



Temperature-dependent structural change of D-penicillamine-capped chiral gold nanoparticles investigated by infrared spectroscopy

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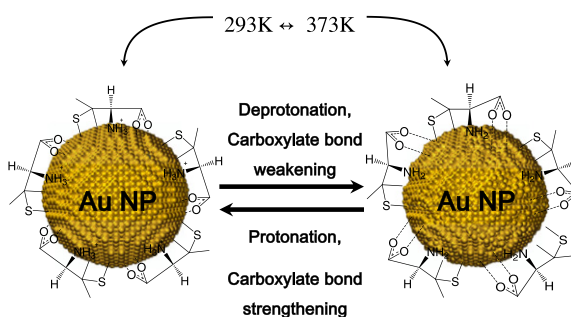
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HIGHLIGHTS

- D-Pen was presumed to interact with gold surfaces by its carboxyl and amino groups.
- Amino groups were deprotonated and carboxylate bonds became weakened at high temperature.
- Such structural changes appeared to be reversible between 293 and 373 K.

GRAPHICAL ABSTRACT



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ABSTRACT

The structure and stability of D-penicillamine-capped gold nanoparticles (D-Pen Au NPs) were studied using spectroscopic tools. The synthesis of D-Pen Au NPs was examined using high-resolution transmission electron microscopy (HR-TEM), UV–vis absorption spectroscopy, and circular dichroism (CD). Temperature-dependent reversible structural changes of D-Pen Au NPs were observed using infrared spectroscopic tools. The three thiol, carboxyl, and amino binding groups of D-Pen were presumed to interact with Au NP surfaces on the basis of the infrared spectral features. D-Pen appeared to form quite a stable structure and desorb at a high temperature above 453 K on Au NPs. Our deconvolution analysis indicated the $\nu_s(\text{COO}^-)$ and $\nu_{as}(\text{COO}^-)$ carboxylate bands at ~ 1392 and ~ 1560 cm^{-1} appeared to be weakened, whereas the amino band at ~ 1595 cm^{-1} remained strong in increasing the temperature from 293 to 373 K. On the other hand, the intensities of the zwitter ionic bands at ~ 999 , ~ 1117 , and ~ 1631 cm^{-1} for NH_3^+ appeared to decrease presumably due to the deprotonation process at 373 K. Our infrared spectroscopic study suggests that the deprotonated amino groups bind stronger, whereas the intra-carboxylate bonds become weaker as the temperature increase. Such structural changes of D-Pen Au NPs appeared to be reversible between 293 and 373 K.

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Introduction

Vibrational spectroscopy is one of the most useful methods to provide structural information of complex molecular systems [1–5]. Temperature-dependent spectral behaviors can provide

information on the energetics or phase transition of adsorbates on metal surfaces. Aromatic monolayers are reported to be stable enough to desorb at a fairly high temperature of 423 K in air, whereas alkanethiols are detached below 373 K [6]. In our previous Raman study, the carboxylate group of L-histidine was predicted to bind rather weakly to Au surfaces [7].

Monolayer-capped optically active nanoparticles (NPs) have attracted significant interest in recent years due to their importance

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in both fundamental science and technological applications such as catalysis, sensing, medicine, drug or gene delivery, optics, photonics, and nanotechnology [8–10]. Penicillamine (Pen) is one of the most frequently used chemical reagents to prepare chiral NPs [11]. In fact Pen is a strong chelating agent and reacts with the majority of heavy metal ions, particularly with an affinity for copper [12–14]. Owing to its outstanding metal-binding capability as a ligand, it has also been employed for the elimination of other heavy metals. D-Pen-capped fluorescence NPs have shown improved colloidal stability in physiological media over the commonly-used 11-mercaptoundecanoic acid-capped NPs [15].

Given the molecular structure of Pen, it is not certain yet whether several binding groups can interact differently with the metal surfaces depending on temperature. This work was motivated by relatively few works related to the structures of the chiral capping materials on NPs using vibrational spectroscopic tools. In this study, with a view to further understanding of physicochemical structural properties of chiral NPs, we investigate the thermal stability and structures of D-Pen Au NPs using temperature-dependent infrared spectroscopy.

Experimental

Preparation of chiral Au NPs

Penicillamine (Pen)-capped Au NPs were prepared by the previous method [11]. Enantiopure D- or L-Pen ($(\text{CH}_3)_2\text{-C}(\text{SH})\text{-CH}(\text{NH}_2)\text{-COOH}$; abbreviated as D-Pen (99%) or L-Pen (99%), respectively) and racemic Pen (abbreviated as DL-Pen (97%)) were received from Sigma Aldrich and used as received. Hydrogen tetrachloroaurate tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99%) and sodium borohydride (NaBH_4 , >90%) were also received from Sigma Aldrich. Each of three kinds of Pen (D-, L-, and DL-form) was used as a surface modifier. Briefly, 0.5 mmol of HAuCl_4 dissolved in water (0.121 M) and 1.0 mmol of Pen (D-, L-, or DL-Pen) were at first mixed in methanol (100 mL), followed by the addition of a freshly prepared 0.2 M aqueous NaBH_4 solution (25 mL) under vigorous stirring. After further stirring for 1.5 h, the solution was stored overnight. Addition of ethanol (300 mL) into the stored solution gave a dark-brown crude precipitate. The precipitate was then thoroughly washed with water/ethanol (1/9) and ethanol.

Physical characterization

The synthesized chiral D-Pen Au NPs were characterized using high-resolution transmission electron microscopy (HR-TEM), UV-vis absorption spectroscopy, and circular dichroism (CD). HR-TEM images were obtained using a JEOL JEM-3010 instrument. The average diameter of D-Pen Au NPs was obtained by counting more than 150 particles. CD spectra were recorded with a JASCO J-720 spectropolarimeter using a bandwidth of 2 nm. The ellipticity resolution is 0.01 mdeg. In the CD measurement, absorption spectrum was simultaneously recorded. Rectangular 1 cm cuvettes made of quartz were used for the measurements. UV-vis absorption spectra were recorded using a Mecasys UV-3220 spectrophotometer.

Temperature-dependent infrared spectroscopy

A portion of the D-Pen Au NP sample was transferred onto a DiffuseIR heated chamber (Pike Technologies) equipped with a temperature controller to control temperatures up to 573 K. The infrared spectra were obtained using a FT-IR spectrometer with a maximum resolution of 0.09 cm^{-1} (Thermo Nicolet 6700). A total of 64 or 128 scans were measured in the range of 800–

4000 cm^{-1} with a nominal resolution of 4 cm^{-1} . The diffuse reflectance infrared Fourier transform (DRIFT) measurements are described in the previous report [16,17]. At each temperature, the sample was heated for approximately 3 min. The spectra were measured by heating up at the given temperature for 5 min. Data processing was carried out using the OMNIC v5.1a software. Spectral parameter and fitting of each spectrum was obtained using a SeaSolve software PeakFit version 4.12.

Results and discussion

Physical characterization

TEM images indicated that the sizes of D-Pen Au NPs are 2–4 nm. The average diameter measured to be around $3.1 (\pm 1.1) \text{ nm}$ and its size distribution are shown in Fig. 1a and b. To obtain information on optical activity of the Au NPs, CD spectra of each chiral Au NP sample were measured in solution in the 200–450 nm wavelength region as exhibited in Fig. 1c. The compounds of Au NPs protected by a racemate did not exhibit any CD signals. On the other hand, the spectrum of the L-Pen or D-Pen-capped compound showed minima and maxima. The optically active surface modifier (D-Pen or L-Pen) contributes to the CD signal only in the UV region. It should be emphasized that the CD signal shows an almost complete mirror image of the ellipticity with respect to each other for the D and L form. The mirror image relationship in CD signals means that enantiomeric surface modifiers can produce the corresponding enantiomeric Au NPs. The structures of our Pen-capped Au NPs appear to be stereochemically controlled. A CD spectrum exhibits the difference of two absorption spectra. D-Pen-capped chiral Au NPs appeared to be quite stable and did not react with other thiol or nitrogen-containing compounds. Absorption spectra of Pen-capped Au NPs were illustrated in Fig. 1d, indicating their small size without showing any surface Plasmon bands.

The surface Plasmon band at $\sim 520 \text{ nm}$ was observed normally for the Au NP formation, [18–20]. In several reports [11,21,22] of small-sized Au NP clusters, the surface Plasmon bands at 520 nm were either absent or blue-shifted. It has to be mentioned that the observed surface Plasmon bands were independent of cluster size with large observation uncertainty in a certain case [21]. It is likely that our TEM images may exhibit only a selected portion of large conspicuous particles. Since we did not treat any polyacrylamide gel electrophoresis separation, our samples contained a mixture of Au NPs smaller than 2 nm.

Infrared spectra of D-Pen Au NPs

Infrared spectral analysis of the prepared samples may clarify the chemical and surface properties of Pen-capped Au NPs. The infrared spectral features as shown in Fig. 2 appeared to be quite analogous to those in the previous report [11]. The vibrational modes that can be ascribed to the CH_3 asymmetric stretching and symmetric band were found at ~ 2960 and $\sim 2920 \text{ cm}^{-1}$, respectively. The CH_3 deformation modes at ~ 1453 , ~ 1341 , and $\sim 1085 \text{ cm}^{-1}$ and the CH_3 wagging band at $\sim 1186 \text{ cm}^{-1}$ were also observed in the infrared spectrum. On the other hand, the NH_2 bending mode at $\sim 1595 \text{ cm}^{-1}$, the COO^- asymmetric stretching band at $\sim 1560 \text{ cm}^{-1}$, and the COO^- symmetric stretching band at $\sim 1392 \text{ cm}^{-1}$ appeared prominently at room temperature. Pen has a similar structure to an amino acid related to either cysteine or valine. The spectral positions with appropriate vibrational assignments are summarized in Table 1 on the basis of the previous works of D-Pen, cysteine, and valine [23–30].

Referring from the infrared band analysis for pure D-Pen and D-Pen Au NPs, we could reach the following conclusions on the sur-

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