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PMBA-SAM 膜をコートした銀ナノ粒子の種々の金属イオンによる近接状態形成と SERS 増強

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Flocculation and SERS activation of PMBA-coated Ag nanoparticles by various metal ions
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Carboxylic groups in PMBA adsorbed on AgNPs at the concentration of 1×10^{-6} M-1×10^{-4} M (without addition of H_2SO_4 or NaOH) are considerably dissociated, because pH in the solutions is around 5.5 comparable with pKa of PMBA, 5.8 [1, 2] or 4.79 [3]. Hence, PMBA coated AgNPs remain isolated in dispersed solutions due to electrostatic repulsion between carboxylic anions on neighboring particles. Indeed, we observed PMBA coated AgNPs gave no additional peaks from coupled localized surface plasmons (LSPs), which will appear at longer wavelength than the absorption of LSP at ~410 nm from isolated AgNPs ([4, 5]). Only slight shift of the LSP peak from isolated AgNPs was observed from 410 nm to 433 nm depending on the concentration of PMBA in solutions. The peak shift of isolated AgNPs is caused by adsorption of PMBA [6] that has larger refractive index (n_{PMBA}=1.642 [7]) than surrounding water (n_{H2O}=1.35 [8]). If PMBA adsorbs on Ag surface via a carboxyl group -COO⁻, further –S-Ag bond formation with neighboring particles inducing the flocculation should be observed. This was not the case, thereby PMBA adsorbs on Ag surfaces by forming a covalent bond of -S-Ag.

Adsorbed quantity of PMBA molecules on each AgNP was evaluated using a method of subtractive absorption [5]. The saturation coverage of PMBA on AgNP was found to be ~1.5×10^5 molecules/particle, which is larger than that for rhodamine on AgNPs by about 10 times [4], and is explained by smaller occupation area of PMBA ~0.2 nm² compared to ~1.2 nm² of rhodamine molecules. Under the concentration of AgNPs, 1.3×10^{11} particles/mL [4], SAM film formation eliminates ~100 % and ~30 % of entire PMBA molecules in 1×10^{-5} M and 1×10^{-4} M PMBA solutions, respectively. This was supported by the observation that pH is almost neutral ~7 in 1×10^{-5} M PMBA solutions after adsorption on AgNPs, which is larger than pH~5.5 in 1×10^{-5} M PMBA solutions without containing AgNPs. Interestingly, we observed adsorption isotherm of PMBA on AgNPs is significantly deviated from the Langmuir adsorption for rhodamine on AgNPs [4], and on AuNPs [5], suggesting intermolecular interaction between adsorbed PMBA molecules. For instance, the surface coverage of PMBA rose more slowly than that for rhodamine at concentrations less than 2×10^{-5} M, which is probably due to electrostatic repulsion between dissociated PMBA anions neighboring on Ag surfaces. Also, the surface coverage of PMBA decreased at concentrations above 2×10^{-5} M, which is presumably attributed to steric hindrance of hydrogen bonding between neighboring PMBA molecules for further adsorption.

AgNPs adsorbed by PMBA at 1×10^{-4} M solutions were flocculated by the addition of NaCl and NaOH as confirmed by the appearance of coupled LSP peaks at 600-700 nm ([6]). Addition of Na⁺ ions gradually decreases the thickness of electrical double layer so that van der Waals force attracts neighboring AgNPs while suppressing repulsion between dissociated PMBA anions [9]. Also electrostatic force between dissociated PMBA molecules on neighboring AgNPs and counter Na⁺ ions plays an important role in stabilizing the flocculates. Indeed, the flocculates of AgNPs in 10 mM NaCl or 6 mM NaOH solutions were stable for more than one hour without varying their LSP spectra. In contrast, coagulates of AgNPs, which are much larger than flocculates and often accompanies precipitation, were formed at the concentration of NaCl or NaOH higher than 30 mM. In this case, ionic strength is markedly large thereby thickness of double layer is small enough to cause the coagulation of AgNPs, where van der Waals attractive force is dominant [4, 9]. These observations support our presumption that PMBA adsorbs via an –S-Ag bond on Ag surfaces. If PMBA adsorbs via a carboxylic anion, the addition of Na⁺ ions would not perturb an –S-H bond or an isolated state of AgNPs.

SERS intensity of PMBA was largely enhanced in the flocculates of AgNPs. For example, Raman bands of protonated PMBA with a –COOH group [10, 11] were clearly observed at 694, 799, 1291, 1400, 1652, and 1702 cm⁻¹ in 10 mM NaCl solutions, while significantly distinct spectra of dissociated PMBA with a –COO⁻ group [10, 11] were detected at 340, 716, 1137, 1430 cm⁻¹ in 6 mM NaOH solutions. Among these, Raman bands at 1702 cm⁻¹ and 1430 cm⁻¹ are assigned to vC=O in –COOH and vCOO⁻ modes in dissociated PMBA ions, respectively [10, 11], in agreement with theoretical calculations using a DFT method (data not shown, see also [8]). These spectral variations are explained by different pH in solutions yielding distinct dissociation of PMBA molecules; (1) pH (~4.9) in 10 mM NaCl solutions is lower than pKa (5.8 [1, 2]) or similar to pKa (4.79 [3]) yielding abundant -COOH similar to -COO⁻ ions, and (2) pH (~12) in 6 mM NaOH solutions is much higher than pKa yielding –COO⁻ ions almost exclusively. In addition, even extremely small quantity of metal dications such as 0.1 mM Ca²⁺ and Ba²⁺ caused the flocculation of AgNPs as evidenced by 550 nm peak from coupled LSP resonances (data not shown), indicating more effective linking of AgNPs via dications compared to monocations. Because such low concentration of dictation does not decrease the double layer thickness around AgNPs, electrostatic interaction between dissociated –COO⁻ in PMBA molecules on neighboring AgNPs and dications is crucial to form the flocculates of AgNP providing enormous SERS signal intensity. Indeed, Coulomb attractive potential between divalent (monovalent) cations and PMBA anions on AgNPs with a separation of 1 nm is

5.9×10^{-21} (2.9×10^{-21}) J, which is larger than thermal energy kT= 4.1×10^{-21} J of AgNPs. Various divalent cations provided distinct peak positions for the COO$^-$ stretching mode at ca. 1400 cm^{-1} even at the same pH, providing evidence for significantly different interaction between divalent metal ions and PMBA anions.

Van der Waals force between AgNPs, on which PMBA molecules are protonated in acidic conditions, also worked for the flocculation. We used two distinct ways to protonate –COO$^-$ in PMBA molecules; (1) PMBA adsorbed on AgNPs and then incubated in sulfuric acid solutions, (2) PMBA was incubated in sulfuric acid and then mixed with AgNP suspension. When AgNPs were incubated in the PMBA solution at concentration 1×10^{-4} M, and then mixed with sulfuric acid solutions (Protonation (1)), the flocculates of AgNPs were not formed even in 10 mM H$_2$SO$_4$ solutions. Accordingly, dissociated PMBA molecules on AgNPs were neither protonated nor linked via hydronium ions even in such acidic conditions. This is against the feasible flocculation by Na$^+$ ion associating to their distinct hydration properties. For example, the hydration enthalpy of proton (-1150 kJ mol^{-1} [12]), which is much larger than that of Na$^+$ (-400 kJ mol^{-1} [13, 14]). Presumably the hydration shell of proton impinges linking of AgNPs. Also, steric hindrance of neighboring PMBA molecules at monolayer coverage prohibits protonation of PMBA on AgNPs. Indeed, much lower surface coverage of PMBA ($\leq$ ca.1/10 of monolayer coverage), which was adsorbed on AgNPs at the concentrations much less than 10^{-5} M, showed the flocculation in 3-5 mM H$_2$SO$_4$ solutions. Interestingly, adsorbed PMBA molecules on AgNPs are noticeably dissociated even in 1-3 mM sulfuric acid solutions as evidenced by Raman bands of –COO$^-$ ions at 841, 1013, 1133, 1378 cm^{-1}, whereas those from protonated species were simultaneously observed at 696, 801, 1181, 1292, 1649, 1702 cm^{-1}. Apparently, these observations are not consistent with the dissociation equilibrium for Brφnsted acid that PMBA should be protonated at such pH (=2.1-2.9) much lower than the pKa of PMBA (4.79 [3], or 5.8 [1, 2]). Probably, the flocculates of AgNPs were formed, when dissociated PMBA molecules are in part protonated by the addition of H$_2$SO$_4$ solutions. The quantity of protonated PMBA molecules yielding van der Waals attractive force should be large enough to link AgNPs, while suppressing electrostatic repulsion between dissociated PMBAs. Further protonation of –COO$^-$ anions after the formation of flocculation is sterically hindered by hydrogen bonds between protonated PMBA molecules in particular at nanogaps.

By Protonation (2), the flocculation of AgNPs and SERS activation were observed in 0.2-3 mM H$_2$SO$_4$ solutions, whereas isolated AgNPs remained at the concentration of sulfuric acid below 0.05 mM. Similar to the results for samples prepared by Protonation (1), PMBA molecules adsorbed in 2×10^{-6} M solution, which gives 4-5 % of monolayer coverage, are mostly dissociated even in 1 mM H$_2$SO$_4$ solution, of which pH~3 is much lower than the pKa, as evidenced by the νCOO$^-$ band at 1380 cm^{-1}. The intensity of the Raman bands from –COO$^-$ anions diminished while those from protonated –COOH at 694, 779, 1291, 1316, 1652, and 1702 cm^{-1} increased with raising the concentration of PMBA above 3×10^{-6} M. Slight increase in PMBA concentration from 2×10^{-6} M to 3×10^{-6} M does not vary the pH of bulk solutions. Thus, dissociation of PMBA on AgNPs is primarily determined by its surface coverage even in quite acidic solutions. As is widely known, pKa of a carboxylic group in alkyl thiols on metal surfaces is larger than that in bulk solutions [15] due to stabilization of protonated species by hydrogen bonding with neighboring molecules or electrostatic repulsion of dissociated species. Contrary to higher surface pKa of alkyl thiols, the observed results suggest that adsorbed PMBA molecules in the flocculates of AgNPs have much lower pKa compared to that in bulk solutions. Such complicated features have not been elucidated in SERS of PMBA, albeit this molecule is often used to demonstrate SERS activity of various metal nanostructures [10, 11] or to monitor pH distribution in living cells. Thus, there are still essential uncertainties on the surface pKa of aromatic thiols, which is further being investigated.

Accordingly, the flocculates of AgNPs were formed using electrostatic interaction between adsorbed PMBA molecules and hydrated metal ions, as well as using van der Waals interaction between protonated PMBA molecules on neighboring AgNPs. The flocculates of AgNP provided enormous SERS signals of PMBA molecules at the nanogaps, where dissociation of PMBA is determined not only by pH in bulk solutions but also by the surface coverage of PMBA. Consequently, the method of flocculation yielding enormous SERS intensity is crucial to elucidate adsorbed state of PMBA-SAM films on AgNPs.

References

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