Shape-Controlled Synthesis of Gold Nanoparticles Under UV Irradiation in the Presence of Poly(Ethylene Glycol)

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Key Words: Gold nanoparticle, dendritic gold nanoparticle, triangular gold plate, photochemical reduction, poly(ethylene glycol), UV irradiation.

INTRODUCTION

Controlling the size and shape of nanocrystalline materials is a key issue in current nanoscience researches [1]. The unique size- and shape-dependent optical and magnetic properties of metal nanoparticles make the nanoparticles extremely attractive as novel building blocks for constructing a new generation of innovative materials and solid-state devices [2-5]. Many metals can now be processed into nanoparticles with extremely low polydispersity and with controlled composition and structure [6], and the nanoparticles sometimes can be produced at large quantities through solution-phase methods [7,8]. Recently, a great deal of efforts have been directed towards the synthesis of nanomaterials that have well-controlled their morphology [9-14]. However, the challenge of synthesizing the metal nanoparticles with novel structure and shape has been met with limited success.

Previous reports using dendrimer as a stabilizer have proved that the photochemical reduction is an effective method for the preparation of gold and silver colloids [15,16]. The currently issued result of Imae’s group demonstrated that the photo-irradiation yielded not only spherical but also polygonal silver nanoparticles in the presence of poly(amido amine) dendrons with an anthracenyl-focal point [17]. The transformation from gold nanoparticles to triangular and hexagonal microplates proceeded by the aid of poly(amido amine) dendrimer as a reducer as well as a stabilizer [18]. Kim et al. [14] succeeded in synthesizing gold nanorods with controlled aspect ratio by using photochemistry in the presence of silver ions.

Here we describe the synthesis of dendritic gold nanoparticles and triangular gold plates under UV irradiation in the presence of poly(ethylene glycol) (PEG). Moreover, we discuss the shape of the gold nanoparticles (dendritic, triangular or irregular) depending on the PEG concentration and the size of the dendritic gold nanoparticles being controllable by varying the duration of UV irradiation.

EXPERIMENTAL

HAuCl₄ and PEG (MW 200,000) were purchased from Aldrich Chemical Co. and Wako Chemical Co., respectively. For the synthesis of gold nanoparticles, a mixture of HAuCl₄ and PEG in water was UV light-irradiated for a certain duration with a low-pressure mercury lamp (HOYA-SCHOTT, EX250, wavelength 200-450 nm) in a dark box at an ambient temperature (~25 °C). After UV irradiation, the obtained gold nanoparticles were collected by centrifugation.

Transmission electron microscopic (TEM) images were taken on a Hitachi H-7000 equipped with a CCD camera, operating at an accelerating voltage of 100 kV. The specimens for TEM were prepared by dropping the sample dispersions onto the carbon-coated copper grids and air-drying them. Ultra violet-visible (UV-vis) absorption spectra were measured on a Shimadzu UV 2200 spectrometer with a 1 cm quartz cell.
icles, which were obtained after 20 min UV irradiation on the mixed aqueous solution of HAuCl$_4$ and PEG at 0.2 mM and 25 mM, respectively. TEM images reveal that triangular gold plates are produced under this condition. The triangle edges range in sizes of 1–1.8 μm. The electron diffraction pattern (Fig. 3(b), inset) from selected-area of a single gold triangle clearly indicates that the triangle is a single crystal. The hexagonal nature of the diffraction spots is a clear indication that the triangular gold prisms are highly {111}-oriented with the plate surface normal to the electron beam. The {111} spots could be indexed on the basis of the face-centered-cubic (f.c.c.) structure of gold. The inner spots with the weaker intensity (circled), the stronger spots (triangle) and the outer spots with a medium intensity (square) could be indexed to 1/3{422}, {220} and {311} Bragg reflections with lattice spacings of 2.50, 1.44 and 1.23 Å, respectively. The presence of the 1/3{422} reflections indicates that the surface of the gold triangles is flat at an atomic scale [23]. It should be pointed out that in the experiment, a few small spherical nanoparticles (around 7 nm) have also been obtained besides triangular gold plates, but it is easy to separate the nanoparticles from the plates by centrifugation.

On the condition where the concentration of PEG in water was increased to 150 mM but gold ions were kept at a concentration of

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**Fig. (1).** TEM images of gold nanoparticles at different magnifications. Particles were prepared from an aqueous solution of HAuCl$_4$ (0.2 mM) and PEG (40 mM) after 20 min UV irradiation. Inset in Fig. 1(b) is an electron diffraction pattern of the nanoparticles.

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**Fig. (3).** TEM images of triangular gold plates obtained after 20 min UV irradiation to an aqueous mixed solution of HAuCl$_4$ (0.2 mM) and PEG (25 mM). Inset in Fig. 3(b) is an electron diffraction pattern of a single triangular gold plate.

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**Fig. (2).** (a) UV-vis absorption spectra of an aqueous solution of HAuCl$_4$ (0.2 mM) and PEG (40 mM) after UV irradiation for different durations. TEM images of gold nanoparticles after 7 and 12 min UV irradiation are displayed in (b) and (c), respectively.
of obtaining dendritic (or hyperbranched) metal structures of controlled size. Just few papers have been reported on the synthesis of the controlled dendritic gold nanoparticles and on the development of such morphologies. Flat gold nanostructures prepared by the reduction of Langmuir monolayers of hydrophobized chloroaurate ions displayed “fractal dimensions” [28]. “Dendritic microstructures” were also fabricated by the reduction of HAuCl₄ in an aqueous solution of perfluorinated surfactant [29]. The dendritic structures spontaneously grew up with the surfactant concentration and the incubation time. “Spongy gold nanocrystals” were prepared on the basis of a modified-citrate reduction technique of gold salt [30]. The hyperbranched gold aggregates were formed on the process of the growth from nanoparticles to microplates in the presence of poly(ethylene amine) dendrimer [18]. The formation of dendritic aggregates is not only restricted to gold metal but also developed on PbS nanoparticles [31] and CoPt nanopolyods [32]. When Pb(NO₃)₂ was reacted with Na₂S in the presence of poly(amide amine) dendrimer as a stabilizer, PbS nanoparticles formed flocs and finally aggregated to large spherical assemblies. As a generalized insight from the available experimental reports including the present work, the mechanism for morphology variation of nanoparticles should be such that the imperfectly protected small nanoparticles are incited the aggregation by the medium of bare metal surfaces on nanospheres and aggregates grew up with dendritic texture. At the same time or after aggregation, the rearrangement of metal atoms at the binding sites gives rise to the morphology re-variation to larger particles like plates and so on. Therefore, the morphology variation occurs under the restrictive reducers and depends on the amount of stabilizer and the aging time. However, in spite of our assumption, the development of morphologies has remained elusive and additional investigation must be carried out.

CONCLUSIONS

Dendritic and irregularly-shaped gold nanoparticles and triangular plates have been synthesized via simple photochemical reduction in the presence of PEG. The shape of the obtained nanoparticles depends on the concentration of PEG in the aqueous reaction solution. On the other hand, the size of the dendritic gold particle is controllable by varying the duration of UV irradiation. The differently-contributing PEG at different concentrations on the assembling of gold in aqueous solutions may serve as a controller for the formation of shape-controlled gold nanoparticles.

ACKNOWLEDGMENTS

XL is thankful to the 21st century COE program (No. 14COE01-00) in Nagoya University for a financial support. This work was partly supported by a Grant-in-Aid for Scientific Research (B) (15350067) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

REFERENCES