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Ultrathin Gold Nanowires Can Be Obtained by Reducing Polymeric Strands of Oleylamine–AuCl Complexes Formed via Auophilic Interaction

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One-dimensional (1-D) Au nanostructures, especially ultrathin nanowires (diameter <2 nm) with high aspect ratios, are of great interest because of their unusual transport properties¹ and promising applications in nanoscale electronics and sensors.² Current preparation methods for Au nanowires are mainly based on template-assisted synthesis,³ assembly of nanoparticles,⁴ or surfactant-mediated growth.⁵ Those synthetic approaches usually give Au nanowires with poorly defined morphologies, low yields, and large diameters or low aspect ratios. Here we report a facile method for preparing ultrathin Au nanowires using [(oleylamine)AuCl] complex chains formed through auophilic attraction. It has been established that auophilic bonding of organometallic complexes formed from Au^I halides and coordinating ligands (e.g., alkylcyanide,⁶ alkylphosphine,⁷ and alkylamine⁸) can lead to the formation of 1-D polymeric chains.⁹ Because of interactions such as van der Waals attraction between the side chains, the 1-D structure can form polymeric strands with backbones of Au^I ions surrounded by alkyl ligands. When the Au^I is converted to Au⁰ under slow reduction, the nucleation and growth of Au can be mediated by the 1-D polymer strands to generate ultrathin nanowires (Figure 1). On the basis of this concept, we have demonstrated, for the first time, that reduction of Au^I complex polymers using Ag nanoparticles can form ultrathin Au nanowires in high yields.

Figure 2A shows TEM image of Au nanowires obtained by mixing 20 mM AuCl and 0.4 M oleylamine in hexane and then reacting with 10-nm Ag nanoparticles (mole ratio of Au/Ag = 200:1). The product was primarily composed of ultrathin nanowires with an average diameter of 1.8 nm and an estimated yield of ~70%. The nanowires exhibited high aspect ratios with an average length of 2 μm (Figure S1 in Supporting Information). By-products in the form of nanoparticles and nanowires with diameter of ~10 nm were also present in the sample. No Ag was detected in the nanowires using energy dispersive X-ray spectroscopy (EDX) analysis, indicating that the nanowires were composed of pure Au. High-resolution TEM (Figure 2B) showed both single-crystal and polycrystalline nanowires. Most of the single-crystal nanowires were grown along the <111> direction. The polycrystallinity observed for some nanowires might be caused by melting under electron beam heating since it was usually found at the tips of the broken nanowires. The thin nanowires are highly susceptible to the TEM electron beam. A short exposure under TEM electron beam would lead to melting of the nanowires and change of lattice orientation (Figure S2). It was noticed that the thin nanowires on TEM grids usually form parallel bundles. The distance between adjacent wires was determined to be ~2 nm, close to the value calculated from the chain length of oleylamine (Figure 2C), implying that the nanowires are well-passivated by the alkyl chain.

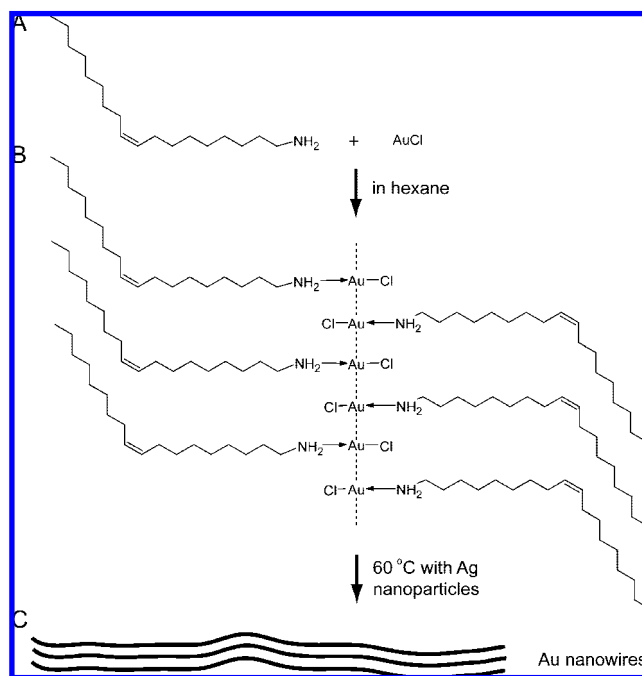


Figure 1. Schematic illustration for the formation of linear chains and then Au nanowires from oleylamine and AuCl in hexane.

Nanowires with similar morphology can also be obtained when the reaction was carried out without adding Ag nanoparticles (Figure 2D), albeit the yield (~20%) is much lower than the reactions with Ag nanoparticles. The role of Ag nanoparticles in promoting the formation of Au nanowires still remains elusive but can probably be attributed to the change of the rate for Au⁰ formation upon introduction of Ag nanoparticles. The decomposition of [(oleylamine)AuCl] complex is relatively slow. Adding Ag nanoparticles will speed up the reduction of Au^I to form Au⁰ at the beginning of the reaction. With the progress of reaction, however, the Ag ions formed through oxidation can also be reduced by oleylamine and cause competition between the reduction of Ag and Au ions. The change of reduction kinetics may alter the rate for the formation of Au⁰ toward favoring the growth of Au nanowires.¹⁰

To confirm the auophilic bonding-assisted growth mechanism of nanowires, we precipitated the polymer by adding acetone to the mixture of oleylamine and AuCl in hexane, followed by centrifugation. Both ¹H NMR (Figure S3) and mass spectra (Figure S4) confirmed the formation of polymer. The TEM image of the white solid collected upon precipitation showed formation of bundled strands (Figure 3A). The low contrast of the strands on the TEM image indicates that they are mainly composed of organic species. EDX analysis of the strands revealed that the compositions of the polymer were Au, 4.7%; Cl, 4.8%; N, 4.7%; and C, 85.8%,

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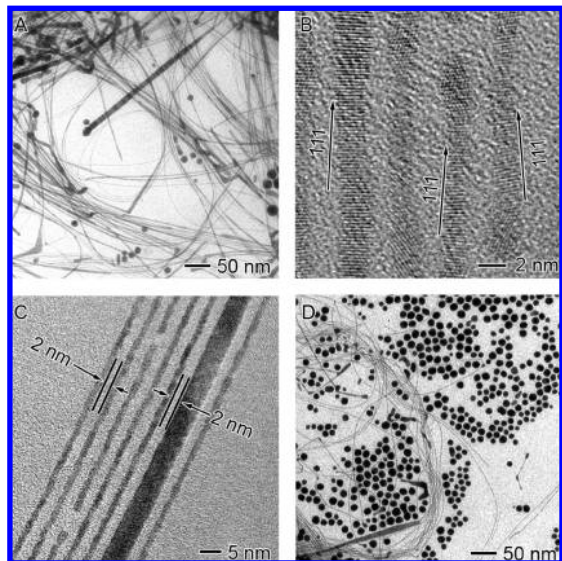


Figure 2. A) TEM image of Au nanowires with an average diameter of 1.8 nm obtained via reactions between [(oleylamine)AuCl] and 10-nm Ag nanoparticles in hexane for 24 h (AuCl to Ag molar ratio = 200:1). (B) High resolution TEM image showing $\langle 111 \rangle$ growth direction for most of the nanowires, although polycrystalline nanowires with twinned planes were also observed. EDX analysis reveals that the nanowires are composed of gold without any detectable silver. (C) A group of parallel nanowires separated by a distance of ~ 2 nm. (D) Au nanowires can also be prepared from oleylamine and AuCl without adding Ag nanoparticles, but with a lower yield. Most of the Au⁰ atoms crystallize into spherical nanoparticles.

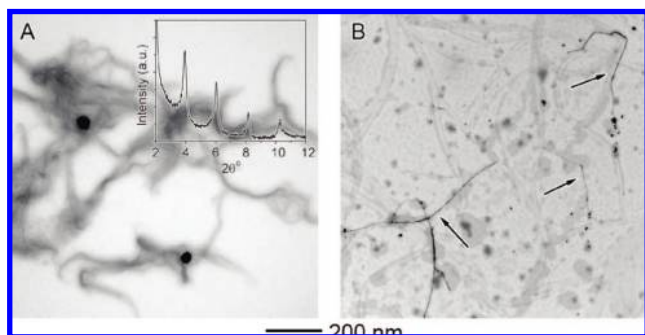


Figure 3. (A) TEM image and (inset) low-angle XRD for the polymer strands formed from oleylamine and AuCl complex in hexane. (B) After heating the polymer at 60 °C for 12 h, Au nanowires started to appear (indicated by arrows) among the polymer strands.

respectively, consistent with their molar ratio in [(oleylamine)AuCl]. Low-angle powder X-ray diffraction (XRD) pattern was also recorded from the precipitate (Figure 3A inset). The series of XRD peaks can be assigned to “ $0k0$ ” ($k = 1, 2, 3, 4, \dots$) with a layer spacing of 4.4 nm. It has been shown that the layer spacing for the supramolecular structures formed through aurophilic bonding is mainly determined by the length of the alkyl chain. The layer spacing of 4.4 nm for poly[(oleylamine)AuCl] is consistent with the data reported for a similar structure.⁶ When the polymer strands were redispersed in hexane and heated up to 60 °C with Ag nanoparticles for 12 h, nanowires started to form among the polymer strands (Figure 3B), clearly indicating that the nanowires were evolved from the [(oleylamine)AuCl] polymer strands.

The selection of solvent was critical to the formation of Au nanowires. When chloroform was used to substitute hexane as the

solvent for the reaction at 60 °C, only particles with sizes of ~ 15 nm were formed with or without the addition of Ag nanoparticles.¹¹ This might be due to the different configuration of the polymer in the solvents. At room temperature, the polymer can be well-dissolved in chloroform, while a viscous gel-like dispersion is obtained in hexane. In addition, it has been reported that aurophilic bonding of the polymer can be broken in some solvents to give oligomers.¹² The different solubility and conformation of the polymer in different solvents determined the formation of either nanowires or nanoparticles.

Although the ultrathin Au nanowires melt under a TEM beam, they are highly stable under ambient environment. Dried Au nanowires or dispersions of nanowires in solvents exhibited long-term (>6 months) stability with no notable morphological change. In addition, considering that other noble metals, such as Pt,¹³ can also form similar 1-D supramolecular chain structures when complexed with appropriate coordinating ligands, the approach reported here should be extendible to other metals. The ultrathin nanowires obtained in this work hold great potential for both fundamental study of their quantum properties and applications including sensors and nanoconnectors in electronic devices.¹⁴

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Supporting Information Available: Experimental procedure; TEM images of nanowires with extended length; TEM images of broken Au nanowires; NMR and mass spectrum of the polymer formed from oleylamine and AuCl. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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