Coordination of Carboxylate on Metal Nanoparticles Characterized by Fourier Transform Infrared Spectroscopy

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The coordination of carboxylate capping agents on silver and gold nanoparticles is investigated by Fourier transform infrared spectroscopy (FTIR). The shift of carboxylate stretching frequency confirmed that carboxylate bound on gold nanoparticle forms unidentate coordination, while that on silver nanoparticle shows ionic bonding. The different coordinations on gold and silver NPs are reasonably interpreted by molecular orbital (MO) calculation based on metal carboxylate molecules.

Size-quantized metal nanoparticles (NPs) exhibit unique electronic, chemical, and optical properties distinct from those of bulk metals, which lead to potential applications in various fields.[1] Most of NPs require surface-passivation to avoid coagulation and fusion of metal cores, since bare NPs are unstable with extremely high surface reactivity. The physical and chemical properties of NPs such as dispersibility in solvents are also known to be controllable by capping organic agents, thus different capping agents have been utilized as stabilizers depending on the polarity of dispersion solution. Brust et al. has developed a representative preparation method of gold nanoparticle (AuNP) by the reduction of $HAuCl_4$ with $NaBH_4$ in aqueous phase and extraction into toluene phase with tetraoctylammonium bromide (TOAB) as a stabilizer.[2] In the case of the Frens method, AuNP is prepared in aqueous solution with citrates as a stabilizer.[3] Recently, we have developed a powerful preparation method for monodispersed silver nanoparticles (AgNP) in large quantities by thermal decomposition of silver acetate and myristic acid, where myristate plays a role as both a reaction matrix and capping agent.[4]

Looking over all these preparation methods, a fundamental question concerning carboxylate arises to us–why do carboxylate work so well as a stabilizer for both AuNP and AgNP? Sulfur compounds such as thiol and disulfide are known as a strong ligand against novel metals forming stable self-assembled monolayers (SAMs) by chemisorption.[5] However, to the best of our knowledge, carboxylates do not form stable monolayers on novel metals unlike thiol at least at room temperature. The strong bond formation of carboxylate on metal NP seems to happen only at high temperature during particle preparation.

In this study, we closely investigate the coordination of carboxylate on AuNP and AgNP by Fourier transform infrared spectroscopy (FTIR) (Figure 1). Infrared spectra of various metal carboxylates (molecule) have been studied extensively over a long period of time.[6] As the fruit of these efforts, the coordination of carboxylate to metal ion are reasonably categorized as ionic or covalent (unidentate, bidentate, or bridging) by their stretching frequencies.[7,8] In contrast, the coordination of carboxylate on metal surface or NPs has never been systemati-
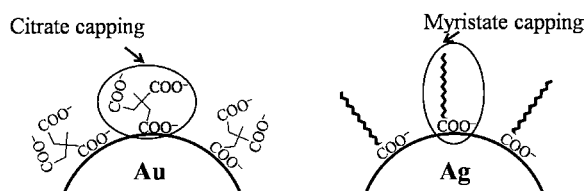

Figure 1. Carboxylates on AgNP and AuNP.

cally studied. The IR data of AuNP and AgNP are compared with that of corresponding metal carboxylate (molecule) obtained experimentally and/or by molecular orbital (MO) calculation.

Citrate-capped AuNP and myristate-capped AgNP were prepared as described in our previous study.[4,9] The reaction temperatures were ca. 100 °C for AuNP and ca. 250 °C for AgNP. The TEM diameters of metal cores are 24 nm[9] for AuNP and 5 nm for AgNP.[4] FTIR measurements of AuNP and AgNP are conducted by KBr method in transmission mode with 8 cm^{-1} of resolution and 100 scans in the region of carboxylate vibration modes (1300–1800 cm^{-1}). MO calculation of metal carboxylates is carried out by using metal acetates as model compounds. Optimized structures of metal acetate and their vibration mode were calculated by Gaussian 98 program[10] in vacuum at 298.2 K, and the results were displayed as 3D images by MolStudio software.

The IR spectra of myristic acid and myristate on AgNP are shown in Figure 2a. The stretching mode of carboxylic acid ($\nu(COOH)$) at 1700 cm^{-1} completely disappeared on AgNP, and the asymmetric ($\nu_{as}(COO^-)$) and symmetric ($\nu_s(COO^-)$) stretching peaks of carboxylate appeared instead at 1561 and 1412 cm^{-1}. The vibration modes of CH_3COOH and CH_3COOAg calculated by MO program are shown in Figure 2b. The experimental and simulated results of carboxylic acid are in perfect agreement with a model of covalent bond formation (unidentate) as reported in refs 7 and 8. In contrast
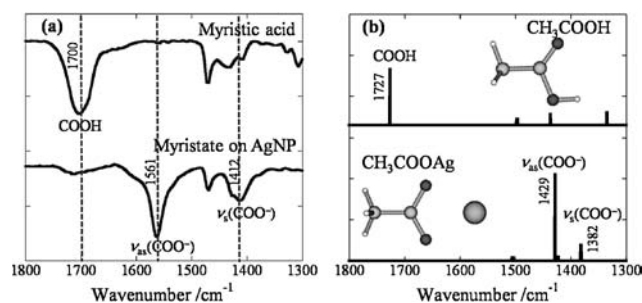

Figure 2. (a) IR spectra of myristic acid and myristate on AgNP and (b) MO calculation of CH_3COOH and CH_3COOAg.
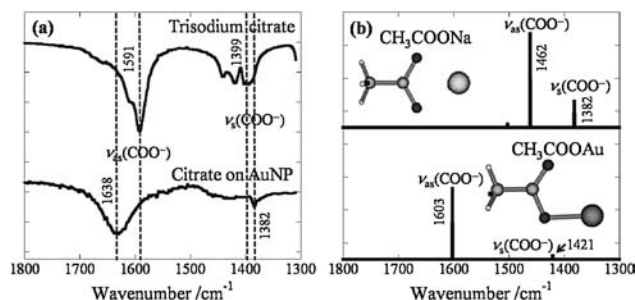
Figure 3. (a) IR spectra of trisodium citrate and citrate on AuNP and (b) MO calculation of CH_3COONa and CH_3COOAu.

to carboxylic acid, carboxylate forms ionic bonding with Ag atom as schematically shown in Figure 2b. The IR data of myristate on AgNP is not exactly the same as the result of MO calculation for CH_3COOAg; however, both exhibit similar tendencies of low frequency shifts.

IR spectra of trisodium citrate and citrate on AuNPs are shown in Figure 3a and the results of MO calculation for CH_3COONa and CH_3COOAu are shown in Figure 3b. Trisodium citrate, the raw material for preparation of citrate-capped AuNP, exhibits ionic coordination with Na as predicted by MO calculation for CH_3COONa, also as reported in the literature.[8] More remarkable is the data of gold carboxylate. The MO calculation predicts unidentate bonding of carboxylate with Au atom along with high frequency shift of $\nu_{as}(COO^-)$, that is completely different from the case of Ag. In fact, the experimental data of $\nu_{as}(COO^-)$ for citrate on AuNP appeared at high frequency ($1638\,cm^{-1}$) compared to trisodium citrate ($1591\,cm^{-1}$), that is in good agreement with MO calculation. The weakened $\nu_s(COO^-)$ on AuNP is also as predicted by MO calculation.

To clarify the point, all the data of $\nu_{as}(COO^-)$ obtained experimentally and by MO calculation are summarized in Figure 4. Interestingly, the data for both metal carboxylate and carboxylate adsorbed on metal NPs lay on the same straight line. The results imply that the coordination of carboxylate on NPs exhibits no significant difference from the corresponding metal carboxylate (molecule) and is predicted by simple MO calculation. To conduct direct comparison between metal carboxylate and carboxylate on NP, the IR datum of CH_3COOAg taken in our laboratory ($\nu_{as}(COO^-)$, $1581\,cm^{-1}$) is plotted together with myristate on AgNP. The data are not identical; however, the difference is relatively small compared with the result for different metals.

In Figure 4, the higher frequency vibration ($>1700\,cm^{-1}$ on x axis) conforms to unidentate (covalent) bond formation, while the lower frequency vibration ($<1500\,cm^{-1}$ on x axis) conforms to ionic bond formation. The peak position of Ag carboxylate close to alkali metals at low frequency is classified into the ionic bonding, while that of Au carboxylate located between the two regions is classified into the intermediate coordination between ionic and covalent bondings even though it has the unidentate structure.

When we consider the adsorption of thiol (–SH) derivatives on metal, they form quite identical self-assembled layers on both Au and Ag by chemisorption. On the other hand, Au has quite different properties from other novel metals such as Ag and Cu. For example, Au does not form stable surface oxidized layer unlike them. Various Ag carboxylates such as CH_3COOAg are identified as isolated molecules, while Au carboxylates are not
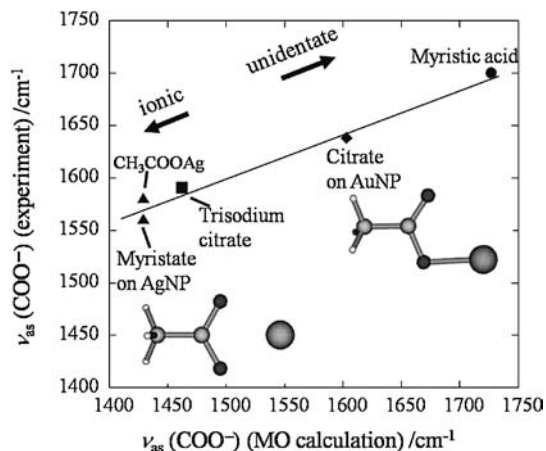

Figure 4. Summarized $\nu_{as}(COO^-)$ data for both metal carboxylate and carboxylate on metal NPs.

(probably our data on AuNP is the first effort to confirm the coordination of carboxylates with Au). It is possible that the larger ionic radius (at $1+$/pm) of Au contributes to these results. In fact, Au atoms cannot locate stably at the center position of carboxylate unlike Ag and Cu during MO calculations, giving errors in the optimization process. Electronegativity of Au which is close to the electronegativity of O may also contribute to the formation of covalent (unidentate) bonding. The detailed mechanism needs to be investigated in the future.

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