Ultrathin Gold Nanowires Can Be Obtained by Reducing Polymeric Strands of Oleylamine–AuCl Complexes Formed via Aurophilic 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 properties and promising applications in nanoscale electronics and sensors. Current preparation methods for Au nanowires are mainly based on template-assisted synthesis, assembly of nanoparticles, or surfactant-mediated growth. 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 aurophilic attraction. It has been established that aurophilic bonding of organometallic complexes formed from Au halides and coordinating ligands (e.g., alkylcyanide, alkylphosphine, and alkylamine) can lead to the formation of 1-D polymeric chains. 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 ions surrounded by alkyl ligands. When the Au complex 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 ultrathin Au nanowires 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 reactivity 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.

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 Au0 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.

To confirm the aurophilic 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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solvent for the reaction at 60 °C, only particles with sizes of ∼15 nm were formed with or without the addition of Ag nanoparticles. 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. 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, 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.

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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.

References

14. After submission of our manuscript, we became aware of that Prof. Peidong Yang’s group had also independently developed a similar synthesis. See: Huo, Z.; Tsung, C.; Zhang, X.; Yang, P. Nano Lett. 2008, 8, DOI 10.1021/nl0813549.