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Preparation and Characterization of Gold Nanoparticles with Reactive Thiocarbonyls: A Proposal for Active Size Control of Nanoparticles

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We have firstly prepared gold nanoparticles using methyl-substituted 1,3-oxathiole-2-thione as a stabilizing reagent by hydride reduction of tetrachloroaurate(III) ions. UV-vis absorption spectra and electron microscope observations show that the particle size can be controlled in a wide range from subnanometer to nanometer scale. Comparison of the results for these particles with those formed using methyl-substituted 1,2,4-trithiolane leads us to attribute the initial process of the formation of subnanometer-sized particles to the dimerization of 1,3-oxathiole-2-thione derivatives. In the reaction process, nascent particle surface is passivated with dimerization intermediates and the particle growth is terminated by sulfide formation.

Key words: gold nanoparticles, thiocarbonyls, dimerization, reaction control, size control

1. INTRODUCTION

Metal nanoparticles are of great interest because of their uniqueness in chemical and physical properties such as catalytic, optical, electronic and magnetic ones differing from their bulk metal [1,2]. As their properties are strongly dependent on their size either regularly or irregularly, the size control of nanoparticles is essential for research and development of them. Since the pioneer work on gold nanoparticles by Brust et al. [3], geometrical and electronic structure of thiol-protected gold nanoparticles have been studied as a function of their size through various approaches such as electron microscopy, X-ray diffraction, X-ray absorption spectroscopy, electron absorption and X-ray photoelectron spectroscopy [4,5]. The particle size has been passively controlled so far by the following procedure. In the procedure, nanoparticles are formed by reducing metal ions in the presence of thiol molecules. Then particle size depends on the ratio of thiol molecules to metal ions. Thus the particle size decreases with increasing the ratio because the nascent particles are rapidly covered and protected with the thiol molecules around them. In contrast, it increases with decreasing the ratio since the particles grow up until the thiol molecules are brought close together. The size control is passive because the reaction probability is dependent on statistical encounter limited by the initial ratio of [thiol]/[metal]. Recently, parameters such as reduction temperature and speed have been fine-tuned for the statistical encounter [6]. As another approach to this limitation, the use of the organic compounds with photo- or thermal reactivity may work for elaborate size controlling. When such a sulfur compound transforming into thiol or disulfide one is used for particle stabilization, one can control the size by regulating the reaction condition without changing the concentration ratio.

2. EXPERIMENTAL

2.1 Synthesis of 1,3-oxathiole-2-thione (OTT) and 1,2,4-trithiolane (TTL)

A solution of diazo carbonyl compound (3.00 mmol) in dry benzene (15 cm^3) was added over a period of 1.5 h to a refluxing suspension of rhodium(II) acetate (1.5 mg, 3.4×10^{-3} mmol) in carbon disulfide (25 cm^3) under nitrogen atmosphere. The solution was heated at 46 °C until no more diazo compound was detected by TLC. The resulting reaction mixture was concentrated under reduced pressure. The residue was separated by column chromatography (silica gel, eluted with ethyl acetate-hexane) to give 1,3-oxathiole-2-thione as pale yellow crystals and 1,2,4-trithiolane as colorless needles. For the following nanoparticle preparation, methyl-substituted 1,3-oxathiole-2-thione (MeOTT) is used as a reactive stabilizing reagent.

2.2 Preparation and Characterization of MeOTT-stabilized gold nanoparticles

Gold nanoparticles were prepared by a catalytic reduction process in organic and water two-phase system. A typical procedure at room temperature is given as follows. A toluene solution of tetraoctylammonium bromide (TOABr: 5 mmol dm^{-3}, 4 cm^3) was poured on an aqueous solution of hydrogen tetrachloroaurate(III) ($HAuCl_4$: 2 mmol dm^{-3}, 2 cm^3). After vigorous stirring, $AuCl_4^-$ was transferred as

$TOA^+AuCl_4^-$ into the organic phase from the aqueous phase. Then assigned quantity of MeOTT was dissolved in the organic phase followed by addition of a fresh aqueous solution of sodium borohydride ($NaBH_4$: 25 mmol dm^{-3}, 2 cm^3). With vigorous stirring, the color of the solution rapidly turned to reddish brown from yellow. After further stirring for 1 h, the organic phase was separated and concentrated. MeOTT-stabilized nanoparticles were precipitated from the concentrate by dilution with methanol and excess thiol and TOA-stabilized nanoparticles were removed. After centrifuging, the dark precipitate was washed with methanol, and dissolved in toluene (4 cm^3). The MeOTT-stablized nanoparticles prepared in this way were characterized by transmission electron microscopy (TEM), UV-vis and IR absorption spectroscopy. Observations by TEM were performed at an accelerating voltage of 300 kV. The diameters of about 300 particles were measured and the particle size distribution was obtained as histograms.

3. RESULTS AND DISCUSSION

Fig. 1 shows the UV-vis spectra of MeOTT-stabilized nanoparticles prepared with three different [MeOTT]/[$HAuCl_4$] ratios. Whereas the nanoparticles with the ratios of 1 and 10 exhibit a surface plasmon absorption at ~530 nm, the particles with the ratio of 100 have no such absorption. The absorption intensity decreases with decreasing particle size and the absorption band disappears at ~1 nm [7]. Thus a large excess of MeOTT forces the particles to be in subnanometer scale. In addition, as the ratio icreases, an absorption band in the UV region is shifted to longer wavelengths. Since MeOTT absorbs light at wavelengths shorter than 360 nm, this absorption is ascribed to inter-band transitions in metal core [8] and charge transfer absorptions from ligands to metal core [9].

Fig. 2 (a)–(c) shows typical TEM images and particle size distributions of the samples (a)–(c) in Fig. 1, respectively. The average diameters of the samples are determined to be (a) 3.5±0.8, (b) 3.1±0.8, and (c) 0.9±0.2 nm with standard deviation σ. Only the sample (c) is in subnanometer scale in contrast to the samples (a) and (b). This coincides with the observation of a surface plasmon absorption band [7]. The image contrast of sample (c) is worse than that in samples (a) and (b). This is because the nanoparticles could not be homogeneously dispersed on a TEM grid due to organic residues in the background. Before discussing the formation of the nanoparticles, we shall argue the dimerization mechanism of OTT.

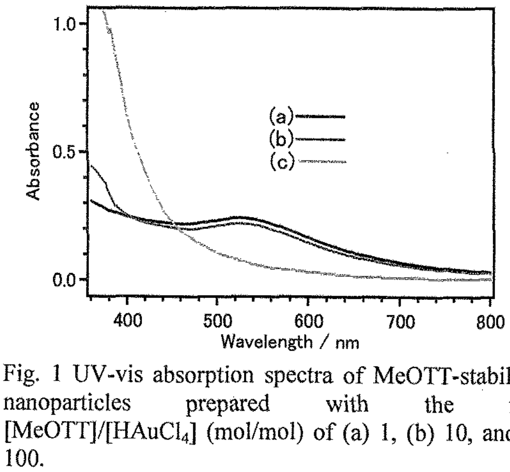


Fig. 1 UV-vis absorption spectra of MeOTT-stabilized nanoparticles prepared with the ratio [MeOTT]/[$HAuCl_4$] (mol/mol) of (a) 1, (b) 10, and (c) 100.

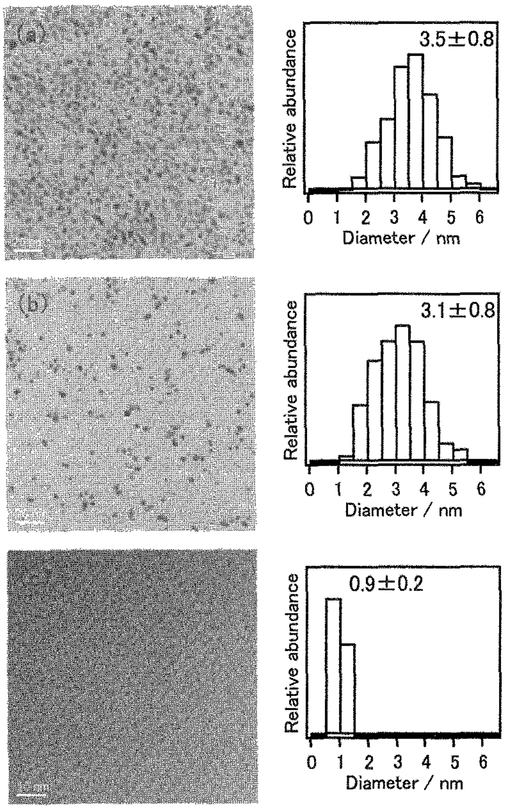
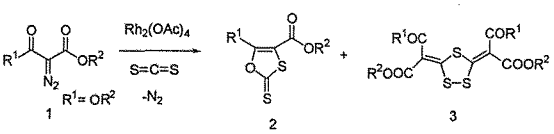
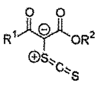


Fig. 2 Typical TEM images and size distributions of MeOTT-stabilized nanoparticles prepared with the ratio [MeOTT]/[$HAuCl_4$] (mol/mol) of (a) 1, (b) 10, and (c) 100.

We reported that the rhodium(II) acetate-catalyzed reaction of diazo malonic esters **1** with carbon disulfide gave 1,3-oxathiole-2-thiones (OTT) **2** and 1,2,4-trithiolanes (TTL) **3**, respectively [10].



The formation of 1,3-oxathiole **2** was explained by the 1,3-cyclization of thiocarbonyl intermediate **4** formed by the electrophilic attack of carbenoid on sulfur atom of carbon disulfide. The formation mechanism of 1,2,4-trithiolane **3** was not clear at that time. So, we examined the mechanism with trapping experiments of thioketene **5** and thiocarbonyl *S*-sulfide (thiosulfine) **6** [11].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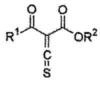
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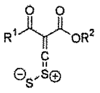
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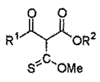
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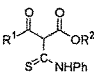
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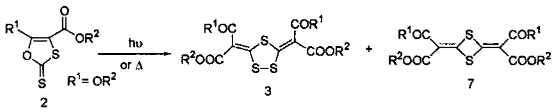
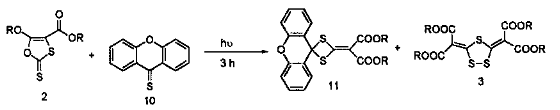
The photoreaction or thermal reaction in refluxing chlorobenzene of 1,3-oxathiole-2-thione **2** gave the 1,2,4-trithiolane **3** and 1,3-dithiane **7**.

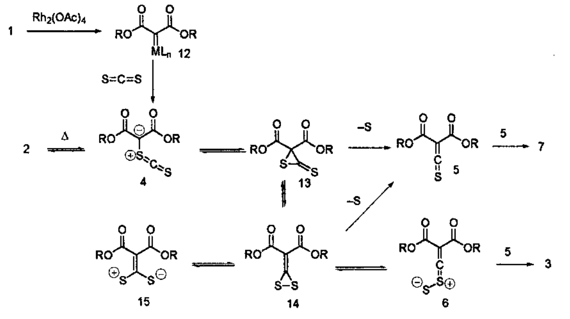


The photoreaction of 1,3-oxathiole-2-thione **2** in the presence of methanol or aniline afforded thioester **8** or amide **9** which was formed by trapping thioketene **5** with methanol or aniline. The thioketene **5** was also trapped by xanthene-9-thione **10** to give **11** without trapping thiocarbonyl *S*-sulfide **6**.



The trapping experiments of thiocarbonyl *S*-sulfide **6** with *N*-phenylmaleimide, dimethyl acetylenedicarboxylate, phenyl isocyanate, methyl isothiocyanate, and di(*t*-butyl)thioketene were failed.

A plausible mechanism for the formation of 1,2,4-trithiolane **3** and 1,3-dithiane **7** is shown below. Photolysis or thermolysis of 1,3-oxathiole-2-thione **2** generates thiocarbonyl ylide **4**, which is equilibrium with thiirane-2-thione **13**, 3-methylenedithiirane **14**, twitter ion **15** and thiocarbonyl *S*-sulfide **6** by ring-opening and ring closure. Desulfurization of **13** or **14** generates thioketene **5**, which dimerizes to give **7**. 1,3-Dipolar cycloaddition of **6** with **5** affords 1,2,4-trithiolane **3**.



The formation rate of 1,2,4-trithiolane **3** from 1,3-oxathiole-2-thione **2** was dependent on the substituent of 5-position of **2**. MeOTT under the thermal reaction conditions was not converted to the corresponding trithiolane **3**. Alkoxy group on **2** accelerates the ring-opening reaction to ylide **4** due to resonance effect of the electron-releasing substituent.

As shown in the previous section, OTT can dimerize into TTL through disulfide intermediates. However, MeOTT cannot dimerize at room temperature due to high activation energy. In addition, MeOTT scarcely has the ability to stabilize nanoparticles in a form of thiocarbonyl. And thus on the nanoparticle formation, dimerization of MeOTT and then bonding with disulfide group of MeTTL at the surface of particles is catalytically activated, which leads to rapid passivation of the particle surface and cessation of the particle growth. This can be the main reason why the subnanometer-sized particle formed at the higher [MeOTT]/[HAuCl$_4$] ratio. Indeed the reaction control of MeOTT dimerization has a potential for active size control of nanoparticles, but that depends on the reactivity. To examine the photochemical reactivity for MeOTT dimerization, absorption changes were observed as a function of irradiation time of high-pressure Hg lamp to a MeOTT solution. Fig. 3 shows such changes with a MeTTL spectrum. As the irradiation time proceeds, the absorption intensity of the peak at ~325 nm decreases and the other one at ~370 nm increases. Thus the MeOTT spectrum changes slowly into the MeTTL one. However, the photo-dimerization efficiency is only 10 % even for 5 h irradiation.

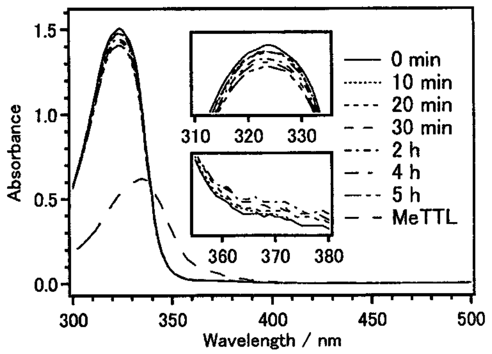


Fig. 3 Absorption changes of a MeOTT solution as a function of irradiation time of high-pressure Hg lamp.

To examine whether MeOTT-stabilized particles are surely formed with MeOTT changing into MeTTL, we have tried to generate nanoparticles by using MeTTL instead of MeOTT. The UV-vis absorption spectra of MeTTL-stabilized nanoparticles prepared with three different [MeTTL]/[HAuCl$_4$] ratios in Fig. 4. The (a)–(c) spectra are on the ratio conditions of 1, 2, and 10 respectively. The peak intensity of a plasmon absorption band decreases with increasing the ratio indicating size-controllable nanoparticle formation. In addition, the dependence of the peak intensity on the ratio is large in contrast to the dependence in Fig. 1. We note that direct evidence of dimerization on the particle formation is given in the following experiment: observation of smaller particle formation with higher energy such as higher temperature and longer irradiation given at a constant [MeOTT]/[HAuCl$_4$] ratio.

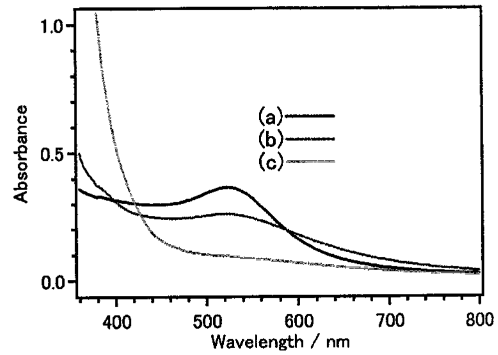


Fig. 4 UV-vis absorption spectra of MeTTL-stabilized nanoparticles prepared with the ratio [MeTTL]/[HAuCl$_4$] (mol/mol) of (a) 1, (b) 2, and (c) 10.

Elemental mapping of the particles by energy dispersive X-ray spectroscopy proves that the particles are coordinated with sulfur atoms around them. Hence the possibility of the coexistence of TOA-stabilized nanoparticles is excluded. We also observed infrared spectra of MeTTL and MeTTL-stabilized particles to investigate the binding form of sulfur atoms on the particle formation. However, the disappearance of the S–S stretching bands of MeTTL was not confirmed on the particle formation due to their weak absorbance. Since the polarization change for the stretching mode is expected to be observably large for Raman spectroscopy, the spectroscopy should prove that the particle formation involves S–S bond cleavage. At this stage, we can speculate the mechanism of nanoparticle formation by using MeOTT. First, MeOTT is photo- or thermochemically excited during the reduction of $AuCl_4^-$ with $NaBH_4$. Then the nascent gold nanoparticles catalyze the dimerization from MeOTT to MeTTL around them. Finally, disulfide intermediates from MeOTT bind to the surface of the particle through either sulfide of the cleaved disulfide residue.

In the future work, we are planning to control particle size more actively by regulating the dimerization reactivity of OTT: changing electron acceptance and donation, or size of the substituent of OTT, and parameters such as irradiation time and ambient temperature. In particular, esteric derivatives are key compounds for their high reactivity.

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