

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

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Abstract: Dendritic gold nanoparticles and triangular gold plates were synthesized via a simple photochemical reduction protocol. The shape of nanoparticles depended on the concentration of poly(ethylene glycol), which was used on the preparation in an aqueous solution. On the other hand, the size of nanoparticles was controlled by the duration of UV irradiation. The mechanism of morphology variation was discussed.

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 optoelectronic 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 controllable 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 nanostructures 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-radiation 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 Adrich 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.

RESULTS AND DISCUSSION

When a mixed aqueous solution of HAuCl₄ (0.2 mM) and PEG (40 mM per repeating unit) was UV light-irradiated for 20 min, the solution colored from yellow to baby pink. Shown in Fig. (1) is the TEM images of the obtained nanoparticles at different magnifications. It can be seen that under this condition, the obtained gold nanoparticles are dendritic. The TEM image (Fig. 1(c)) of single nanoparticle clearly shows that the dendritic gold nanoparticle consists of many pods. The size of pods is 5 - 7 nm, while that of nanoparticles is 135 ± 15 nm. The electron diffraction pattern of the particles (Fig. 1(b), inset) demonstrates that the dendritic gold nanoparticles are in polycrystal state.

A UV-vis absorption spectroscopy was used to monitor the photoreduction process of HAuCl₄ in the solution. It has been known that the spectroscopic properties of metallic nanoparticles depend on the size and shape of the particles [19-21]. For example, a surface plasmon resonance band of gold nanospheres changes from 510 to 550 nm with increasing a particle size from 3.2 nm to 7.3 nm [20]. UV-vis spectra of dispersions in the present work were recorded as a function of UV irradiation duration, as shown in Fig. 2(a). The spectrum after 7 min UV irradiation displayed a broad surface plasmon band at about 580 nm with a full width at half-maximum (fwhm) of around 115 nm. The band then shifted to 600 nm involving an increase in fwhm with time, in addition to be intensified in intensity. These time-dependent features are characteristic in the formation of anisotropic particles, whose aspect ratio increases with time [22].

Both TEM images (Fig. 2(b) and 2(c)) from the solutions after 7 and 12 min UV irradiation, respectively, show the presence of a large number of dendritic gold nanoparticles. The size of the nanoparticles increases with the duration of UV irradiation. The sizes are 17.5 ± 7.5 nm and 40 ± 10 nm for 7 and 12 min UV irradiation, respectively. This implies that the size of the dendritic gold nanoparticles is controllable by varying the duration of UV irradiation. It should be noted that when the duration of UV irradiation is longer than 25 min, the dendritic particles are apt to aggregate and form bigger particles.

The effect of PEG concentration on the shape of gold nanoparticles was examined on aqueous solutions of different PEG concentrations. Shown in Fig. (3) are TEM images of the gold nanoparti-

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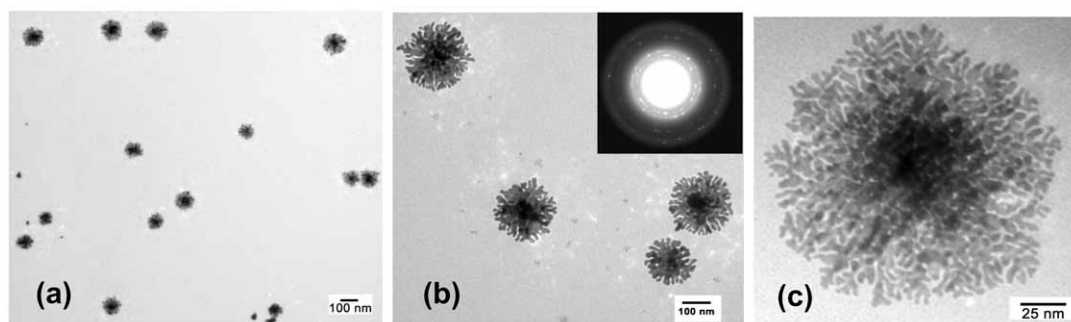


Fig. (1). TEM images of gold nanoparticles at different magnifications. Particles were prepared from an aqueous solution of HAuCl_4 (0.2 mM) and PEG (40 mM) after 20 min UV irradiation. Inset in Fig. 1(b) is an electron diffraction pattern of the nanoparticles.

cles, 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,

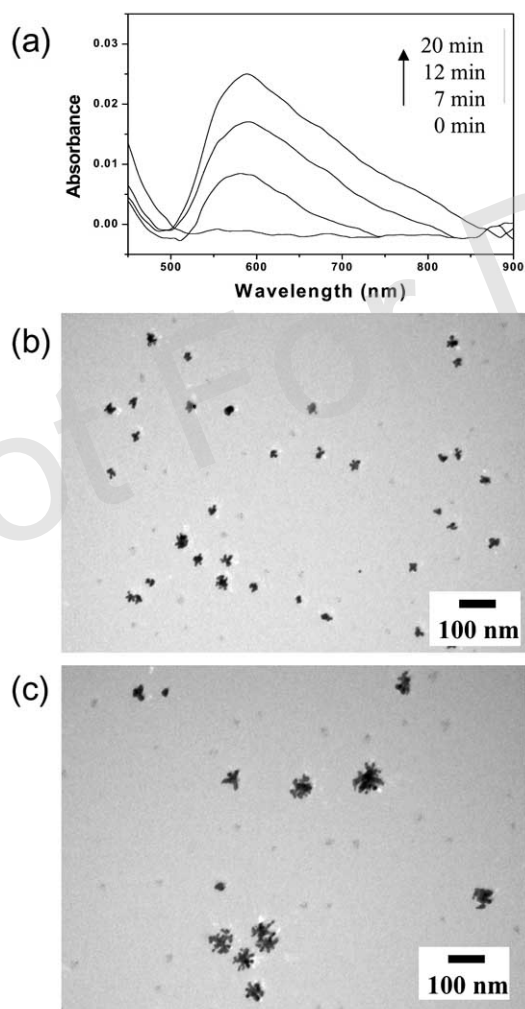


Fig. (2). (a) UV-vis absorption spectra of an aqueous solution of HAuCl_4 (0.2 mM) and PEG (40 mM) after UV irradiation for different durations. TEM images of gold nanoparticles after 7 and 12 min UV irradiation are displayed in (b) and (c), respectively.

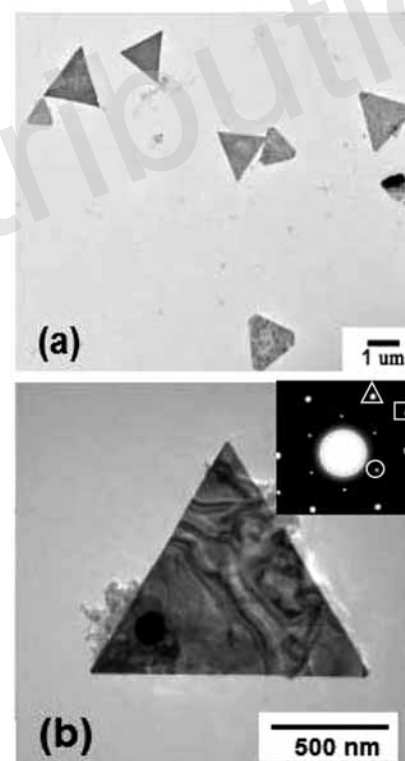


Fig. (3). TEM images of triangular gold plates obtained after 20 min UV irradiation to an aqueous mixed solution of HAuCl_4 (0.2 mM) and PEG (25 mM). Inset in Fig. 3(b) is an electron diffraction pattern of a single triangular gold plate.

1.44 and 1.23 \AA , 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

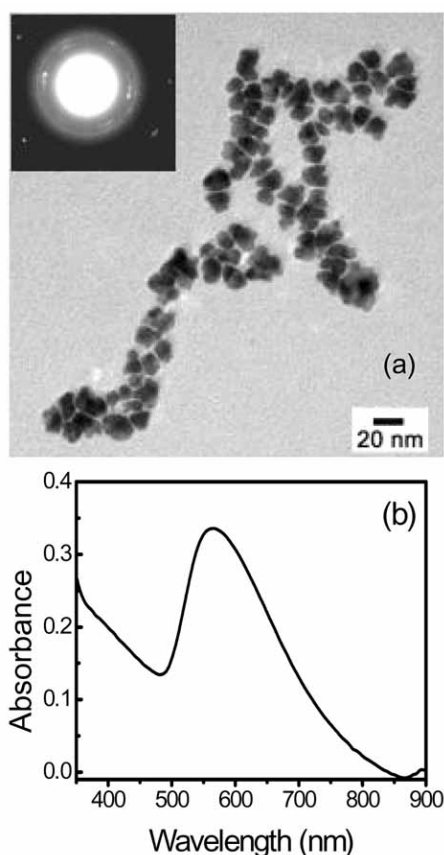


Fig. (4). A TEM image (a) and a UV-vis absorption spectrum (b) of nanoparticles obtained after 20 min UV irradiation to an aqueous mixed solution of HAuCl₄ (0.2 mM) and PEG (150 mM). Inset in Fig. 4(a) is an electron diffraction pattern of the nanoparticles.

0.2 mM, the shape of gold nanoparticles was different from those mentioned above. Fig. 4(a) is a TEM image of particles obtained from this aqueous solution after 20 min UV irradiation. It can be seen from a TEM photograph that only irregularly-shaped gold nanoparticles were obtained. The size of the particles was 17.5 ± 7.5 nm. An electron diffraction pattern of the particles (Fig. 4(a), inset) reveals that the particles are in polycrystal state. A UV-vis absorption spectrum (Fig. 4(b)) of this dispersion after 7 min UV irradiation indicates the appearance of a broad surface plasmon band at about 580 nm with a fwhm of around 180 nm, implying the aggregation of the obtained nanoparticles [24], which is in agreement with the result observed from TEM.

The role of PEG on the preparation of nanoparticles must be discussed now. There is a prospect for it. The kinetic results on the gold nanoparticle formation were explained under the assumption that Au(III) complexes bound to pseudocrown ether structures on the polymers are reduced by the polymers [25]. The involvement of oxyethylene groups in the polymers on the reduction of metal complexes was also supported [26], and the dominant contribution of poly(ethylene oxide) blocks in poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers and their high efficiency in comparison with poly(ethylene oxide) homopolymer systems were indicated [27]. Even in the present work, it is suggested that similar mechanism of the reduction by PEG is progressing. However, in spite of energetic investigation as described above, there was no previous investigation of the morphology variation of nanospheres prepared in the presence of PEG, except the demonstration in the present report.

The most emphatic result in the present work is the possibility

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(amido amine) dendrimer [18]. The formation of dendritic aggregates is not only restricted to gold metal but also developed on PbS nanoparticles [31] and CoPt nanopolypods [32]. When Pb(NO₃)₂ was reacted with Na₂S in the presence of poly(amido 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 nanospheres 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.

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