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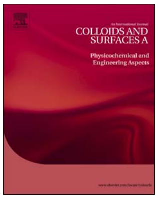

Preparation and length control of water-dispersible ultrathin gold and silver bimetallic nanowires

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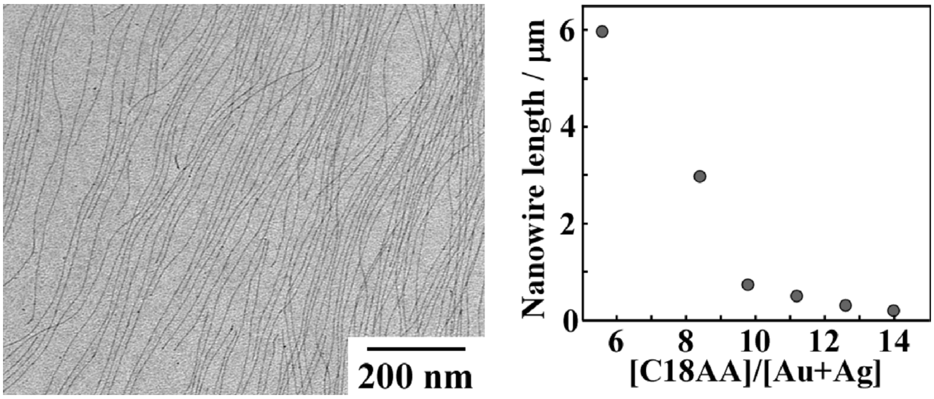
GRAPHICAL ABSTRACT



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ABSTRACT

Ultrathin nanowires are very attractive because they have unique catalytic and optical properties. Ultrathin nanowires are generally prepared in organic solvents; hence, the preparation of water-dispersible ultrathin nanowires is necessary in order to expand their areas of application. Furthermore, bimetallic nanocrystals are emerging as a new class of material. Herein, we report the preparation of water-dispersible Au–Ag bimetallic ultrathin nanowires by the orient-attachment method using a long-chain amine (C18AA) as the capping agent. These nanowires have an average diameter of 2 nm and lengths of a few micrometers; these lengths are controlled within the nanometer-to-micrometer range by adjusting the [C18AA]/[Au + Ag] molar ratio. In addition, these ultrathin nanowires exhibit a surface-plasmon band in the infrared region.

1. Introduction

Noble metal nanocrystals are very important for applications in fields such as electrochemistry, electronics, magnetic storage, catalysis, and biotechnology [1–10]. The properties of metal nanocrystals strongly depend on their morphologies, including size and shape [1–3]. Consequently, there are many reports on the fabrication of various shape-controlled metal nanocrystals such as cubes [11], plates [12], rods [13], and flowers [14–16]. In particular, the preparation and application of ultrathin (2-nm-diameter) Au nanowires (NWs) as catalysts,

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optical materials, and electronics are attractive [17–28]. The Xia [17], Yang [18], and Ravishankar [19] groups reported the preparation of ultrathin Au NWs by the soft-template and/or orient-attachment methods using oleylamine as the capping agent. The orient-attachment method involves the aggregation of single-crystalline nanoparticles (NPs) using oleylamine, which is selectively adsorbed on Au(100) and Au(110), and only weakly on Au(111) [19]. The Xing et al. improved the method of synthesis, and succeeded in preparing ultrathin Au NWs at room temperature over a few hours [20]. Recently, ultrathin Au NWs have been easily prepared using oleylamine as the capping agent, however, oleylamine-capped ultrathin Au NWs are only dispersible in organic solvents such as hexane.

The formation of water-dispersible ultrathin Au NWs is desirable both from a fundamental point of view and for practical applications by hybridization with hydrophilic functional molecules, especially biomolecules such as peptides or other biopolymers. Generally, a ligand-exchange method is used to change the dispersion solvent [29,30]; however, it is very difficult to change the dispersion solvent for ultrathin Au NWs by ligand exchange due to their fragility [21,22]. Previously, we reported the preparation of ultrathin Au NWs in toluene using a long-chain amine (C18AA, Fig. 1) as the capping agent, and water-dispersible ultrathin Au NWs were obtained by phase transfer of the NWs from toluene into water without ligand exchange [21–23].

Bimetallic nanocrystals, composed of two distinct metal elements, are emerging as new a class of materials [31–33], especially Au–Ag bimetallic nanocrystals that are expected to be applied as optical materials [34–39]. The surface-plasmon (SP) bands of Au–Ag spherical NPs are tunable in the 420–520 nm range by adjusting the Au/Ag molar ratio [34–36]. Moreover, Au–Ag bimetallic NPs exhibited high catalytic activities as alcohol oxidation catalysts compared to Au NPs [37–39]. Therefore, ultrathin Au–Ag bimetallic NWs are very interesting and are expected to be novel optical materials and nanocatalysts. The Li et al. [40] reported the preparation of ultrathin Au–Ag bimetallic NWs using the orient-attachment method in an organic solvent with octadecylamine as the capping agent; this amine-bearing capping agent is known to weakly adsorb on the (111) surface compared to the (100) and (110) surfaces of gold and silver, respectively [19,41,42]. However, to the best of our knowledge, there are no reports of the preparation of water-dispersible ultrathin Au–Ag bimetallic NWs.

This study reveals that water-dispersible ultrathin Au–Ag bimetallic NWs are prepared in aqueous solution by the orient-attachment method using a long-chain amine (C18AA, Fig. 1), which has selective adsorption properties, as a capping agent, for specific gold and silver surfaces. In addition, we show that the lengths of the ultrathin NWs can be controlled by the [C18AA]/[Au + Ag] molar ratio.

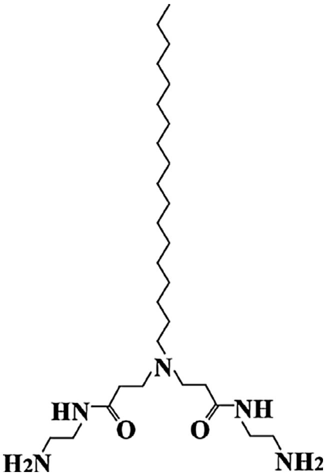

Fig. 1. Molecular structure of C18AA.

2. Materials and methods

2.1. Materials

Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was obtained from Nacalai Tesque. Silver nitrate ($AgNO_3$), ascorbic acid, and sodium borohydride were purchased from Kanto Chemicals. C18AA was synthesized using a previously reported method [21–23,33].

2.2. Preparation of ultrathin Au–Ag bimetallic NWs

Aqueous solutions of $HAuCl_4$ (24 mM, 150 µL, 3.6 nmol) and $AgNO_3$ (24 mM, 150 µL, 3.6 nmol) were added to a 2 wt% aqueous solution of C18AA (1 mL). In addition, 10 mM ascorbic acid (150 µL), as the reducing agent, was added to the mixture, after which it was left at room temperature for 1 d. The [C18AA]/[Au + Ag] molar ratio was 5.6.

2.3. Effect of reduction rate

2.3.1. Reaction temperature

Three mixtures were prepared as described in 2.2 (above). The mixtures were left to stand for 1 d at 50, 70, or 90 °C (instead of room temperature).

2.3.2. The use of $NaBH_4$

Three mixtures were prepared as described in 2.2 (above), with the exception that 10 mM aqueous $NaBH_4$ solutions (70, 150, and 720 µL) were used for the reduction step (instead of ascorbic acid).

2.4. Effect of the [C18AA]/[Au + Ag] molar ratio

Aqueous solutions of $HAuCl_4$ (8–24 mM, 150 µL) and $AgNO_3$ (8–24 mM, 150 µL) were added to 2 wt% aqueous solutions of C18AA (1 mL). Equimolar ratios of Ag to Au were used in these experiments. In addition, 10 mM ascorbic acid (150 µL), as the reducing agent, was added to each mixture, after which it was left at room temperature for 1 d.

2.5. Effect of the [C18AA] and [Au + Ag] molar concentrations

Aqueous solutions of $HAuCl_4$ (8 or 12 mM, 150 µL) and $AgNO_3$ (8 or 12 mM, 150 µL) were added to aqueous solutions of C18AA (4 or 8 wt%, 1 mL). In addition, 10 mM ascorbic acid (150 µL), as the reducing agent, was added to each mixture, after which it was left at room temperature for 1 d. The molar [Au]/[Ag] and [C18AA]/[Au + Ag] ratios were either 1 or 5.6.

2.6. Characterization

Transmission electron microscopy (TEM) was carried out using a JEOL JEM-1011 instrument operating at 100 kV. High-resolution TEM (HR-TEM) was performed using a JEOL 2100 instrument equipped with 200 kV energy-dispersive spectroscopy (EDS) capabilities. UV–vis spectra were acquired using a JASCO V-570 instrument.

3. Results and discussion

Aqueous solutions of $HAuCl_4$ and $AgNO_3$ were added to 2 wt% aqueous C18AA, and the Au and Ag ions were reduced by ascorbic acid. Fig. 2a displays a representative TEM image of the ultrathin NWs obtained using C18AA as the capping agent. The average diameter of the ultrathin NWs was 2.0 nm, while they were a few micrometers in length (Fig. 2a). TEM-EDS experiments reveal that the ultrathin NWs are composed of gold and silver (Fig. 2b). In addition, the Au/Ag molar ratio was determined to be 1.05, which is in good agreement with ratio used during preparation. The Cu peaks observed are from the TEM