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Sub-Two Nanometer Single Crystal Au Nanowires

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ABSTRACT

Ultrathin single crystal Au nanowires with diameter of ∼1.6 nm and length of few micrometers were synthesized with high yield by simply mixing $HAuCl_4$ and oleylamine at room temperature. High resolution transmission electron microscopy studies revealed that all of these nanowires are single crystalline and grew along the [111] direction. The valency evolution of the gold species during the synthesis was studied by X-ray photoelectron spectroscopy, which showed a clear $Au^{3+} \rightarrow Au^{+} \rightarrow Au$ stepwise reduction at different reaction stages. Small angle X-ray scattering and small-angle X-ray diffraction suggest mesostructure formation upon $HAuCl_4$ and oleylamine mixing. The slow in situ reduction of this mesostructure leads to the formation of ultrathin nanowires in solution. This novel nanowire growth mechanism relies on cooperative interaction, organization, and reaction between inorganic precursor salts and oleylamine.

One-dimensional nanostructures have continuously drawn significant research attention in the past decade because of their unique electrical, optical, and magnetic properties as well as their potential applications in mesoscopic device research.[1,2] Various synthetic methods in gas phase and solution phase have been developed for the growth of semiconductor and metal nanowires.[3–10] Studies on these semiconductor and metal nanowires have led to a rich collection of novel optoelectronic properties and an impressive array of functional device platforms.[11–15] It is, however, interesting to note that for most of these early studies nanowires with relatively large diameters (typically above 5 nm) have been the common research subject. This partly reflects the fact that the synthesis of single crystal sub-5 nm nanowires has been challenging and examples of such in the literature have been quite rare.

Herein, we report a simple solution method for the production of high quality ultrathin Au nanowires with uniform diameter of approximately 1.6 nm and length up to ∼4 μm. The actual synthetic procedure is unusually simple, and only two chemicals ($HAuCl_4$ and oleylamine) were used throughout the entire synthetic process. The nanowire growth happened at room temperature. As evidenced by our experimental results, oleylamine here served as solvent, reducing agent, and surface capping agent. In a typical synthesis, 0.2 mmol of $HAuCl_4 \cdot 3H_2O$ (from Aldrich) and 20 mL of oleylamine (≥70%, technical grade from Aldrich) were mixed together by ultrasonication for 15 min. The resulting transparent yellowish red solution was aged at room temperature (20−25 °C) for 4 days. During this aging process, purple precipitation was formed and can be separated from the bulk solution by centrifugation at 3500 rpm for 20 min. This purple product requires thorough washing with mixed solvents (1:3) of toluene and ethanol for several times in order to remove the excess oleylamine. The surfaces of the as-made Au nanowires are capped by oleylamine; hence, the nanowires are hydrophobic and can be readily dispersed in solvents such as hexane or chloroform. More importantly, this synthetic protocol can be readily scaled up toward subgram quantity nanowire production.

The morphologies of the products were examined by transmission electron microscopy (TEM, FEI Tecnai G^2 S-Twin at an accelerating voltage of 200 kV and Hitachi H9500 at an accelerating voltage of 300 kV) at low and high magnification. As shown in Figure 1a−c, the product typically consists of uniform, continuous, and ultrathin nanowires although larger nanowires and nanoparticles were also observed. Such uniform ultrathin nanowires can have length up to 4 μm. The diameter of these nanowires is measured to be uniformly below 2 nm. The aspect ratio of

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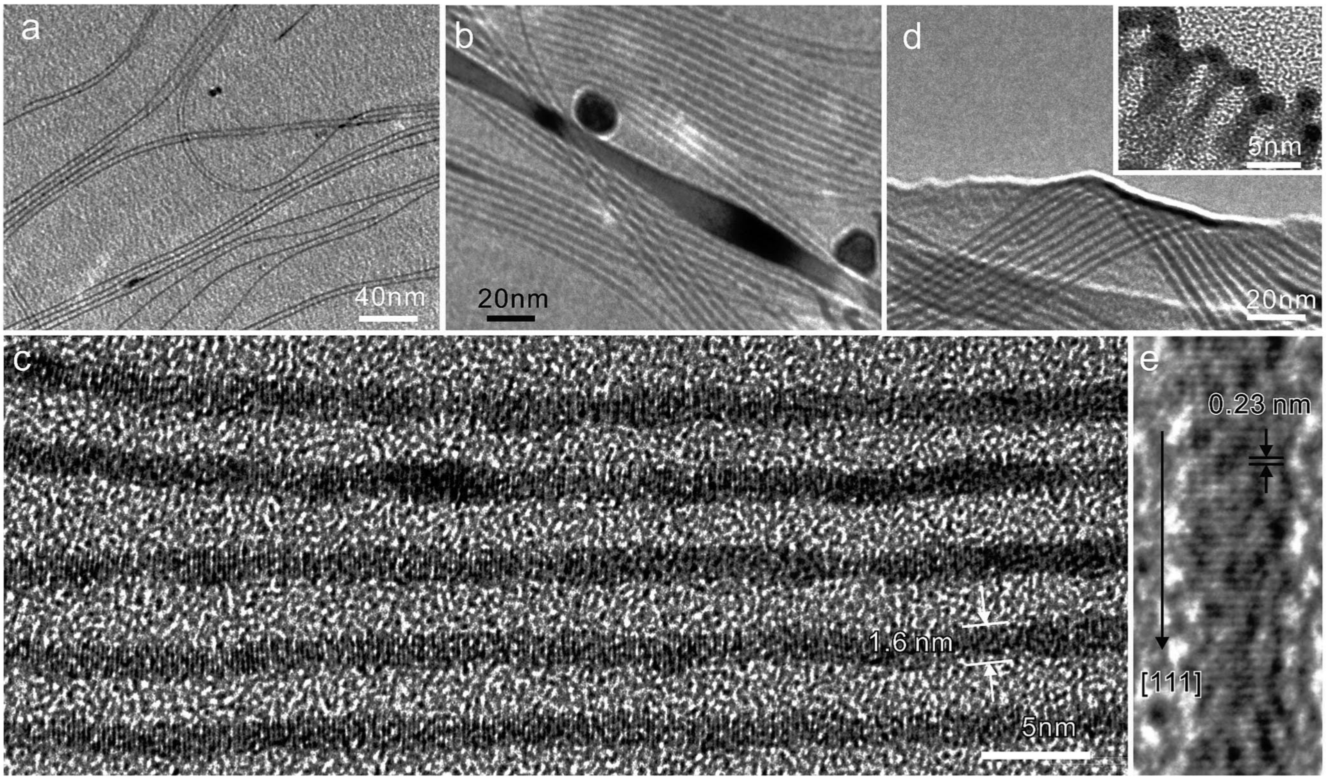

Figure 1. (a−d) TEM images of the ultrathin Au nanowires; (e) HRTEM image of an individual Au nanowire showing the (111) lattice planes.

these nanowires easily approaches 2000. A survey of several tens of nanowires in high magnification TEM image showed that the diameters of these nanowires are in the range of 1.5 to 1.8 nm, with an average of 1.6 nm. In addition, these nanowires are also frequently looped or bent on TEM grid (Figure 1d), a clear indication that these nanowires are highly flexible.

Despite the ultrathin nature of these Au nanowires, they are also single crystalline. High resolution transmission electron spectroscopy (HRTEM) results provided additional insight into the nanowire's crystallinity and their growth characteristics. Most of these nanowires grow along the [111] direction. Figure 1e shows a nanowire with lattice fringe of 0.23 nm corresponding to the 111 lattice spacing. To the best of our knowledge, this is the first time that single crystal Au nanowires with such thin diameters were synthesized with such a simple procedure, namely, by simply mixing the gold precursor with oleylamine at room temperature. We note that nanowires with similar dimension have been reported previously in one case;[10] however, an oriented-attachment mechanism was invoked, and the synthesis procedures were quite different by using oleic acid and ascorbic acid at relatively high temperature.

In order to find out the possible nanowire growth mechanism, X-ray photoelectron spectroscopy (XPS) was used to probe the valency evolution of the gold species at different reaction/reduction and growth stages. After adding $HAuCl_4•3H_2O$ to oleylamine, the reaction mixture was sampled at different time during the reaction and deposited on silicon wafer for the XPS measurement. The measured XPS spectra were fitted using XPSPEAK Ver. 4.1, as shown in Figure 2, and the relative ratio of different Au valance states (Au^{3+}, Au^{+}, and Au^{0}) were summarized in Table 1. After dissolving $HAuCl_4•3H_2O$ in oleylamine by ultrasonication for 15 min, the solution became yellowish red (Figure 2a inset). At this stage, Au^{3+} was found to be the dominant species (55.7%) while substantial amount of Au^{+} and Au^{0} (31.4 and 12.9%, respectively) were already present in the

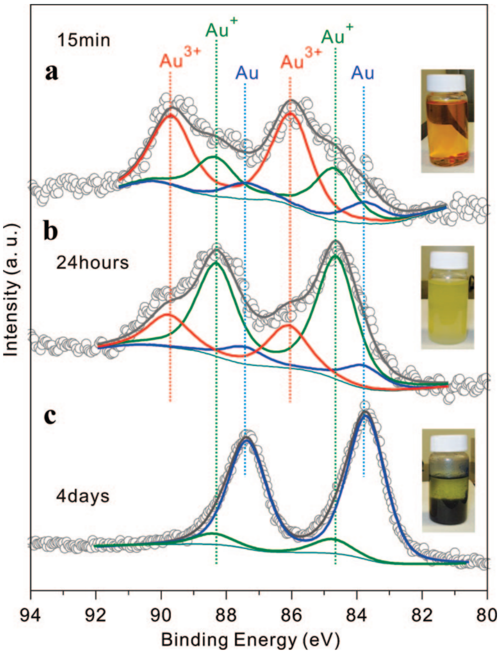

Figure 2. XPS spectra for Au species at different reaction times. Insets show the corresponding digital camera images of the resulting solutions, respectively.

Table 1. Evolution of the Au Species at Different Stages of the Reaction

	relative ratio of XPS Au 4f peak		
reaction time (h)	Au^{3+}	Au^{1+}	Au^{0}
0.25	55.7	31.4	12.9
24	22.9	65.0	12.1
96	0	9.1	90.9

reaction mixture. This suggests that, within the first hour of the reaction, the Au precursor was already partly reduced by amino group in the oleylamine. After 24 h of reaction, a whitish gel (Figure 2b inset) was formed within the reaction mixture and can be separated from the solution via centrifugation. XPS analysis indicates that the relative ratio of Au^{3+} decreased dramatically from 55.7 to 22.9% and Au^{+} became the dominant Au species (65.0%) in the reaction mixture, while the relative ratio of Au^{0} remains the same over this time. After 96 h, purple product precipitates out (Figure 2c inset). 90.9% Au^{0} and 9.1% of Au^{+} were observed in this reaction mixture and no Au^{3+} species was detected, a sign of complete reduction of Au^{3+} to Au^{0} and Au^{+}.

We hypothesized that the structure of the white Au^{+}−oleylamine gel might hold the clue for the nanowire growth mechanism. Small angle X-ray scattering (SAXS, Brüker Hi-Star, Cu K radiation) and small-angle X-ray Diffraction (SAXRD, Siemens D5000 powder diffractometer, Cu K radiation) were used to probe whether there is any mesoscopic ordering of the Au^{+}−oleylamine complexes within this white gel. Figure 3 shows the combined SAXS and SAXRD spectra recorded on the whitish Au−oleylamine gel. Interestingly, six diffraction peaks with *d*-spacings of 4.720, 2.336, 1.533, 1.176, 0.922, and 0.784 nm were recorded. These six peaks can be readily indexed as (00l) series for a mesostructure where Au^{+} assemblies were separated by 4.7 nm, roughly the width of an oleylamine bilayer. The SAXS spectrum shown in the inset displays a bright diffraction ring, again supporting the notion of high degree of ordering within this mesostructure. These small angle diffraction experiments unambiguously demonstrated that ordered mesostructures were formed in the synthetic process upon mixing Au precursor with oleylamine.

On the basis of our TEM, XPS, SAXS, and SAXRD results, a possible growth mechanism for these ultrathin Au nanowires can be proposed. We suggest that this process involves a cooperative assembly between the inorganic metal salt and the oleylamine synchronized with a stepwise reduction of gold precursor within the mixture (Figure 4). In the first step after the mixing the two chemical reagents, $HAuCl_4$ was partially reduced by oleylamine to AuCl (Au^{+}).[16,17] The newly formed Au^{+} species can then be complexed with oleylamine to form an ordered mesostructure that can be readily detected by our small angle diffraction experiments. Within this mesostructure, the charged Au^{+} assemblies are separated by an oleylamine bilayer. This assembly process bears some similarity with the mesoporous material synthesis.[18] It is noted that the formation of such complex between the Au^{+} species and the oleylamine is not uncommon. Because of the aurophilic interaction, similar ordered mesostructures have been reported previously in the literature.[19–21] In addition, the Au^{+}-amine mesostructure observed here is also similar to the surfactant induced mesoscopic assembly of inorganic molecular chains $[Mo_3Se_3^{-}]_\infty$ reported earlier from this laboratory.[22] This Au^{+}-amine mesostructure with long-range order can serve as a highly confined and high-aspect-ratio template for further in situ reduction of Au^{+}. As the last step, the Au^{+} species within the mesostructure can be slowly reduced to form Au nanowires with [111] growth direction,[23] a thermodynamically favorable growth direction. Because of high regularity and the confined space of the Au^{+}-amine mesostructure, the resulting nanowires are uniform and ultrathin. This new nanowire growth mechanism has two important features: (1) the formation of ordered mesostructure between the ionic inorganic precursor and the oleylamine and (2) the slow in situ reduction of metal ions within the mesostructure. As

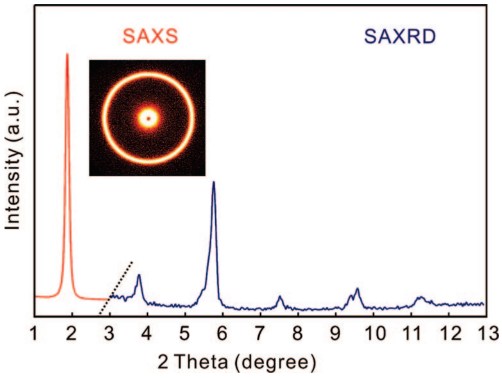

Figure 3. Combined SAXRD (blue) and SAXS spectra (red) recorded on the whitish Au^{+}−oleylamine gel. The inset shows the corresponding SAXS pattern.

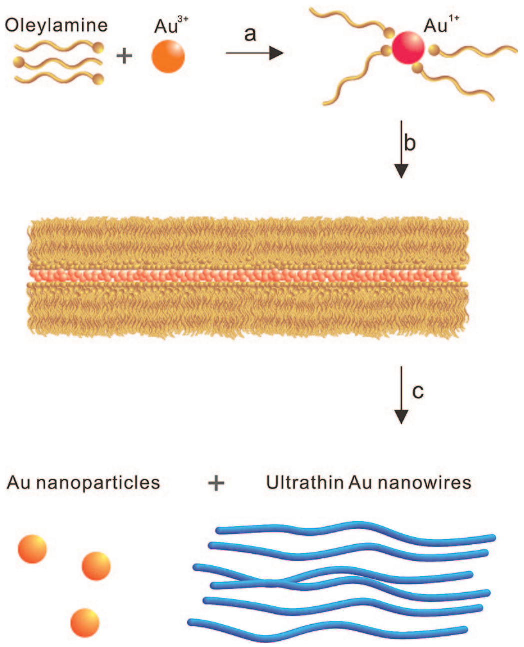

Figure 4. Schematic illustration of the ultrathin Au nanowire growth process. The cooperative interaction between the gold precursor and the oleylamine leads to a mesostructure formation followed by slow in situ reduction. It is believed that the mesostructures of the Au^{+}−oleylamine complex serve as growth template and govern the anisotropic growth in nanoscale.

many inorganic species can form complexes with oleylamine, this newly discovered nanowire growth strategy can be potentially applied to other systems to generate ultrathin metal (e.g., Pt, Ag, Pd) or even semiconductor nanowires.

In conclusion, ultrathin (1.5−1.8 nm) and high aspect ratio (up to 4 μm) gold nanowires were successfully synthesized by simply mixing a gold precursor with oleylamine. The cooperative interaction between the gold precursor and the oleylamine leads to a mesostructure formation followed by slow in situ reduction. It is believed that the mesostructures of the Au^+−oleylamine complex serve as growth template and govern the anisotropic growth in nanoscale. This simple synthetic strategy and underlying mechanism could be applicable for the synthesis of other metal and semiconductor nanowires with similar dimensions reported here. These ultrathin nanowires hold promises for novel physical properties and functional devices.

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