. We investigated to solve these issues using AgNP/thiol-SAM/Ag films/prism samples. Here, AgNPs were immobilized on thiol-self assembled monolayer (SAM) films, formed on a dove prism coated with an Ag film, through electrostatic interaction between ammonium ( $-\text{NH}_3^+$ ) in p-amino thiophenol (PATP) and

<sup>☆</sup> Selected paper presented at 7th International Conference on Advanced Vibrational Spectroscopy, Kobe, Japan, August 25–30, 2013.

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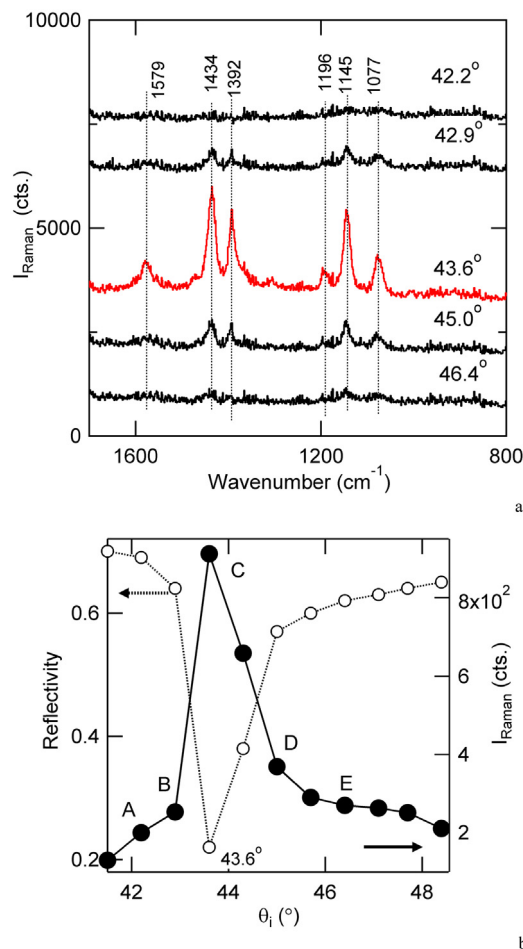
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negatively charged AgNPs [3,5], and van der Waals force between Ag films and AgNPs via thiophenol (TP) [16].

Next, we applied a gap mode under an attenuated total reflection (ATR) configuration to analyze a photochemical reaction of PATP-SAM on Ag films. PATP has been often used to demonstrate SERS activity of various metal nanostructures. It is well-known that PATP on Ag or Au surfaces shows complicate SERS spectra, which are perturbed by laser illumination, pH in solutions, and the potential of Ag and Au electrodes. First, Osawa et al. reported that SERS spectra of PATP are governed by  $b_2$  modes pronouncedly enhanced by charge-transfer (CT) interaction between PATP and Au, Ag films in addition to electromagnetic enhancement [12]. Alternatively, Wu et al. reported that a photochemical reaction occurs in PATP adsorbed on Au or Ag surfaces providing those bands assigned to  $b_2$  modes, which is evidenced by gradual spectral changes under laser illumination depending on laser power [13]. They also confirmed the Raman spectra modified by laser illumination are identical with those for an azodimer molecule (p-diazobenzenthio). As an aside, Kim et al. reported that the dimer bands vary to those of monomer PATP by laser illumination, while suggesting predominant CT effect of PATP [14]. Thus, attribution of SERS spectra of PATP is still under discussion. Here, we investigated a plausible photochemical reaction of PATP using p-dimethylamino thiophenol (PDATP) and PATP with a deuterated amino group using a gap mode under an ATR geometry.

## 2. Experiments

Silver nanoparticles with an average size of 40 nm were prepared by chemical reduction using trisodium citrate [3,5,7]. PATP, PDATP and TP molecules were purchased from Wako Pure Chemicals, and used without further purifications. Deuteration of an amino group in PATP was achieved by dissolution and immersion of PATP for 2 h in  $D_2O$ . PATP-SAM films were formed on Ag films (45 nm thickness), evaporated on a Dove prism of BK-7, at pH  $\sim 3$  to suppress a photochemical reaction of PATP [13]. Unbound thiols were thoroughly washed out by repeated rinsing with Millipore water (18 M $\Omega$ ). Similarly, TP-SAM films were formed on Ag coated prisms using 1 mM ethanol solutions. AgNPs, on which residual species like citrates were replaced by  $Cl^-$ , were immobilized on thiol-SAM/Ag films/prism. Distinct surface coverage of AgNPs ( $\theta_{AgNP}$ ) was obtained for different thiols, such as 10% for TP and 3.5% for PATP molecules, which is determined by specific interaction between thiols and AgNPs. Scanning electron microscope (SEM), Hitachi S-4100, was used to evaluate the surface coverage of AgNPs,  $\rho_{AgNP}$  (particles/ $\mu m^2$ ) and  $\theta_{AgNP}$  (%), immobilized on metal substrates. Here,  $\theta_{AgNP}$  is a ratio of overall cross section of AgNPs per unit area of Ag films. Reflectivity and Raman spectra of PATP- or TP-SAM/Ag films/prism and AgNPs/PATP- or TP-SAM/Ag films/prism were measured at various angles of incidence to evaluate the enhancement in Raman scattering of thiols by a PSP resonance and a gap mode with a solid laser at 532 nm ( $\sim 20$  mW), a Chromex polychromator (250is), conventional optics and a rotation stage. Enhancement in Raman scattering averaged over samples illuminated by a laser, and that at a nanogap were evaluated by using a Raman band at  $\sim 1070$   $cm^{-1}$  ( $\nu_{C-S}$ ) in PATP and TP. For this purpose, weighted bulk PATP (powder) and TP (liquid) samples were adsorbed on neat Si surfaces to estimate Raman scattering intensity per molecule. The results were compared with those estimated for single molecule at a nanogap under a coupling of a PSP and a gap mode. An FDTD method (FDTD Solutions, Lumerical Co.) was employed in evaluation of local electric field at a nanogap between AgNPs and Ag films on a prism under an external and an ATR geometry, while varying the angle of incidence to the prism base.



**Fig. 1.** Experimentally observed Raman spectra at a PSP resonance of PATP-SAM/Ag film (45 nm)/prism (a), and reflectivity ( $R$ ) and Raman scattering intensity ( $I_{Raman}$ ) vs. angle of incidence ( $\theta_i$ ).

## 3. Results and discussion

We investigated enhanced Raman scattering using a gap mode under an ATR configuration. In particular, a focus was placed on the effect of AgNPs immobilized on thiol-SAM/Ag film ( $t_{Ag} = 45$  nm)/prism on PSP resonance conditions, and also on the enhancement in Raman scattering of thiols compared with that under an external geometry.

First, we evaluated the enhancement factor in Raman scattering under a PSP resonance of Ag films on a dove prism. Reflectivity was measured for PATP-SAM/Ag film (45 nm)/BK-7 prism with a solid laser at 532 nm at p-polarization while tuning the angle of incidence to prism base. The reflectivity showed the sharp minimum at  $\sim 43.6^\circ$  in air, which is the resonance angle of a PSP excitation (Fig. 1a and b). This observation was in good agreement with  $43.2^\circ$  obtained by theoretical evaluation using Fresnel equations (Fig. 2a) as well as using FDTD calculations. The Raman enhancement factor for a PATP peak at  $1077$   $cm^{-1}$  ( $\nu_{C-S}$ ) was estimated to be  $7 \times 10^3$  at the resonance angle, which was consistent with  $2.2 \times 10^4$  predicted by theoretical calculations [15]. We noted that SERS spectra observed for PATP on Ag film contains so-called dimer bands at  $1434$ ,  $1392$ ,  $1196$  and  $1145$   $cm^{-1}$  although we kept pH  $\sim 3$  during the formation of a PATP-SAM film. This is probably because we observed Raman spectra of the samples in air and thereby pH was not always sustained to be acidic. For this reason, we used the Raman band at  $1077$   $cm^{-1}$  from a C–S stretching mode, of which spectral features were not affected by a plausible photochemical

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