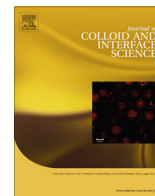




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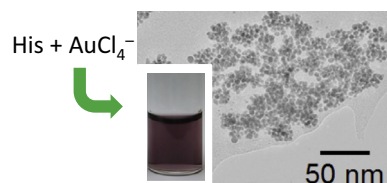


Synthesis of gold nanoparticles using various amino acids

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GRAPHICAL ABSTRACT



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ABSTRACT

Gold nanoparticles (4–7 nm) were synthesized from tetrachloroauric acid using various amino acids as reducing and capping agents. The gold nanoparticles were produced from the incubation of a AuCl_4^- solution with an amino acid at 80 °C for 20 min. Among the twenty amino acids tested, several amino acids produced gold nanoparticles. The color of the nanoparticle solutions varied with the amino acids used for the reduction. We adopted L-histidine as a reducing agent and investigated the effects of the synthesis conditions on the gold nanoparticles. The His and AuCl_4^- concentrations affected the size of the gold nanoparticles and their aggregates. The pH of the reaction solution also affected the reaction yields and the shape of the gold nanoparticles.

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1. Introduction

There are a number of reports describing a broad range of nanomaterials and nanoparticles still play a major part in nanotechnology. In particular, metal [1,2] and semiconductor nanoparticles [3–5] exhibit unique optical and electronic properties beyond their bulk analogs, offering great potential for incorporation into photonic and electronic devices, sensors, diagnostics and bioimaging. Their unique properties are derived from their composition, nanoparticle size and size distribution. Gold nanoparticles, a well-studied type of metal nanoparticle, have been synthesized by various methods. Conventionally, the Turkevich method is widely used to produce water-soluble gold nanoparticles, in which AuCl_4^- is reduced by sodium citrate in water [6]. In the last decade, various organic compounds (e.g. amines, polymers and proteins) were found to act as reducing agents for AuCl_4^- [7–10]. Aslam

et al. reported that oleyl amine acted as a reducing and capping agent for the synthesis of gold nanoparticles [11]. Habib et al. investigated the synthesis of gold nanoparticles using Good's buffers and proposed that the nitrogen of the buffer played an important role in the reduction of AuCl_4^- [12]. Newman and Blanchard reported that various amines that have a reduction potential between AuCl_4^- and Au^0 are good reducing agent candidates for synthesizing gold nanoparticles [13]. Selvakannan et al. demonstrated that gold nanoparticles could be obtained from tryptophan reduction of AuCl_4^- and discussed the importance of the indole group of tryptophan in the reduction of AuCl_4^- [14]. The use of amino acids, peptides and proteins as reducing and capping agents for the synthesis of gold nanoparticles has attracted attention as a “green” and “biocompatible” approach because biomolecule-functionalized gold nanoparticles can be applied to biosensors and biomedical devices. Although there are also several reports of the synthesis of gold nanoparticles using amino acids, only a limited number of amino acids were examined [14–20].

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In the present study, we attempted to synthesize gold nanoparticles using 11 kinds of amino acids. The successfully synthesized gold nanoparticles were evaluated using UV–vis spectroscopy, dynamic light scattering and transmission electron microscopy.

2. Experimental section

2.1. Materials

Gold(III) chloride acid (HAuCl_4) was purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). Amino acids and other chemicals were from Wako Pure Chemical Industries (Osaka, Japan). The water used in all experiments was prepared using a Milli-Q® Integral water purification system (Millipore, Bedford, MA) and had a resistivity of 18.2 M Ω cm.

2.2. Synthesis of gold nanoparticles using amino acids

Typically, an aqueous solution of gold(III) chloride acid (1 mL, 1.0 mM) and an aqueous solution of an amino acid (His, 1 mL, 100 mM) were mixed and incubated at 80 °C for 20 min using an oil bath, followed by pH adjustment using 1 M NaOH or 1 M HCl to pH 7.1–7.8. Spectra of the prepared solutions were measured using a UV/vis spectrophotometer, V-630 (Jasco, Tokyo, Japan). DLS measurements were carried out using ELSZ-2 (Otsuka Electronics Co., Ltd., Osaka, Japan) equipped with a quartz cell (10 mm light path length), after removing Au^{3+} ions using a PD-10 column (GE-Healthcare, Little Chalfont, UK).

2.3. Transmission electron microscope (TEM) observation

A sample solution was applied to a PD-10 column to remove Au^{3+} ions and loaded on a 200-mesh copper grid coated with carbon. The sample was dried in vacuo overnight. A high resolution transmission electron microscope (JEM-2010, JEOL) was used for the observation of nanoparticles. The accelerating voltage was 200 kV.

2.4. Measurement of AuCl_4^- conversion

After removing Au^{3+} ions from gold colloidal solutions using a PD-10 column, the concentrations of the metal ions in the samples were measured using inductively-coupled plasma-optical emission spectrometry (ICP-OES, SPS-3100, SII Nano Technology Inc., Tokyo).

3. Results and discussion

Fig. 1 shows the photos of gold colloidal solutions prepared using various amino acids. Some of amino acids yielded colored solutions typical of a gold colloidal solution. For example, Asn produced a red¹ solution. Ala, Gly, His, Leu, Lys, Ser and Tyr gave purple solutions. However, some (Ala and Lys) also produced precipitates. Among the 20 amino acids, the use of Arg, Cys and Thr did not result in a gold colloidal solution. Although Met, Phe and Trp produced colloids, the products were easily precipitated.

Using His (50 mM, final concentration) as a reducing agent, the effect of AuCl_4^- concentration on the synthesis of gold nanoparticles was investigated (Fig. 2a). The absorbance around 550 nm derived from the surface plasmon resonance (SPR) of gold nanoparticles was observed above 0.75 mM AuCl_4^- . The absorbance increased with the increase of the AuCl_4^- concentration. The wavelength of the maximum absorption also increased with the increase of the

AuCl_4^- concentration, implying the diameter of the gold colloids or the aggregate size increased.

Fig. 2b shows the DLS measurements of gold colloidal solutions prepared using 0.38 mM, 0.5 mM and 0.75 mM AuCl_4^- , which revealed the synthesized colloids were less than 1 μm in diameter (nanoparticles). The lower the AuCl_4^- concentration was, the smaller the colloids were. Because His was considered to act as a reducing and capping agent, the high AuCl_4^- concentration would result in a shortage of His for capping the surface of the nanoparticles, leading to aggregation of the nanoparticles. Indeed, the addition of sodium dodecyl sulfate decreased the colloid size to several nm from tens of nm as observed in DLS measurements (Supplementary material, Fig. S1). This indicates the redispersible aggregates of the gold nanoparticles.

TEM observations also show that the nanoparticles of several nm in diameter were aggregated (Fig. 2c–e). The average diameters of the nanoparticles were 4.1 nm (C.V. 22%) for 0.38 mM AuCl_4^- , 4.8 nm (C.V. 20%) for 0.5 mM AuCl_4^- and 4.3 nm (C.V. 26%) for 0.75 mM AuCl_4^- with the His concentration of 50 mM. The AuCl_4^- concentration seemed not to affect both the diameter and the size-distribution of discrete nanoparticles. The aggregation sizes observed in TEM images were in good agreement with the results of DLS measurements.

To verify that the nanoparticles consisted of crystalline gold, high-resolution TEM was performed (Fig. 2f). The high-resolution TEM revealed lattice fringes with an interlayer spacing of 0.236 nm, which corresponds to the lattice spacing of the gold (111) planes [21].

We then investigated the effect of the His concentration on the synthesis of the gold nanoparticles (Fig. 3a). The AuCl_4^- concentration was set at 0.5 mM in the mixture. The absorbance around 550 nm increased with the increase of the His concentration up to 50 mM. Use of His at 100 mM resulted in reduced absorbance around 550 nm. The wavelength of maximum absorption decreased with increasing His concentration, also indicating the decrease of the diameter of the gold nanoparticles.

The DLS measurements also show how changes in the nanoparticle size are induced by the His concentration (Fig. 3b). The higher the His concentration used, the smaller the nanoparticle size (observed by DLS). Fig. 3c and d shows the TEM images of nanoparticles prepared at 25 and 100 mM His. The average diameters of the nanoparticles were 4.6 nm (C.V. 22%) for 25 mM His, 4.8 nm (C.V. 20%) for 50 mM His and 7.4 nm (C.V. 32%) for 100 mM His with the AuCl_4^- concentration of 0.5 mM. The diameter of discrete gold nanoparticles increased with the increase of the His concentration while there was little influence of the AuCl_4^- concentration on the diameter. This indicates that His acted as a reducing agent and affected the growth of the nanoparticles. Since His also acted as a capping reagent for the nanoparticles, the increase of the His concentration contributed to the reduction of the aggregate size, which was observed in the DLS measurements.

In the present study, amino and carboxy groups in amino acids are considered to play major roles in the reduction of AuCl_4^- and also in capping the nanoparticle surfaces [10,19]. During synthesis, the solution pH was expected to affect the yield and size of the gold nanoparticles. We then examined the effect of solution pH on the synthesis of gold nanoparticles. Because the pH of a mixture of AuCl_4^- and His solutions (0.5 mM AuCl_4^- and 50 mM His, final concentrations) was 7.3 without pH adjustment, 1 M NaOH or 1 M HCl was added to the mixture to achieve the desired pH. Fig. 4a shows the absorbance spectra of gold colloidal solutions prepared at various pHs. A typical SPR-derived absorbance was only observed for the gold colloidal solution prepared at pH 7.3. Fig. 4b shows the inverted glass vials of gold colloidal solutions. The preparations at pH 1.2 and 3.0 resulted in precipitates that were adsorbed on the glass and the resultant supernatants were transparent (no

¹ For interpretation of color in Figs. 1 and 4, the reader is referred to the web version of this article.

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