Ultrathin Gold Nanorods: Controlled Synthesis and Characterization
(極細金ナノロッドの構造制御と物性評価)

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1. Introduction

Gold nanostructures have attracted researchers in variety of fields owing to their unique physicochemical properties dependent on the sizes or shapes. In case of isotropic gold nanospheres (AuNSs), their structures and properties change drastically at a critical diameter of ~2 nm [1]. The atomic structures of AuNSs undergo a transition from face-centered-cubic (fcc) to icosahedral- or decahedral-based structures when the diameter becomes smaller than 2 nm. The optical response of AuNSs changes at this size region from collective oscillations of the free electrons (localized surface plasmon resonance: LSPR) at 520 nm to single electron transitions between quantized levels. Gold nanorods (AuNRs) with a diameter of several tens of nm and the aspect ratios in the range of <50 have been studied extensively as representative anisotropic Au nanostructures [2]. AuNRs exhibit two modes of LSPRs along longitudinal and transverse axes. The resonant wavelength of the longitudinal mode is widely tuned from visible to near IR region by changing the aspect ratio, while that of the transverse mode remains similar regardless of the aspect ratio. Although AuNRs are stable in ambient conditions, they can be transform into AuNSs upon heating or laser irradiations via melting spheroidization and fragmentation due to Rayleigh instability. These unique transformations are useful for photothermal therapy and one-dimensional assembly of AuNSs.

In 2007, synthesis of anisotropic Au nanostructures with diameters smaller than 2 nm and lengths of µm-scale (ultrathin Au nanowires: AuUNWs) was reported by several groups [3,4]. Fundamental questions arise as to how the structures, stabilities and physicochemical properties of AuUNWs and ultrathin Au nanorods (AuUNRs) are different from those of conventional AuNRs due to the reduction of the diameter below ~2 nm. In order to answer these questions, we must overcome technical challenges that include removal of impurities of AuNSs and control of the length while keeping the diameter constant. In my doctoral study, I successfully
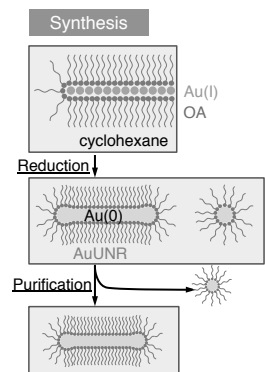

Figure 1. Synthesis scheme of AuUNRs

synthesized AuUNRs, a new class of anisotropic Au nanostructures, with systematically-controlled lengths and chemically modified surfaces. The fundamental aspects of AuUNRs including, atomic structures, morphological stability, and optical properties, were investigated.

2. Controlled synthesis

It was proposed that the AuUNWs are formed by reduction of Au(I) ions pre-aligned one-dimensionally via aurophilic interaction in a template made of oleylamine (OA) (Figure 1 [4]). According to this scheme, the length of AuUNRs will be affected by the length of the template. On the hypothesis that length of the template can be tuned by the concentration of OA, tetrachloroauric acid ($HAuCl_4 \cdot 4H_2O$) was mixed with different concentrations of OA. A weak reducing agent of triisopropylsilane was added to this mixture and the mixture was stirred for 30 h. The color of the solutions slowly changed to brown, suggesting that the reduction of Au(I) proceeded slowly. The condensed dispersions of AuUNRs obtained by solvent evaporation were diluted by hexane and stored under –20 °C overnight to remove AuNSs. Figure 2 shows typical transmission electron microscope (TEM) images of OA stabilized AuUNRs (AuUNR:OA) synthesized with the different concentration of OA. The images showed that the samples of AuUNRs are not contaminated by AuNSs and their morphologies are monodisperse. The lengths of AuUNRs increase from 5 to 370 nm with the increase in the concentration of OA, whereas the diameters are below 2 nm in all the samples. The surface modification methods of AuUNR:OA by thiolate were developed. Briefly, thiols solution with excess amount of OA such as glutathione (GS) in MeOH or dodecanthiol in

	Diameter	Length
a)	1.7 nm	370 nm
b)	1.6 nm	40 nm
c)	1.7 nm	24 nm
d)	1.6 nm	13 nm
e)	2.0 nm	5.2 nm

Figure 2. TEM images of AuUNRs synthesized in different concentration of OA. Scale: 20 nm

	Diameter	Length
a)	1.7 nm	5.2 nm
b)	2.1 nm	8.3 nm
c)	2.0 nm	15 nm
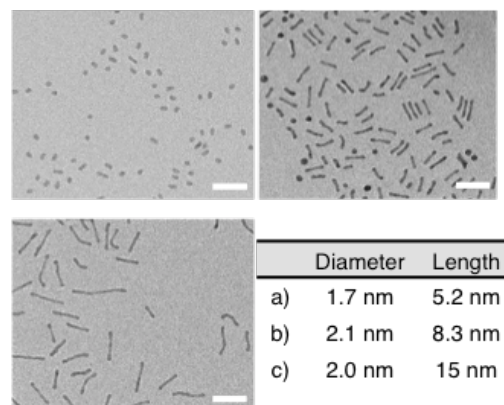
Figure 3. TEM images of AuUNR:SG ligand exchanged with different length of AuUNR:OA. Scale: 20 nm

$CHCl_3$ was added to dispersion of AuUNR:OA dispersed in $CHCl_3$ with excess amount of OA. The ligand exchange from OA to thiolates was confirmed by IR spectroscopy. The typical TEM images of SG-protected AuUNRs (AuUNR:SG) in Figure 3 indicate that using AuUNR:OA with different length as starting materials, AuUNRs are synthesized with lengths in the range 5–15 nm, while keeping their diameters of ~2 nm.

3. Atomic structures

The atomic structures of AuUNRs were examined using aberration-corrected high-resolution TEM (AC-HRTEM). AuUNRs with a diameter of ~1.8 nm and a length of ~18 nm were used for this purpose. HRTEM images of individual AuUNRs were composed of one or two different domains of crystal fringes. Intensive analysis of the images of ~500 AuUNRs revealed that the domains are categorized into six types as shown in Figure 4. The images of types I–III correspond to those projected from different directions of twin crystals grown along the [111] direction of the fcc structure. The
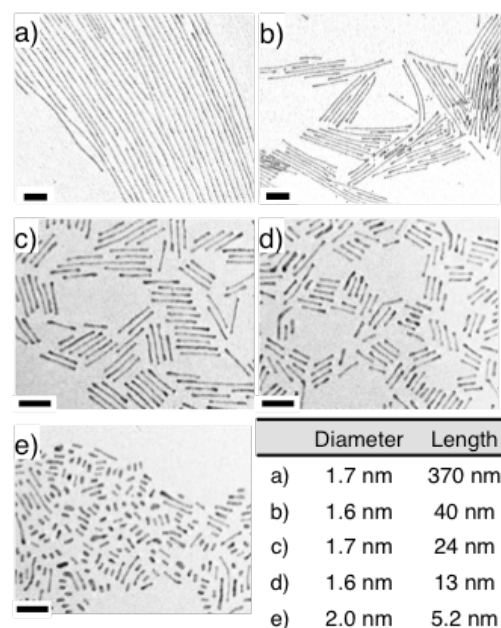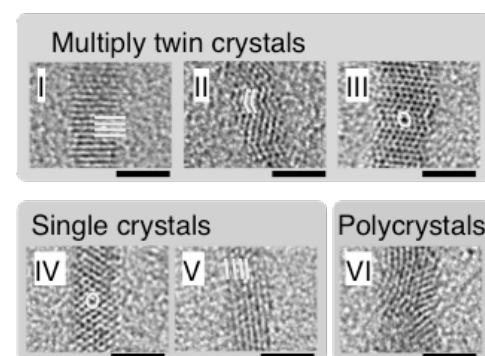

Figure 4. High-resolution TEM images of AuUNRs with different crystal domains.

images of types IV and V are assigned to fcc single crystals grown along the [110] direction. The image of type VI is obtained from polycrystalline. The area percentage of individual types, which is defined as the area occupied by domain type divided by the total area of crystalline domains, are analyzed using 500 rods. The area percentages of multiply twin crystals (types I–III), single crystals (types IV and V), and polycrystals (type VI) were 82, 7, and 11%, respectively. This statistical analysis leads us to conclude that the

Figure 5. An ideal model of AuUNRs –cuboctahedral Au_{147} oligomer–.

most abundant structure of the AuUNRs is multiply twined crystals. The sizes of fractions separated by twin boundaries were also analyzed statistically. The average diameter and length of a single domain separated by twin boundaries were determined to be 1.9 ± 0.3 and 1.4 ± 0.8 nm, respectively. One of the plausible candidates for a single domain is the cuboctahedral Au_{147} cluster. I propose that the AuUNRs consist of one-dimensional oligomers of cuboctahedral Au_{147} connected via twin boundaries (Figure 5). The crystal structures of AuUNR:GS were also examined using AC-HRTEM. Although the crystal structures were partly distorted due to the ligand exchanges, AuUNR:GS have the multiply twinned crystals as a dominant structures.
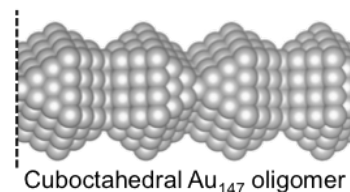
4. Optical properties

The AuUNWs and UNRs did not exhibit any distinct bands of transverse mode of LSPR at around ~520 nm, but intense bands in the IR region which are assigned to the longitudinal mode of LSPR. Polarized extinction spectroscopy for the aligned AuUNWs on a glass plate confirmed that the IR band is assigned to the longitudinal mode of LSPRs. The assignment was further confirmed by the length dependence of the resonance wavelength. Three samples of AuUNR:OA with the lengths of 5.2, 8.7 and 13 nm exhibited intense extinction band at ~1300, 1600, 2100 nm, respectively. The samples of AuUNR:SG also exhibit single band in NIR, although their intensities decrease due to the electron withdraw by thiolates. Figure 6d compares the correlation between aspect ratios and LSPR wavelengths between AuUNRs (AuUNR:OA: gray circle, and AuUNR:SG: black circles) and conventional AuNRs. The plots clearly indicate that the resonance wavelengths of both rods are redshifted with the increase of aspect ratios. However, the longitudinal modes of LSPR of AuUNRs are significantly redshifted with respect to those of the conventional AuNRs with the comparable aspect ratio. The redshift behavior could not be reproduced by the

Figure 6. Optical spectra of a) AuUNWs and UNRs with lengths of b) 5.2 and c)13 nm. Plot of LSPR wavelength as a function of aspect ratio.

classical electromagnetic simulations and TDDFT calculations on model structures of the AuNRs [5]. One possible scenario to explain the redshift is reduction of electron density due to the surface passivation by OA. However, X-ray photoelectron spectroscopy indicated that the AuUNRs are negatively charged probably due to, electron transfer from the amine group of OA and did not explain the redshift of the resonance wavelengths. Although the origin of the redshift is not clear at this moment, these findings demonstrate remarkable effect of the miniaturization of diameter below ~2 nm on optical response of AuUNRs.
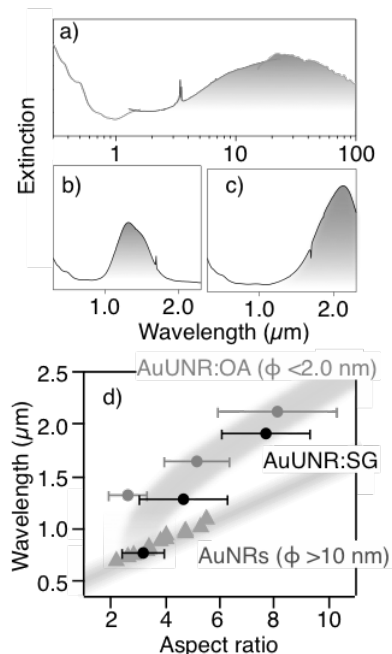
5. Morphological stability

The morphology of AuUNR:OA was retained when the solution contained an excess amount of OA. However, I found that AuUNR:OA was transformed into AuNSs in the absence of excess OA in dispersing

media or at elevated temperatures. Figure 7 shows the time course of the UV–vis–NIR spectra of AuUNR:OA (diameter 2 mm; length 5.8 nm) dispersed in toluene at 80 °C containing a small amount of OA (0.75 mg/mL). The SPR band originally observed at 1600 nm is gradually blue-shifted. The intensity of the SPR band decreases with time. The inset of Figure 7 shows TEM images of AuUNRs recorded after 0, 1800, and 3600 s. It appears that the initial AuUNRs became shorter with time. The results of time-resolved optical spectroscopy and TEM analysis indicated that the AuUNRs were gradually shortened by releasing AuNSs with the diameters of 2 nm. Since the

Figure 7. a) Time course of UV-vis-NIR extinction spectra during breakups.

diameters of the released AuNSs are comparable to that of the cuboctahedral Au_{147} clusters, it is proposed that the breakup occurs at the twin boundaries. The lifetime of AuUNRs, defined as the time at which the extinction at 1600 nm becomes half of the original value, was reduced dramatically by decreasing OA concentration. This behavior indicates that the OA surfactants play an essential role in stabilizing the morphology of AuUNRs by suppressing the diffusion of surface Au atoms. On the other hand, based on the time-resolved optical spectroscopy, AuUNR:SG retained their morphologies in pure $CHCl_3$. Therefore morphological stability of AuUNR:OA is remarkably enhanced by the thiolation due to the suppression of diffusion of Au atoms.
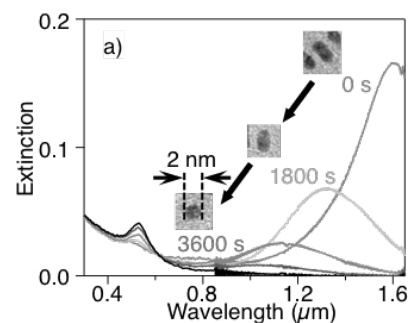
6. Conclusion

I developed a method of synthesizing purified AuUNRs with controlled lengths in the range of 5–370 nm and surface modifications by OA or thiolates. AuUNR:OA possesses unique multiple twin crystal structures with a periodicity of 1.4 nm. A model structure of the cuboctahedral Au_{147} connected via twin boundaries is proposed for AuUNRs. AuUNR:SG also exhibits similar multiple twin crystal structures. The wavelengths of LSPRs observed in AuUNRs are drastically red-shifted with respect to those of conventional AuNRs with the comparable aspect ratio. These results reveal that AuUNRs with the diameters in the range of <2 nm exhibit the unique properties which are different from that in the conventional thick AuNRs. AuUNRs break up into AuNSs at the twin boundaries. The OA surfactants play an important role in stabilizing the morphology of AuUNRs by the suppressing the diffusion of surface Au atoms. The stability of AuUNRs was further enhanced by the thiolation due to the formation of the strong chemical bonds with the surface Au UNRs.

References
[1] Negishi, Y. *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 1206. [2] Vigderman, L. *et al.*, *Adv. Mater.* **2012**, *24*, 4811. [3] Halder, A. *et al.*, *Adv. Mater.* **2007**, *19*, 1854. [4] Lu, X. *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 8900. [5] Sinha-Roy, R. *et al.*, *ACS Photonics* **2017**, *4*, 1484.