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Research paper

Elucidation of hydrated metal ions using flocculation-surface enhanced Raman scattering

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Hydrated metal ions such as Na^+, Mg^{2+}, and Cu^{2+} in addition to surface species like citrate, p-mercaptobenzoic acid (PMBA), and halide anions were identified by exploiting coupled localized surface plasmons of flocculated silver nanoparticles (AgNPs). Indeed, SERS spectra provided clear evidence for the formation of citrate complexes of Co^{2+} and Cu^{2+} as well as ion pairs of metal ions and $PMBA^-$ anions on AgNPs. For the first time, we have detected pronounced Raman bands from hydrated metal ions in flocculates of halide-covered AgNPs assigned to restricted rotation and translation at 600–200 cm^{-1} and O—H stretching bands at 3500–3600 cm^{-1}. Interestingly, the peak frequencies of O—H stretching mode from hydrated metal ions are sensitive to metal and halide species, proving the observed water molecules are sandwiched between trapped metal ions and halide ions on adjacent AgNPs while forming a solvent shared ion pair.

1. Introduction

Vibrational spectroscopy inherently provides us with straightforward information on hydration structure or configuration surroundings of metal ions in concentrated solutions or at various interfaces [1,2]. For instance, recent developments in phase sensitive sum frequency generation (SFG) spectroscopy enable us to determine the orientation of water at solid/liquid or liquid/vapor interfaces [3]. Adsorption features of dehydrated anions are indeed along the order of Hofmeister series at the surface of lipid amines, in contrast to those of hydrated metal cations at surfaces of dissociated fatty acid [4]. Conventional IR absorption spectroscopy is also employed to investigate hydrated ions in concentrated salt solutions above ~1 M [5] using multicomponent analysis (MCA) or double difference infrared spectroscopy (DDIR) using semiheavy water (HDO) to derive intrinsic spectra of O—H stretching mode for hydrated species. From a series of IR spectra, Stangret addressed the fact that intermolecular hydrogen bonding largely varies with the charge density of anions providing distinct νO—H band at 3200–3600 cm^{-1}, whereas metal cations at the same valences give almost constant νO—H frequency [5]. Besides, low frequency modes of libration and restricted translation of water molecules against associating metal ions are observed at 700–100 cm^{-1} in Raman [6] and THz/FTIR [7] spectroscopy, which afford compelling evidence for the detection of hydrated metal ions. Concerning the interaction between metal cations and counter anions, Rudolph et al. persisted that contact ion pair (CIP) is formed for Li^+ and CH_3COO^- anions instead of solvent shared ion pair (SIP) or solvent separated ion pair (2SIP) for Na^+ and CH_3COO^- based on the Raman spectral modifications against those of deprotonated (free) CH_3COO^- anions [8,9]. We have a limited number of reports on structural variations of ion pair, such as from 2SIP to SIP and CIP with increasing concentration of salts. This is partly due to experimental constraints such as serious disturbance of neat water in MCA or DDIR analyses even at such high concentrations, and also due to low sensitivity for water in conventional Raman spectroscopy.

The low sensitivity in conventional Raman spectroscopy to observe νO—H stretching mode of water is markedly improved by using surface enhanced Raman scattering (SERS), in which Raman enhancement by a factor of 10^4–10^5 is obtained for various molecules on roughened Ag, Au or Cu surfaces [10]. Nevertheless, there are few reports on water molecules even with SERS. It was often addressed that water or other small molecules rather than dye molecules must be observed in SERS, in particular according to electromagnetic enhancement that should work equivalently for any molecules. The point is, however, markedly low scattering cross section of water (~1/30) compared with other molecules like nitrobenzene [11,12] as reported in this paper. Concerning this, nanogap of flocculates, closely adjacent state, of silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs), provides much larger enhancement factor such as 10^6–10^{10} compared to roughened

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metal surfaces [13]. One of MNPs in flocculates can be replaced with smooth metal substrates even with large damping like Pt, Ni, Co, Al, or non-metal substrates like Si, TiO_2 with sufficiently high refractive indices [14–19]. Li et al. reported potential dependence of Raman bands from water adsorbed on Ag, Au and Pt film electrodes, composed of these nanoparticles immobilized on the same metal substrates, in particular on hydrogen bonding interactions and Stark effect [20], suggesting higher enhancement is essential to detect water molecules adsorbed on electrode surfaces.

In the present study, sufficiently high enhancement in flocculates of AgNPs was exploited to elucidate hydrated metal ions and relevant surface species. We indeed succeeded in trapping and characterizing hydrated metal ions like Li^+, Na^+, Cs^+, Ca^{2+}, Fe^{2+}, Cu^{2+}, and Co^{2+} between a nanogap of halide-covered AgNPs. Water molecules bound to metal ions gave Raman bands at 3500–3600 cm^{-1} for O—H stretching modes, which are significantly higher than those in concentrated salt solutions at 3200–3400 cm^{-1}, and sensitive to metal species and halide species, indicating solvent shared ion pair is formed in flocculates.

2. Experimental

Silver nanoparticles (AgNPs) were synthesized by a method of citrate reduction [21,22], in which citrate molecules reduce Ag^+ ions, and also stabilize AgNPs in suspensions. The surfaces of as-prepared AgNPs are covered by residual citrate anions [22] with a surface coverage of $\theta \sim 0.1$ [23,24], binding one of ten metal atoms with citrate anions, which are replaced by various thiol molecules and also by halide ions. Aqueous solution of p-mercaptobenzoic acid (PMBA, 1 mM) added to as-prepared suspensions thus forms self-assembled monolayer (SAM) on AgNPs. In a similar way, sodium halide (Cl^-, Br^-, I^-) solutions (1 mM) were mixed with as-prepared suspensions to form halide adsorbed AgNPs. The pH in AgNP suspensions was selected to keep these surface species deprotonated. Namely pH value was kept to be 4–6 for citrate-AgNPs, while that for PMBA-AgNPs was kept to be 12 to capture Na^+ ions and to be 5–6 for Rb^+, Cs^+, Mg^{2+}, Ba^{2+}, Cu^{2+} and Co^{2+}. These pH values are compatible with deprotonation of citrate (pKa = 3.09, 4.75, 6.41) and PMBA (5.8), and dissolution of transition metal ions. Flocculates of AgNPs were then formed by the addition of metal halide or metal sulfate, in which much different concentrations are necessary for monovalent and divalent metal ions to sufficiently diminish the thickness of double layer and the surface potential [25]. Here, we used different metal ions like Li^+, Na^+, Ka^+, Cs^+, Mg^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+} to find the effect of their charge density on the structure of hydration and interaction with halide and $PMBA^-$ anions. Subtractive absorption spectroscopy [14] (JASCO, V550) and ICP-AES (Perkin-Elmer, Optima 5300DV) analysis were employed to assess the number of metal ions captured on each AgNP. An optical microscope was combined with home-built collective optics and with a polychromator (Bunkokeiki KK, M-25) to detect SERS signal from flocculates of AgNPs with hydrated metal ions in a thin solution cell [14] using a He-Ne laser (~20 mW). DFT calculations were employed to obtain optimized structures and theoretical Raman spectra for hydrated metal ions and their complexes with $PMBA^-$ and halide anions in water.

3. Results and discussion

3.1. Citrate covered AgNPs (as prepared AgNPs)

As-prepared AgNPs, covered by residual citrate anions as evidenced by ζ-potential of −45 mV [22], are isolated in suspensions. At low ionic strength like ≤1 mM, interparticle interactions are primarily governed by electrostatic repulsion of hydrated metal cations in their electrical double layer rather than van der Waals attractive force between AgNPs. Many cations are accumulated around AgNPs at higher ionic strength, which reduces surface potential and its decay length, and thereby attenuate interparticle repulsions. Accordingly AgNPs flocculated at the concentration of metal chloride of 40 mM and 2 mM for monovalent (Na^+, Cs^+) and divalent (Mg^{2+}, Co^{2+}) metal ions, respectively (Fig. 1), as evidenced by decreased intensity of an extinction peak at ~400 nm from isolated AgNPs, and by increased intensity of broad peaks at 600–800 nm (Fig. S1). Much lower critical concentration for multivalent ions is explained by the Schultz-Hardy rule along with the Debye-Hückel theory. The average number of trapped metal (Co^{2+}) ions was found to be 3700–3900 ions per AgNP (r = 15 nm) by subtractive absorption and ICP-AES analysis (Table 1) in accordance with those (~5000 ions/AgNP) predicted from surface coverage of citrate [22].

Citrate anions adsorb on AgNPs via one or two carboxylate anions, as evidenced by AFM and electrochemical measurements [22,24], even under appreciably acidic conditions. The ζ-potential of −28 mV at pH2 is notably smaller than −45 mV at pH7, but still large enough for AgNPs to be isolated. Deprotonated state of citrate on AgNPs at pH2 was confirmed also by SERS band at ~1400 cm^{-1} from $\nu_{sym}COO^-$ mode (Fig. 1). We observed Raman spectra from adsorbed citrates at 1397, 1090, 1026, 951, 838, 800, 300, and 218 cm^{-1} identical for monovalent and divalent typical metal ions at pH = 4–6 (Na^+, Rb^+, and Mg^{2+}), corresponding well to those of bulk trisodium citrate powder only slightly modified by adsorption on Ag surfaces. In contrast, transition metal ions such as Co^{2+} and Cu^{2+} showed spectra at 1600, 1487, 1370–1360, 1318, 1160–1150, 1020, 935, 810, and 790 cm^{-1}. These spectral differences observed for typical and transition metal ions are attributed to complex formation of transition metal ions with citrate on AgNPs as supported by the peak shift of $\nu_{sym}COO^-$ from 1397 cm^{-1} to 1370–1360 and ~ 1320 cm^{-1} [26].

3.2. PMBA-coated AgNPs

We adjusted pH in suspension to 12, which is much higher than pKa (5.9) of PMBA in bulk solutions, to deprotonate PMBA com-

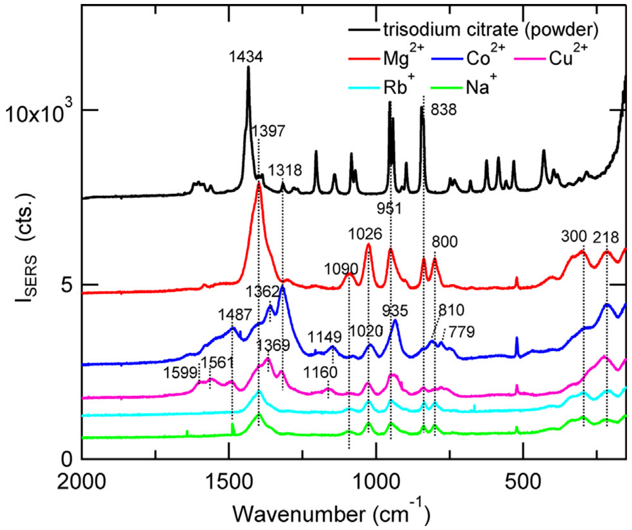

Fig. 1. SERS spectra from metal cations (M^{n+}) trapped on as-prepared AgNPs: M^{n+} = Na^+, Rb^+, Cu^{2+}, Co^{2+}, Mg^{2+} as well as from bulk trisodium citrate (powder). Here, concentrations of metal ions are 2 and 40 mM for divalent (Cu^{2+}, Co^{2+}, and Mg^{2+}) and monovalent (Na^+ and Rb^+) ions, respectively. Most of solutions possess pH ~ 6 except those containing Cu^{2+} ions (pH = 4.1) to suppress precipitations of $Cu(OH)_2$.