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CHEMICAL PHYSICS LETTERS

Chemical Physics Letters 428 (2006) 93-97

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Local structural characterization of gold nanowires using extended X-ray absorption fine structure spectroscopy

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> Received 6 June 2006 Available online 23 June 2006

Abstract

Gold nanowires were prepared via seed-mediated growth process. Standard X-ray powder diffraction pattern of nanowires and foil are nearly identical. The intensities of the (220) and (111) diffraction peaks was higher than the conventional value, which implied that the nanowires were abundant in {110} facets. This is in accordance with electron diffraction analysis of mature nanowires, the wires grow along the [110] directions. X-ray absorption spectroscopy indicates that coordination number of gold nanowires was slightly smaller than that gold foil. Moreover, the Debye–Waller factor of the refinement result of gold nanowires implies that there were some structural defects.

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1. Introduction

Several characteristics of nano-materials depend on size and shape, including their catalytic, optical and physical characteristics [1-3]. Spherical particles can be prepared easily by wet chemical methods. Anisotropic metal nanoparticles have been prepared using electrochemical means [2], photochemical reduction in aqueous system [4], bubbling hydrogen with capping polymer [5], and the polyol process [6]. Au nanorods with a small aspect ratio are of particular interest because of their optical properties. They exhibit transverse and longitudinal plasmon bands in the visible region of the spectrum, making them applicable in sensing and imaging fields [7]. 1-D nanoparticles can be prepared using templates that constrain the direction of growth of the crystal. Various chemical methods have been actively investigated to process metal into 1-D nanostructures [8]. Gold nanorods have been synthesized by electrochemical reduction in the presence of cetyltrimethylammonium bro-

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mide (CTAB) [9], and by seed-mediated growth in a surfactant template [3].

More recently, the electrochemical method and seedmediated growth method have been used with CTAB as the soft template, demonstrating the fabrication of gold nanorods dispersed in aqueous solution. The growth mechanism of 1-D gold nanoparticles in the presence of CTAB has been extensively examined [10-15]. The direction of growth of gold nanorods has been confirmed by analyzing the electron diffraction pattern and transmission electron microscopy (TEM) images [10]. Busbee et al. investigated the pH conditions of ascorbic acid for synthesizing of gold nanorods [11]. The ascorbate monoanion over the acid or dianion increased the aspect ratio of the nanorods. Murphy et al. studied the concentration of silver ions, the $(Au^{3+})/$ (ascorbic acid) ratio, and the concentration of CTAB [12,13]. Branch Au nanoparticles, including tetra-pods, star-shaped nanoparticles and multi-pods, can be prepared at various (seed)/ (Au^{3+}) ratios. The surface structure of gold nanorods capped with cationic surfactants was investigated by IR. The results reveal the formation of a new bond, which shows the binding of the surfactant headgroups to the surface of nanorods [14]. Additionally, various surfactants such

as alkyltrimethylammonium bromides and cetylpyridinium chloride have been investigated and used for synthesizing gold nanorods [15]. The results demonstrate that the aspect ratio of the resulting gold nanorods increased with the length of the surfactant chain. The surfactant binds as a bilayer to the growing nanorods and promotes the elongation of the nanorods via a 'zipping' mechanism. Moreover, multifield ²H relaxation has been used to quantify the effect of solubilization of alkanes on the size and shape of the micelles in aqueous solutions of haxadecyltrimethylammonium bromide, C₁₆TAB [16]. Recently we had described a new approach, based on the seed-mediated method, which could extend the length of the resultant products using a simple procedure [17]. Since the local structures of nanomaterials are greatly important for future applications. Although TEM has been shown to be a powerful tool for the analysis of nanoparticles, it is limited to study the chemical bonds and structural characteristics of multicomponent materials. However, X-ray absorption spectroscopy (XAS) can provide information about the nanostructure (e.g. coordination number, interatomic distance, and oxidation state of absorption atoms). This structural information is averaged over all of the X-ray-excited atoms in the entire sample, but since a large percentage of the atoms in nanoparticles are at the interface. Extended X-ray absorption fine structure (EXAFS) was useful for identifying the random or preferred occupation of sites around specific atoms, many studies about nanostructural analysis have been reported using EXAFS [18-22]. Thus, the local structures of gold nanowires was demonstrated in present study.

2. Experimental

2.1. Materials

Hydrogen tetrachloraurate(III) hydrate, trisodium citrate dehydrate (99%), silver nitrate (99%), ascorbic acid (99%), cetyltrimethylammonium bromide (CTAB) (99%) were obtained from Across Organics and used without further purification. The water used throughout this work was reagent-grade water produced by a Milli-Q SP ultrapurewater purification system of Nihon Millipore Ltd., Tokyo.

2.2. Preparation of gold nanowires

In a typical synthesis, 300 mL of 0.025 mM HAuCl_4 aqueous solution was prepared, and then 9 g of solid CTAB was added to the gold salt solution. The solution was heated to 40 °C with stirring to dissolve the CTAB. The solution was used as a growth solution after it was cooled to room temperature. The growth solution was used within 1 min of its preparation. After 10 min, gold clusters formed in the solution. 3–4 nm gold seed particles were prepared, as already reported by other researchers, using the trisodium citrate capping method.³ 0.02 mL of gold seeds were placed in a beaker. 0.1, 1, 10 and 100 mL of freshly prepared ascorbic acid (10 mM) solutions were mixed with

0.2, 2, 20 and 200 mL of growth solutions, respectively. After ascorbic acid had been added, the growth solution became colorless as gold ions were reduced to gold atoms. These three colorless solutions were added to the gold seed solution one by one at 45 s intervals. The solutions turned from pink to violet within 10 min.

2.3. Characterization of gold nanowires

The surface morphology of the samples was examined by TEM (JEM-2000EX, 200 kV). The specimens were obtained by placing several drops of the colloidal solution onto a Formvar-covered copper grid and evaporating it in air at room temperature. Before the specimen was prepared, the colloidal solutions were sonicated for 1 min to improve the particle dispersion on the copper grid. A series of X-ray diffraction (XRD) patterns were recorded at room temperature using BL01C2 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan ($\lambda =$ 0.07749 nm). The flux of BL01C2 is ~10¹⁰ which is about four orders of magnitude than in-house X-ray sources. As a result, it is possible to perform XRD analysis even with very small amount of sample.

In the XAS measurement, the gold nanowires solution was centrifuged for 10 min at a speed of 4000 rpm. The upper part of the colorless solution was removed and the solid portion was collected. The nanowires powder was mounted in aluminum cells and pasted on a plastic tape. Au L₃-edge X-ray absorption spectra were recorded on the Wiggler-C beam line of the National Synchrotron Radiation Research Center, in Taiwan, which was designed for such experiments. The data were collected in transmission mode using gaseous nitrogen and argon-filled ionization chambers as detectors. Energy calibrations were undertaken using Au metal foils, designating the first inflection point as 11,918 eV. X-ray absorption spectra for Au metal foils were measured simultaneously in each measurement when the metal foils were positioned before the window of the third ion chamber to eliminate any energy shift problem. The EXAFS data analyses were carried out by the standard procedure [23]. The normalized k^3 -weighted EXAFS spectra, $k^3x(k)$, were Fourier transformed in the k range from 3.0 to 13 Å⁻¹ to show the contribution of each bond pair to the Fourier transform (FT) peak. The S_0^2 (amplitude reduction factor) was fixed at 0.8 for the Au atoms to determine the structural parameters of each bond pair. The structural parameters, such as the coordination number, the interatomic distance and the Debye–Waller, were adjustable parameters in the fitting of the EXAFS spectra.

3. Results and discussion

Nanowires with aspect ratios 40–70 were synthesized by our previous report [17]. However, synthesis of nanowires alone was not possible, and the fact that particles form in mixed shapes suggests that those gold seeds that can grow



Fig. 1. TEM micrographs of gold nanowires. (a) As-prepared nanowires and electron diffraction pattern (inset). (b) HRTEM image of nanowires.

preferentially along their longitudinal axes posses a unique crystal configuration to favor an axial growth. Fig. 1a shows a typical gold nanowires image. Electron diffraction (inset in Fig. 1a) from the single rod shows it to be along the [110] crystallographic zone axis. Electron diffraction analysis of mature nanowires showed superpositions of two specific pairs of crystallographic zones, either (112)and $\langle 100 \rangle$ or $\langle 110 \rangle$ and $\langle 111 \rangle$, which were consistent with a cyclic penta-twinned crystal with five {111} twin boundaries arranged. The nanowires have an idealized 3-D prismatic morphology with 10 {111} end faces and five $\{100\}$ or $\{110\}$ side faces, or both. This structure was similar to previous result about gold nanorods prepared by seed-mediated growth method in CTAB [10]. TEM image of a single gold nanowire at high resolution is shown in Fig. 1b. The HRTEM image reveals that these nanowires show single crystalline nature, as indicated evidently by atomic lattice fringes. Most interestingly, the image provide the direct evidence of twin defect structures on the (100) crystal face (arrowed in Fig. 1b). The atomic structural detail in Fig. 1b demonstrates that the defects are twin lamellae with the dimension of the lamellae of about 5 nm. This has important implications in the applications of nanowires in the molecular device technology. In the wet synthesis described here, all nanowires were observed to contain the twin defects.

The change of the internal crystal structure is seen in wide angle X-ray diffraction (XRD) studies. Fig. 2 shows representative XRD patterns of as-prepared gold nanowires and gold foil, respectively. The XRD patterns of the foil and nanowires were assigned to the (111), (200), (220), (311), and (222) reflections of the face-centered cubic structure of gold. The lattice constant calculated from this pattern was 4.081(3) Å, a value in agreement with the literature report (a = 4.079 Å, Joint Committee on Powder Diffraction Standards file No. 65-2870). Note that the standard XRD patterns of nanowires and foil are nearly identical. It is worthwhile to note that the ratio between the intensities of the (220) and (111) diffraction peaks was higher than the conventional value (0.16 versus 0.19), which implied that our nanowires were abundant in $\{110\}$ facets, and thus their $\{110\}$ planes tended to be preferentially oriented parallel to the substrate. Accompanying with the growth of gold, the {110} facets increased due to the growth preferentially along their longitudinal axes. This is in accordance with electron diffraction analysis of mature nanowires, the wires grow along the [110] directions.

To obtain better evidence of the structural parameters of gold nanowires, EXAFS was performed. The curve-fitting



Fig. 2. XRD patterns of as-prepared gold nanowires and gold foil.

result of gold nanowires at the Au L₃-edge is shown in Fig. 3a. Fig. 3b shows the Fourier-transformed EXAFS spectra at the Au L₃-edge of gold foil and gold nanowires. respectively. In the case of the gold nanowires and gold foil, the main peak is attributed to the Au–Au metal bond. Just like the corresponding foil case, the shape of main peak was consistence with gold foil, indicating that the local structure of as-prepared gold nanowire was similar to gold foil. Structural parameters (e.g., interatomic distance, coordination number, and Debye-Waller factor) for the gold foil and gold nanowires are obtained from EXAFS refinement (Table 1). This result suggests that the interatomic distance between the Aucore and the nearest neighboring Au atom is 2.86 Å which is consistent with the value for the bulk of gold (2.88 Å). The EXAFS data clearly confirms that gold nanowires prepared by our method are indeed of a face-centered cubic (fcc) phase of gold, it corresponds to that of observation in XRD. Coordination number of gold nanowires was slightly smaller than that gold foil, it was owing to the nano-materials nat-



Fig. 3. (a) Curve-fitting results of gold nanowires using FEFF7-calculated amplitude and phase shift. Solid and circle lines are observed and calculated data, respectively. (b) Fourier transformed EXAFS spectra at the Au L_3 -edge of gold foil and gold nanowires.

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Curve-fitting analyses of EXAFS data for gold foil and gold nanowires

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	Path	CN	<i>R</i> (Å)	σ^2 (Å ²)	$\Delta E (eV)$	
Foil	Au–Au	11.8(2)	2.88(2)	0.0065(7)	1.3(3)	
Nanowires	Au–Au	11.0(3)	2.86(4)	0.015(2)	2.1(6)	

ure. As size of materials reduced, increase of surface-to-volume ratio leads to the decrease of coordination number. It should be noted that the Debye-Waller factor of gold nanowire was significantly different from that of gold foil. In general, the Debye-Waller factor represent thermal disorder since every real system vibrates even at very low temperature due to the zero-point energy. The Debye-Waller factor is given by $\sigma^2 = \sigma^2_{vib} + \sigma^2_{stat}$, where σ_{vib} and σ_{stat} are the vibrational and static disorder [23]. Usually the absolute of Debye-Waller factor between the standard and unknown compounds is important. The refinement result shows that the Debye-Waller factor of gold nanowires was greatly larger than that of gold foil, which imply that there were some structural defects in local structure. The twin defects have been observed in the result of HRTEM, which was consisted to the result of EXAFS refinement. These structural defects were usually obtained in nano-materials since the 'bottom up' synthesis process. On the other hand, the surface nature of seed particles plays an important role in this synthesis process. Surface facet of seed particles determined the shape of resulting product, and zeta potential (surface charge) results in the aspect ratio of nanorods [24]. Besides the above-mentioned factors, several reaction parameters also determined the shape and aspect ratio of resulting product, including size of seed particles, reaction temperature, crystalline of seed particles, and concentration of seed solution. A number of synthesized factors have influence on the product, some structural defects were formed easily. Thus the structural parameters have been analyzed.

4. Conclusion

High aspect ratio of gold nanowires have been synthesized in our previous report. The TEM result reveals that these nanowires show the direct evidence of twin defect structures on the (100) crystal face. The atomic structural demonstrates that the defects are twin lamellae with the dimension of the lamellae. XRD result suggests that the ratio between the intensities of the (220) and (111) diffraction peaks was higher than the conventional value, indicating that nanowires were abundant in $\{110\}$ facets, the {110} facets increased due to the growth preferentially along their longitudinal axes. Structural parameters and gold nanowires are obtained and discussed from the EXAFS refinement. The Debye–Waller factor was involved with structural defects, the cause of these defect were also discussed. The ability to make and modify nanocrystals continues to improve, the creative uses of these materials are sure to increase.

Acknowledgement

This work was performed under contract No. NSC 94-2113-M-002-030 from the National Science Council of the Republic of China.

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