Ultrathin and stable AgAu alloy nanowires

Jianbo Wu¹, Yung-Tin Pan¹, Dong Su² and Hong Yang^{1*}

Stable sub-two nanometer AgAu nanowires were synthesized using a CO-mediated gas reducing agent in liquid solution (GRAILS) method. These AgAu nanowires are stable, and do not readily break into short nanorods upon heating or electron beam irradiation. The surfaces along the longitudinal direction of the AgAu nanowires were largely bounded by the stable {111} facets. This structure differs from those ultrathin Au nanowires made without the use of CO gas, which were bounded by the {100} facets and unstable under e-beam irradiation. These differences in structure and composition lead to enhanced stability.

One-dimensional metal nanostructures have interesting optical, electronic, catalytic, and transport properties [1–8]. Among the different metals, Au and Ag nanowires and nanorods show strong absorption in the range from visible to near infra-red (NIR) region. They also possess excellent thermal and electrical conductivity, which are useful in a variety of applications, such as interconnects in electronic system [9,10], optical devices [11,12], spectroscopic enhancers [13–15], and electrochemical [16–19] and biological sensors [20]. For instance, electronics in an integrated circuit need to work properly above 100°C, thus the suitable metal nanowires have to be electrically highly conductive and thermally stable. For this purpose, Au nanowires are used despite the high cost. Ag has been considered as an alternative due to its relative cheaper price and high electrical ($6.3 \times 10^7 \text{ S m}^{-1}$) and thermal ($429 \text{ W m}^{-1} \text{ K}^{-1}$) conductivity [21]. In recent years, a large amount of flexible transparent conductive film was made based on Ag nanowires [22]. Thin wires are desirable in terms of ductile property. In addition, Ag and Au nanomaterials also attract much attention for their applications in photo-thermal cancer therapy and near infrared light, which offers deeper penetration than the visible light [23]. The unique localized surface plasmon resonance (LSPR) produced by Ag and Au nanostructures, especially Ag, is strong and thus also of great importance for bio-imaging [24–26]. However, Ag is prompt to be oxidized by oxygen in air or other oxidant, thus Ag-Au alloy, which is more stable than either pure Au or Ag [27], should have the ad-

vantages in this regard. The synthesis of AgAu nanowires, however, has been unsuccessful, especially when the diameter approaches 2 nm, at which point metal nanowires become very ductile [28].

One-dimensional metal nanomaterials are typically made using surfactant-mediated growth method [29], although template approach and oriented attachment are also used [30,31]. These methods often yield metal nanorods with diameter larger than 5 nm. A liquid crystal mesophase-assisted approach was developed recently for producing ultrathin Au nanowires (<2–3 nm) [32–35]. These ultrathin Au nanowires, however, were not stable and readily broken into short nanorods even under moderate electron beam (e-beam) irradiation, making them practically impossible to be utilized otherwise intriguing plasmon properties from the longitudinal component of these metal nanowires [36,37]. Metal nanostructures are known to have different thermal properties from their bulk counterparts due to surface energy difference [38]. The size-dependent thermal stability of Au nanoparticles including rods has been studied experimentally using ultrafast lasers [39–42], and by theoretical modeling [43–45]. In the case of ultrafine Au₃₈ nanoparticles, the melting point lowers to 180°C [46,47]. Nanowires however can undergo various structural changes at temperatures lower than the estimated melting points for spherical nanoparticles due to the Rayleigh instability [48]. In this case, the driving force for the structural change is the chemical potential gradient (capillarity or surface tension) induced by a perturbation in the radial direction of the nanowires [48].

Recently, thin Au nanowires were made by using carbon monoxide at a low flow rate [49]. Unlike the Au nanowires made by using mesophase-template alone, these Au nanowires seem to be stable under e-beam irradiation and no short rods were shown in the TEM micrograph. This result suggests that structural stability of nanowires could be closely related to the surface tensions of the nanowires, and both facet and surface capping ligands may be important. Herein, we report the synthesis of high aspect ratio AgAu

¹ Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

² Brookhaven National Laboratory, Center for Functional Nanomaterials, Upton, NY 11973-5000, USA

* Corresponding author (email: hy66@illinois.edu)

nanowires with an average diameter of ~ 2 nm via a low temperature solution phase synthesis assisted by CO gas and present a study on the stability of these alloy nanowires under e-beam irradiation and at elevated temperatures.

Fig. 1a shows representative transmission electron microscopy (TEM) micrographs of AgAu nanowires obtained from a mixture of 0.05 mmol of HAuCl_4 and 0.05 mmol of silver trifluoroacetate (AgTFA) in 5 mL of oleylamine (OAm) and 5 mL of oleic acid (OAc). The reaction took place at 60°C for 1 h using the CO-assisted gas reducing agent in liquid solution (GRAILS) method [50]. The population of nanowires was about 90% and had a high aspect ratio of ~ 100 , with an average diameter of 2.1 ± 0.3 nm and length of 200 nm (Fig. 1a inset and Fig. S1). Nanoparticles with diameter of ~ 6 nm made up the rest. High CO flow rate (190 sccm) and elevated temperature (60°C) are required to produce AgAu nanowires. Only Au nanowires were obtained either at a lower CO flow rate or a temperature less than 45°C .

The sides of these nanowires are largely enclosed by the $\{111\}$ surfaces, as shown in Fig. 1b. The d -spacing of these planes is 0.23 nm, which indicates that the sides of nanowires are not enclosed by $\{100\}$ surfaces, nor are the single

crystalline nanowires that grow along the $\langle 100 \rangle$ direction and are bounded with $\{100\}$ and $\{110\}$ facets on the side, as in the cases of previous reports [51]. The tips of AgAu nanowires could have the twinned structures bounded by the $\{111\}$ surfaces (Fig. S2) [52]. Formation of the $\{111\}$ surface-enclosed nanowires could be ascribed to facet-dependent preferential adsorption of CO gas on metal surfaces [16,50,53,54]. In the absence of CO, Au nanowires grew along $\langle 111 \rangle$ direction, rather than bounded by $\{111\}$ surfaces [32,33]. Fig. 1c shows a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the nanowire, and Fig. 1d is the corresponding line scan profiles of Au and Ag elements across a nanowire based on the energy-dispersive X-ray (EDX) analysis. The EDX linear scan shows that both Au and Ag elements are fairly evenly distributed across the nanowire (Fig. 1d). The shapes of EDX line scans for the two elements are similar and have a peak in the central region, indicating the one-dimensional structure is wire, not ribbon. EDX analysis further shows that the atomic ratio between Au and Ag is about 1:1, close to the feeding ratio between the two metals in the precursors (Fig. S3).

OAm and OAc were needed to form a liquid crystal

Figure 1 (a) Low and (b) high magnification TEM micrographs, (c) HAADF-STEM image, and (d) corresponding EDX line scans of Au (gold line) and Ag elements (green line) of AgAu nanowires. The size distribution is shown as the inset in (a).

phase and to assist the binding of metal ions to facilitate the growth of AgAu nanowires [32,33]. The aspect ratio of the nanowires was controllable by adjusting the OAm/OAc ratio. When 5 mL of OAm and 5 mL of OAc were used, nanowires with a length of 100–150 nm were obtained (Fig. S1). The length of the nanowires shortened to 50–80 nm if the volumetric ratio between OAm and OAc increased to 7:3 (Fig. S4a). 7 nm nanoparticles were obtained when this ratio was changed to 3:7 (Fig. S4b). Reaction temperature is critical for the morphology of the nanowires. Fig. S5 shows the nanowires were around 100 nm long and 2.2 ± 0.4 nm in diameter when the reaction temperature was 45°C. These nanowires were shorter than those obtained at 60°C with the same reaction time period of 30 min. The Au:Ag atomic ratio of the final product was close to 1:1, which was the feeding ratio between the two metal precursors, indicating that Au and Ag precursors could almost completely be reduced even at 45°C (Fig. S6). When the reaction temperature was lowered to 25°C, the nanowires formed was made of mostly Au (Figs S7a and S8). The reduction of Ag precursor appeared to be slower than Au at this temperature. Noticeably, these Au nanowires had a similar average diameter of 2.2 ± 0.3 nm, but an average length of 50–80 nm. Moreover, only Au nanowire could be obtained at 60°C, if the flow rate of CO gas was lower than 100 sccm. The as-made Au nanowires in presence of CO were also enclosed predominantly by {111} due to the surface selective adsorption of CO (Fig. S7b) [50,53–55]. These results indicate that AgAu nanowires can only be synthesized at elevated temperature and with a sufficiently high flow rate of CO gas.

The stability of {111} facet-enclosed AgAu nanowires

and {100} facet-enclosed Au nanowires were investigated using field emission TEM (FEI Tecnai F20) at an accelerating voltage of 200 kV. The AgAu nanowires were stable under the e-beam for an extensive period of time (~30 min). In contrast, the sub-2 nm Au nanowires made without CO gas were highly susceptible to e-beam damage. They broke up within 1–5 min exposure under e-beam irradiation at a dose level of 8 pA cm^{-2} , even if they were embedded in the thick surfactant media (Fig. S9). These ultrathin Au nanowires broke into short rods in about 5 s under the e-beam irradiation if there was no imbedded media (Fig. S10). Thick OAm and OAc surfactant media could in part prevent the Au nanowires from breaking up rapidly under the e-beam irradiation. Au nanowires less than 2 nm in diameter and with the longitudinal direction along $\langle 111 \rangle$ were previously shown to readily break into short rods upon e-beam irradiation [32,33]. Those ultrathin Au nanowires primarily grew along $\langle 111 \rangle$ direction and bounded by {100} facets on the sides when CO gas was not used [33,56]. Au nanowires made under those conditions were unstable and could result in shape transformation into shorter but thicker nanorods due to Rayleigh instability [43,48,52]. In comparison, both Au and AgAu nanowires generated under CO gas were predominately enclosed by {111} surfaces and stable under the e-beam irradiation.

The thermal stability of {111} surface-enclosed AgAu and Au nanowires was investigated with the heat treatment. AgAu nanowires remained largely intact after heating at 60°C in chloroform for 1 h, though the diameter increased slightly to 2.5 ± 0.4 nm, which is close to eight unit cell length (Fig. 2a). The longitudinal surfaces were still primarily bounded by {111} facets (Fig. 2b). The length of

Figure 2 (a) High and (b) low magnification TEM micrographs of AgAu nanowires after annealing at 60°C. Inset shows the size distribution of diameter of the nanowires.

Au nanowires made by using CO gas was largely preserved after the heat treatment at 60°C in chloroform for 1 h, although some nanowires show uneven contrast along the longitudinal direction within the wire (Fig. S11). This unevenness is likely caused by the Rayleigh instability [48].

Fig. 3 shows the TEM micrographs of {100} facet-enclosed Au nanowires. After thermal treatment at 60°C in chloroform for 1 h, these Au nanowires, which were hundreds of nanometers long originally, broke into 20–50 nm short rods. These nanowires showed both single-crystalline and polycrystalline features and were enclosed by {200} and {110} facets. Noticeably, the latter two metal surfaces are generally less stable than {111} surfaces [57]. Reconstruction of these thin nanowires occurred far below the melting temperature of Au. Upon heating, such nanowires underwent a shape transformation to either short and widened rods or spherical nanoparticles (Fig. 3b). Figs 3c and d show high resolution TEM micrographs of these Au nanowires having the reconstruction at both center and tip regions after annealing. Two sets of lattices separated by a planar defect were observed within the nanowire. One is projected along $\langle 111 \rangle$ direction, showing (200) surface that

has a d -spacing of 0.20 nm. The other is projected along $\langle 110 \rangle$ direction, with d -spacing of 0.234, 0.200 and 0.144 nm for (111), (200) and (110) planes, respectively. Fig. 3d shows the TEM micrograph of the surface reconstruction at the tip region. The atoms at the outer layer turned into {111} surface structures, while those in the interior kept the same structure in {200} lattice. This structural change could be driven by the requirement for minimizing the surface energy. The tips of Au nanowires have high surface energy with large curvature and the surface atoms are prompted to the reorganization from the high energy {110} surfaces to the low energy {111} surfaces.

The thermal stability of AgAu nanowires was also studied using *in situ* variable temperature TEM (Fig. 4). These ultrathin alloy nanowires were stable under e-beam irradiation at an accelerated voltage of 200 kV. Some started to break around 50°C at the narrow regions of the nanowires. About 10% of the nanowires (i.e., 5 out of 50 in the micrograph) broke into short rods when the temperature rose to the range of 60–100°C. The tips of the broken nanowires had spherical shapes because of the reconstruction through the Rayleigh process (Fig. S12) [48]. The variation of local

Figure 3 TEM micrographs showing the morphology and structure changes of Au nanowires (a) before and (b, c, d) after a thermal treatment at 60°C in chloroform for 30 min. Inset of (a) shows the lattices of Au nanowires in HR-TEM micrograph. These Au nanowires were made without the use of CO gas.

Figure 4 *In situ* variable-temperature TEM study of morphological changes of AgAu nanowires during heat treatment at different temperatures.

composition might contribute to the thermal instability of nanowires. The rest of alloy nanowires were fairly stable even when the temperature reached 200°C. These nanowires apparently could tolerate large strain without morphological changes during the cooling process. The convergent evident from the TEM study indicates overall the composition of the wires is homogeneous and no severe phase separation was observed. If there was large phase separation, the local strain would cause the changes in morphology and contrast which were not observed in the TEM images.

Fig. 5 shows the UV-vis-NIR absorption spectra for ultrathin AgAu alloy nanowires. As a comparison, Au nanowires made without CO gas were also examined under the same condition. Both AgAu and Au nanowires show two LSPRs: one around 500 nm associated with the transverse resonance and the other with longitudinal resonance at ~2900 nm [16,58,59]. The AgAu nanowires exhibited essentially the same kind of UV-vis absorption spectra after the heat treatment between 60 and 100°C. This observation indicates that most of the AgAu alloy nanowires should be thermally stable within this temperature range.

On the contrary, after annealing at 60°C the longitudinal resonance of Au nanowires blue-shifted by ~300 nm, and after the treatment at 100°C, a broad band between 1500–2800 nm appeared (Fig. S13), indicating the coexistence of Au nanostructures with huge variations in their dimensions. The background absorption due to the solvent and surfactants can be ruled out (Fig. S14). Thus, the blue shift in the NIR region could be attributed to the fragments of the broken nanowires.

In summary, we developed a CO-assisted synthesis of ultrathin, high aspect ratio AgAu alloy nanowires. These AgAu nanowires, which are largely bounded by {111} planes along the longitudinal surfaces, are much more stable than ultrathin Au nanowires bounded by {100} facets made without the use of CO gas. These ultrathin AgAu nanowires possess stable transverse resonance in the visible and longitudinal resonance in the NIR region. Besides a new synthetic method for making AgAu alloy nanowires, the discovery of facet-dependent stability in ultrathin metal nanowires is important for the design of new classes of stable low dimensional nanomaterials.

Figure 5 UV-vis-NIR absorption spectra for ultrathin (a) AgAu and (b) Au nanowires with and without thermal treatments.

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Author contributions Yang H and Wu J conceived the study and wrote the manuscript. Su D executed the *in-situ* variable temperature TEM study. Pan YT acquired and analyzed the absorption spectra. All authors contributed to the discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Jianbo Wu was born in Zhejiang, China, in 1982. He received his BSc degree in 2005, and MSc degree in 2007, both from Zhejiang University. He received his PhD degree majored in chemical engineering in 2012 under the direction of Prof. Hong Yang at University of Rochester, and then did his postdoc research jointly in Prof. Hong Yang (2012–2014) and Prof. Jian-Min Zuo (2013–2014) groups at the University of Illinois at Urbana-Champaign (UIUC). He received Elon Huntington Hooker Fellowship from the University of Rochester in 2011, and Shen Postdoctoral Fellowship from Chemical and Biomolecular Engineering Department, UIUC in 2013–2014. He was recruited by Shanghai Jiaotong University under the “National Thousand Talents Plan for Young Professionals” in 2014. His research interest is on colloidal chemistry, shape control of platinum-based alloys and intermetallics, and their applications as electrocatalysts.

Hong Yang is a Richard C Alkire Professor of Chemical and Biomolecular Engineering at UIUC. He received his BSc degree from Tsinghua University (1989), MSc degree from the University of Victoria (1994), and PhD degree from the University of Toronto (1998). After working at Harvard University as an NSERC postdoctoral fellow (1998–2001), he started his career at the University of Rochester before joining the Department of Chemical and Biomolecular Engineering at UIUC in 2012. Dr. Yang is an NSERC Canada Doctoral Prize winner and an NSF CAREER Award recipient. His current research interests include control of nanocrystals, surface modification, *in situ* TEM study of nanomaterials in solution and under reacting atmosphere, catalysis and electrocatalysis, and nanomaterials for energy and biological applications.

中文摘要 本文通过一氧化碳辅助GRAILS法(gas reducing agent in liquid solution)制备得到稳定的亚2 nm粗细的银金合金纳米线. 这些银金合金纳米线在加热和在电子束辐照的条件下表现出良好的稳定性. 对其纳米结构进行表征, 我们发现这种纳米线沿纳米线径向主要由{111}晶面组成. 这个结构不同于没有一氧化碳辅助生长的以{100}面为主的金纳米线. 后者在电子束辐照的条件下非常不稳定. 结构和成分上的区别导致了稳定性的提高.