

Raman spectroscopy of gold nanoparticle conjugates of cosmetic ingredient kinetin

Anh Thu Ngoc Lam^a, Erdene-Ochir Ganbold^a, Kwang-Hwi Cho^b, Daeseung Kang^c, Sang-Woo Joo^{a,*}

^a Department of Chemistry, Soongsil University, Sangdo-dong, Dongjak-gu, Seoul 156-743, South Korea

^b School of Systems Biomedical Science, Soongsil University, Sangdo-dong, Dongjak-gu, Seoul, South Korea

^c Department of Electrical Engineering, Soongsil University, Seoul 156-743, South Korea

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ABSTRACT

We performed a feasibility test of the cosmetic ingredient kinetin (KT)-gold nanoparticle (AuNP) conjugates by means of vibrational Raman spectroscopy and quantum mechanical calculations. The adsorptions of KT on AuNP surfaces were examined by absorption spectra and surface-enhanced Raman scattering (SERS). The size of KT at the initial concentrations of 10^{-5} M with the AuNP composites was measured to be 22 nm. Density functional theory (DFT) calculations were performed to estimate the energetic stabilities of KT on an Au cluster atom. The two tautomeric forms of 9H-amino and 7H-amino in KT are predicted to have similar energies on Au. The N3-coordinating geometries in both 9H-amino and 7H-amino forms of KT are predicted to be most stable on an Au cluster. Vibrational analysis also suggested that the two tautomers of KT should coexist in the adsorbed state on Au. The concentration-dependent SERS spectra of KT indicated that 5×10^{-5} M exhibited the highest SERS signals.

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1. Introduction

Among various characterization tools, due to less interference from water and high spatial/spectral resolution, Raman spectroscopy can be utilized to monitor the dermal drug delivery on skin [1,2]. By taking advantage of enormous enhancements of electromagnetic and charge transfer mechanisms, surface-enhanced Raman scattering (SERS) has been used to investigate interfacial behavior of adsorbates on metal nanostructures [3–6]. Quantum mechanical calculations have been introduced to predict the adsorption geometry and conformational change to better explain surface phenomena [7].

Kinetin (N6-furfuryladenine, KT) was one of the first cytokinin compounds in promoting cell growth, development and division [8,9]. Studies on human fibroblasts *in vitro* have demonstrated that KT may have the ability to delay the onset of age-related changes as well as decrease the severity of these changes [10,11]. Although KT has been included in cosmetic compounds to exert its antiaging effects [12–16], the mechanism by which KT exerts its effects on human skin fibroblasts remains elusive.

Gold nanoparticles (AuNPs) have been introduced in drug delivery systems because of their low toxicity and biocompatibility. Although there have been numerous reports of AuNP-based drug delivery systems, there has been no vibrational spectroscopic analysis of cosmetic ingredients in association with quantum mechanical calculations.

Despite numerous AuNP-based drug delivery systems, there has been no report on the SERS study of any cosmetic ingredients to the best of the authors' knowledge. In this work, we attempted to fabricate the KT cosmetic ingredient on AuNPs. Raman spectroscopy was introduced to investigate the interfacial structures and adsorption behaviors. Density functional theory was used to interpret the Raman spectra of both in the solid state and on AuNPs.

2. Experimental

2.1. Preparation of AuNP conjugates and physical characterization

PEGylation was used in NP-based drug delivery systems as in the previous report [17]. KT and thiolated-PEG were purchased from Sigma Aldrich (St. Louis, USA) and Nanocs (New York, USA), respectively. AuNPs were prepared according to the previous report [18]. Absorbance spectra of the AuNP solutions before and after surface

* Corresponding author. Tel.: +82 2 820 0434; fax: +82 2 824 4383.
E-mail address: sjoo@ssu.ac.kr (S.-W. Joo).

modification were taken using a Mecasys 3220 spectrophotometer. The quasi-electrostatic light scattering (QELS) measurements to estimate the hydrodynamic radius and surface potentials of AuNPs were performed with an Otsuka ELSZ-2 analyzer.

2.2. DFT calculations

We performed DFT calculations using a Gaussian 09 software. The energetic stabilities of more than 20 rotamers of KT were first estimated prior to the Au cluster conjugate calculations. The most stable geometries of the 9H-amino and 7H-amino tautomeric forms were selected to compare the vibrational spectra. For the six Au atom cluster models, the energies were calculated using B3LYP/LanL2DZ functional/basis set. The three plausible coordinating geometries were tested to predict the binding structures of the six Au cluster atoms. Raman frequencies and assignments were calculated at the fully optimized geometry having the minima on potential energy surfaces.

2.3. Raman spectroscopy

We obtained Raman spectra using a Renishaw RM 1000 microscope under the excitation wavelength at 632.8 nm. For the solid sample of KT, the Bruker RFS-100 Fourier-transfer Raman spectrometer was used with irradiation of the near-infrared at 1064 nm. The spectra measurements were performed by the method as in a previous report [19].

3. Results and discussion

3.1. DFT calculations of tautomeric forms

Fig. 1 illustrates the molecular structure of KT, which may have a 7H-amino and 9H-amino tautomeric form [20] for the corresponding hydrogen positions as shown in Fig. 1. In this previous report [20], 9H-amino form was calculated to be more stable than that of the 7H-amino form. Our DFT calculations on the basis of B3LYP/6-31G+(d,p) also predict that the 9H-amino form is more stable by 8.33 kcal/mol.

KT may adsorb on AuNPs via its nitrogen atoms of the adenine units. There may be the three binding sites of N1, N3, and N9 and N1, N3, and N7 atoms for the 7H-amino and 9H-amino tautomeric forms, respectively. Based on the present DFT calculations, the N3-coordinating geometries were predicted to be more stable than those of the N1, N7, and N9-coordinating sites. The energetic difference of the 7H-amino-N3 and 9H-amino-N3 with the six Au atoms was calculated as only 0.83 kcal/mol, which was much smaller than that of the gas-phase neutral state. The Au–N distances of 7H-amino-N3 and 9H-amino-N3 were calculated as 2.20 and 2.19 Å, respectively, as shown in Fig. 2. Although our cluster model cannot completely explain the adsorbed structures, more favorable adsorption of the 7H-amino-N3 form may be due to an additional exposure of one more deprotonated nitrogen N9 atom toward Au atoms, differently from the case of the 9H-amino-N3 form. In order to better understand the adsorption behaviors, we performed absorption and Raman spectroscopy for the AuNP-KT conjugates.

3.2. Adsorption of KT on AuNPs

The size of AuNPs was measured to be 22 nm, as shown in Fig. 3a. Considering that the hydrodynamic diameter was measured to be as small as 22 nm, the AuNP conjugates may be appropriated to the cell treatment. Fig. 3b shows absorption spectra of the AuNPs before and after the addition of KT and PEG. The surface Plasmon band of AuNP-KT appeared at 522 nm. After introducing PEG-SH, AuNPs

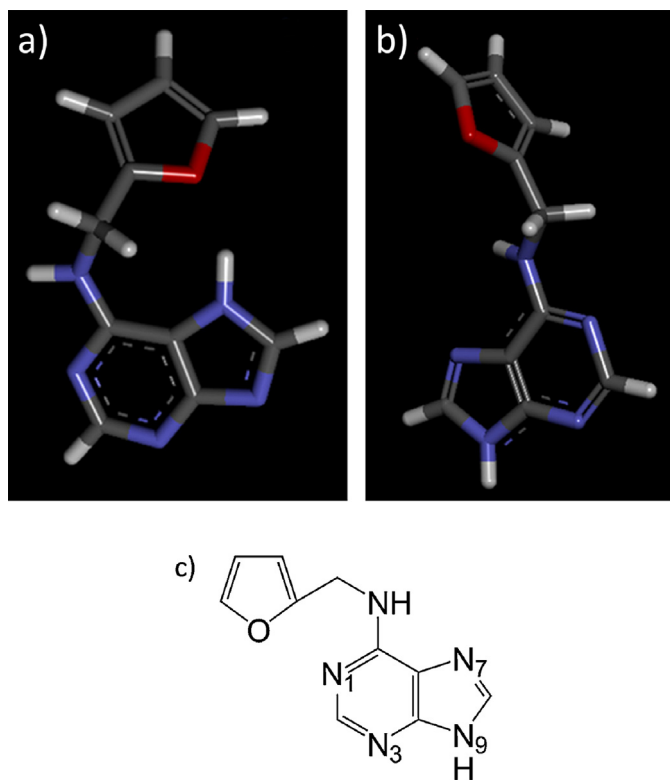


Fig. 1. Molecular structures of (a) 7H-amino and (b) 9H-amino of KT. (c) Numbering of the nitrogen atoms of 9H-amino form of KT. 7H-amino form with the hydrogen atom attached to N7 atom instead of N9 form is omitted.

became slightly aggregated, as indicated by the redshift to 525 nm for the surface Plasmon band along with the increased absorbance between 600 and 800 nm. In order to understand the vibrational structures of KT on AuNPs, we performed Raman spectroscopy with the guidance of DFT calculations.

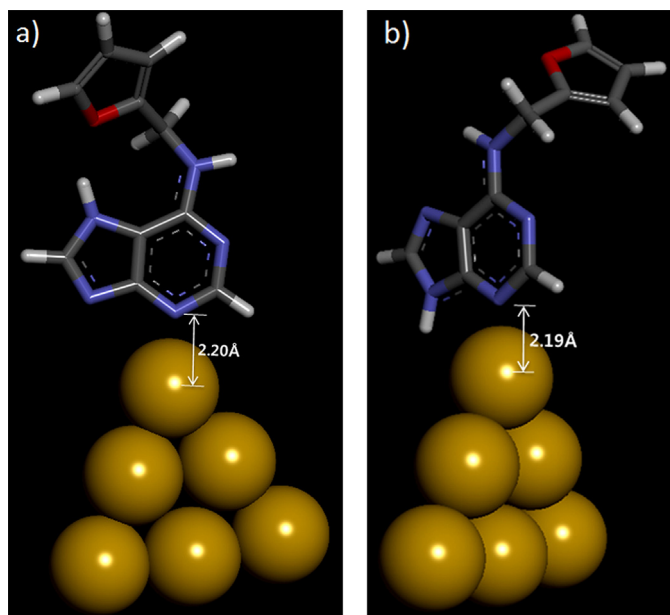


Fig. 2. Molecular structures of (a) 7H-amino and (b) 9H-amino forms by coordinating a six atom Au cluster via the N3 atom of KT. The Au–N distances were depicted in the pictures.

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