



Characterization of citrates on gold and silver nanoparticles



Priastuti Wulandari^{a,b}, Takeshi Nagahiro^a, Nobuko Fukada^c, Yasuo Kimura^a, Michio Niwano^a, Kaoru Tamada^{a,d,*}

^a Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

^b Department of Physics, Institut Teknologi Bandung, Jalan Ganesha 10, Bandung 40132, Indonesia

^c Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba 305-8561, Japan

^d Institute for Materials Chemistry and Engineering, Kyushu University, 6-10-1 Hakozaki, Higashiku, Fukuoka 812-8581, Japan

ARTICLE INFO

Article history:

Received 12 August 2014

Accepted 28 September 2014

Available online 13 October 2014

Keywords:

Vibration of adsorbed molecules

Infrared spectroscopy

Metal nanoparticles

Carboxylate

ABSTRACT

In this paper, we report different coordinations of citrates on gold (AuNP) and silver (AgNP) nanoparticles, as determined using Fourier transform infrared spectroscopy (FTIR) and molecular orbital (MO) calculations. AuNPs and AgNPs are found to have completely different interactions with the carboxylate anchoring groups, as indicated by their unique asymmetric stretching vibrations in the FTIR spectra. The ν_{as} (COO^-) of citrate exhibits a high-frequency shift resulting from the formation of a unidentate coordination on AuNPs, whereas this vibration exhibits a low-frequency shift as a result of ionic bond formation on AgNPs, as predicted from the MO calculations of the corresponding metal complex salts. The enhancement in the IR signals when their vibration direction was perpendicular to the nanoparticle surface revealed the influence of localized surface plasmons excited on the metal nanoparticles.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Colloidal metals or metal nanoparticles (metal NPs) have been intensively investigated in recent years due to their unique electronic, chemical and optical properties, which differ from those of their bulk counterparts [1–4]. These small metal NPs with various functional groups have been reported to have potential applications in microelectronic devices, biosensors, catalysts, solar cells and other fields [5–10].

Capping ligands on metal NPs are quite important for surface passivation to prevent the aggregation and fusion of metal cores [11–18]. It is also well known that the physical and chemical properties of NPs, such as their dispersibilities in solvents, are controlled by the capping organic molecules [18]. Because the specific properties of metal NP architectures are determined not only by the properties of individual particles but also by their assembled structures, it is crucial to control the interactions and the gap distance between the particles through the design of an organic interface on the metal cores [19].

Citrate has been employed as a common reducing and stabilizing agent for colloidal Au dispersions, as reported by Frens in 1973 (Fig. 1) [12]. Following this report, the adsorption of citrate

on Au has been carefully investigated in the field of surface science. Sandroff and Herschbach obtained direct evidence for the presence of citrate anions adsorbed on colloidal Au surfaces using surface-enhanced Raman spectroscopy [20]. Biggs et al. measured the forces between a Au-coated colloidal silica sphere and a pure Au plate as a function of the citrate concentration using atomic force microscopy (AFM) [21]. Floate et al. investigated the specific adsorption of citrates from perchloric acid electrolytes onto Au (111) electrodes using in situ FTIR spectroscopy and proposed a model for the surface coordination of citrate [22]. Recently, Lin et al. succeeded in imaging the structure of citrate on Au (111) through the use of in situ scanning tunneling microscopy (STM) [23].

The study of carboxylates adsorbed on Ag has also become a current research interest for use as a stabilizer in the synthesis of AgNPs. Myristic acid and oleic acid are commonly used as capping molecules for the synthesis of AgNPs via thermal reduction [16–18]. The interaction between carboxylate and a flat Ag substrate has also been investigated. Chau and Porter found that perfluorocarboxylic acid symmetrically bonded with the flat Ag substrate with carboxylates as a bridging ligand [24]. Although many studies have been conducted to investigate the interactions of carboxylates with flat Au and Ag substrates, all of these studies focused on physisorbed molecules (weakly bound carboxylates, which can be rinsed out), i.e. the conformation and structure of the carboxylates in these reports are not required to be identical for the carboxylate ligands to strongly bind to the metal particles.

* Corresponding author at: Institute for Materials Chemistry and Engineering, Kyushu University, 6-10-1 Hakozaki, Higashiku, Fukuoka 812-8581, Japan.

E-mail address: tamada@ms.ifoc.kyushu-u.ac.jp (K. Tamada).

In this study, we attempt to determine the coordinations of carboxylates in citrate-capped AuNPs and AgNPs using FTIR spectroscopy with consideration of the different metal cores. We also discuss the influence of localized surface plasmons excited on the metal cores on the vibration modes of the carboxylates.

2. Experimental

Citrate-capped AuNPs were prepared in water by following the Frens method [12]. 90 mL of an aqueous HAuCl₄ solution (0.05% by weight) was heated to its boiling temperature under reflux. Then, 10 mL of trisodium citrate (1% by weight) in an aqueous solution was rapidly injected into the solution. After 2 min of reaction time, the color of the reaction solution changed from yellow to deep purple, indicating the formation of AuNPs. The AuNP solution exhibited a homogenous red wine color after purification. The synthesis of citrate-capped AgNPs was conducted at room temperature by mixing 100 mL/0.1 mM of AgNO₃ and trisodium citrate aqueous solutions under stirring at 570 rpm. The reaction was completed by adding a 10 mL/2 mM NaBH₄ aqueous solution as a reductant. After 3 h of reaction time, the reaction mixture exhibited a yellow color, indicating the formation of AgNPs. The citrate-capped AuNPs and AgNPs were both purified more than 4 times to completely remove the free citrates in solution [25]. The purified solutions could be stored for several weeks at room temperature without aggregation.

The conformations and coordinations of citrate on the AuNPs and AgNPs were confirmed by FTIR spectroscopy [26–31]. The FTIR measurements were conducted using the KBr method in transmission mode with a resolution of 8 cm⁻¹ and a total of 100 scans. The experimental AuNP and AgNP IR data were compared with the simulation results. The molecular orbital (MO) calculations were performed using the corresponding metal acetates as model compounds [32]. The optimized structures and vibration modes were

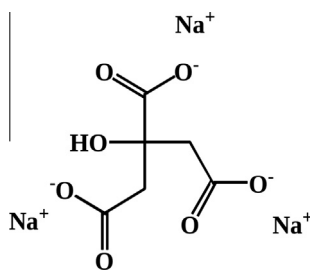


Fig. 1. Molecular structure of trisodium citrate (C₆H₅Na₃O₇).

calculated using the Gaussian 98 program [33] under vacuum conditions at 298.2 K. The results were displayed as 3D images using the MolStudio software.

3. Results and discussion

The syntheses of citrate-capped AuNPs and AgNPs were confirmed by the surface plasmon absorbance bands at 525 nm for AuNPs and at 397 nm for AgNPs in aqueous solutions (Fig. 2). The transmission electron microscopy (TEM) data revealed that the diameters of the spherical NPs were 24 nm for AuNPs and 5 nm for AgNPs (data not shown) [25,34].

Fig. 3 presents the FTIR spectra of the citrate-capped AuNPs and AgNPs. Peaks for carboxylate asymmetric stretching ($\nu_{as}(\text{COO}^-)$) and symmetric stretching ($\nu_s(\text{COO}^-)$) from trisodium citrate appeared at 1591 cm⁻¹ and 1399 cm⁻¹, respectively. For citrate on the AuNPs, the $\nu_{as}(\text{COO}^-)$ peak was found to be largely high-frequency shift from the original peak position. In contrast, the $\nu_{as}(\text{COO}^-)$ appeared to be slightly low-frequency shift in the case of citrate on the AgNPs. The $\nu_s(\text{COO}^-)$ on the AuNPs and AgNPs are both low-frequency shift to 1382 cm⁻¹, and the peak intensity of $\nu_s(\text{COO}^-)$ on the AgNPs is significantly stronger compared to that on the AuNPs.

Fig. 4 presents the comparison between the FTIR data and the MO calculation results of the corresponding metal carboxylates. In our previous study, we found that the coordinations of carboxylates on metallic NPs are reasonably predicted by MO calculations based on the corresponding metal carboxylate molecules [32]. The FTIR data of citrate on the AuNPs exhibited $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ stretching bands at 1638 cm⁻¹ and 1382 cm⁻¹, respectively. On the other hand, the MO calculations of CH₃COOAu resulted in $\nu_{as}(\text{COO}^-)$ at 1603 cm⁻¹ and $\nu_s(\text{COO}^-)$ at 1421 cm⁻¹. The peak positions of both $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ were consistent between the experiment and the MO calculations. The peak intensities were also quite consistent. The optimized structure obtained from the MO calculation revealed covalent bond formation (unidentate), as shown in Fig. 4(a).

The FTIR data of citrate on the AgNPs exhibited $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ stretching bands at 1585 cm⁻¹ and 1382 cm⁻¹, respectively, whereas the MO calculation of CH₃COOAg revealed $\nu_{as}(\text{COO}^-)$ at 1429 cm⁻¹ and $\nu_s(\text{COO}^-)$ at 1382 cm⁻¹. The peak position of $\nu_s(\text{COO}^-)$ was in perfect agreement between the experimental data and the MO calculation; however, the peak position of $\nu_{as}(\text{COO}^-)$ differed by more than 150 cm⁻¹ between the experimental data and the MO calculation. The optimized structure obtained from the MO calculation consisted of an ionic bond between carboxylate and Ag atoms, as shown in Fig. 4(b). The

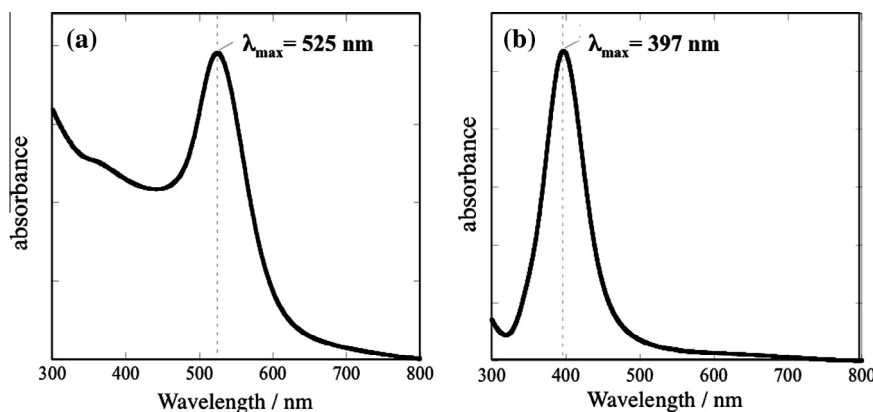


Fig. 2. UV-Vis spectra of citrate-capped AuNPs (a) and AgNPs (b) in aqueous solutions.

Download English Version:

<https://daneshyari.com/en/article/607046>

Download Persian Version:

<https://daneshyari.com/article/607046>

[Daneshyari.com](https://daneshyari.com)