

Simple and rapid synthesis of ultrathin gold nanowires, their self-assembly and application in surface-enhanced Raman scattering†

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A simple and one-step method to rapidly synthesize single crystalline ultrathin gold nanowires at room temperature within a few hours has been developed, and the self-assembled ultrathin gold nanowires demonstrated an intriguing application in surface-enhanced Raman scattering (SERS).

One-dimensional gold nanowires (AuNWs) have attracted considerable interests because of their high aspect ratios, unusual physical properties and potential applications in nanoelectronics, photonics and sensors.¹ The large anisotropy of AuNWs and their subsequent assembly ability make them especially important building blocks for the linkage of nano-scale electronics and molecular devices.² Many standard approaches have been extensively developed to produce AuNWs with desired shapes on the basis of particle assembly,³ surfactant mediation,⁴ template assistance⁵ or physical deposition.⁶ However, most of these early reported techniques usually resulted in the production of polycrystalline or relatively large diameter (>5 nm) nanowires with poor morphology and rough surfaces. The most recent reports by Xia,⁷ Yang⁸ and others^{9,10} delineated the synthesis of ultrathin AuNWs (<5 nm) by using oleylamine (OA) or combined chemicals as both one-dimensional growth templates and reducing agents. The complexes of AuCl (or HAuCl₄) and OA through aurophilic interactions could be reduced to form the ultrathin AuNWs. Despite their significant success with respect to the better control of the dimension of the nanowires and well-defined crystalline structures, a novel and more simplified method for the rapid synthesis of ultrathin AuNWs in large quantities remains highly desirable as most current approaches required a lengthy reaction time (usually up to several days),^{7,8,10} high temperature treatment,^{7,9,10a} or complicated and multistep manipulation^{7,10a} to improve the productivity and quality of the ultrathin AuNWs.

In this paper, we present a quick and simple method for preparing ultrathin single crystalline AuNWs in a solution of HAuCl₄, OA and triisopropylsilane (TIPS) at room temperature within a few hours. This process involved the addition of OA as a stabilizer and one-dimensional growth template, and TIPS as a highly effective reducing agent.¹¹ Especially when deposited onto the substrates such as a copper grid or silicon wafer, the ultrathin nanowires could easily self-assemble into two-dimensional network structures with quantities of closely packed parallel nanowires. These assembled structures could serve as an active substrate for surface-enhanced Raman scattering (SERS) application (Scheme 1).

In a typical synthesis, 100 μL OA was mixed with 3 mg HAuCl₄ in 2.5 ml hexane, followed by the addition of 150 μL TIPS to form a yellow solution. Then the reaction proceeded at room temperature without stirring for 4~5 hours until the color gradually changed to dark red. The final products were centrifuged, washed by ethanol and finally redispersed in hexane for further investigation. Control experiments in different synthetic conditions revealed that TIPS was crucial to accelerate the formation of the AuNWs at room temperature (Fig. S1, ESI†). A large-scale experiment was also successfully conducted by using the same approach (Fig. S2, ESI†). Energy dispersive X-ray spectroscopy (EDX) confirmed that the nanowires were composed of pure gold (Fig. S4, ESI†), and Fourier-transform infrared (FTIR) analysis (Fig. 1(B)) demonstrated that the nanowires were mainly capped with amine groups.

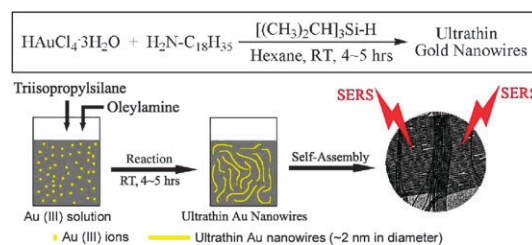
Transmission electron microscopy (TEM) analysis of the ultrathin AuNWs (Fig. 2) demonstrated that the nanowires displayed a relatively high level of flexibility with low thickness down to 1.8 nm and length up to 2 μm (Fig. S3(D), ESI†). Upon evaporation of the solvent, the long and ultrathin nanowires tended to form “stacked” parallel bundles on the substrate. The different layers of parallel bundles were further

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Scheme 1 Schematic illustration for the formation of ultrathin AuNWs and their self-assembly and application in SERS.

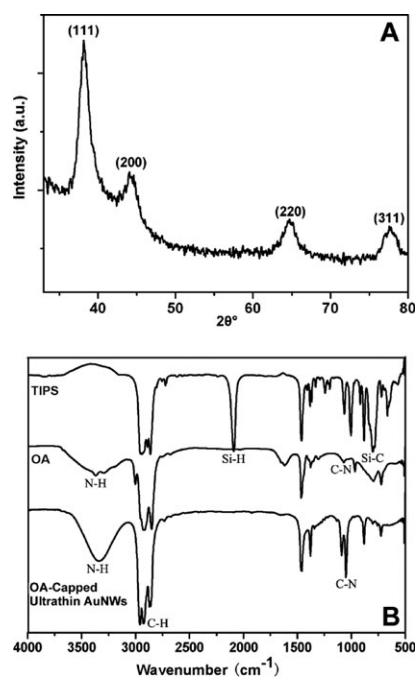


Fig. 1 (A) X-Ray diffraction (XRD) pattern of ultrathin AuNWs, and (B) FTIR spectra analysis of TIPS, OA and OA-capped ultrathin AuNWs.

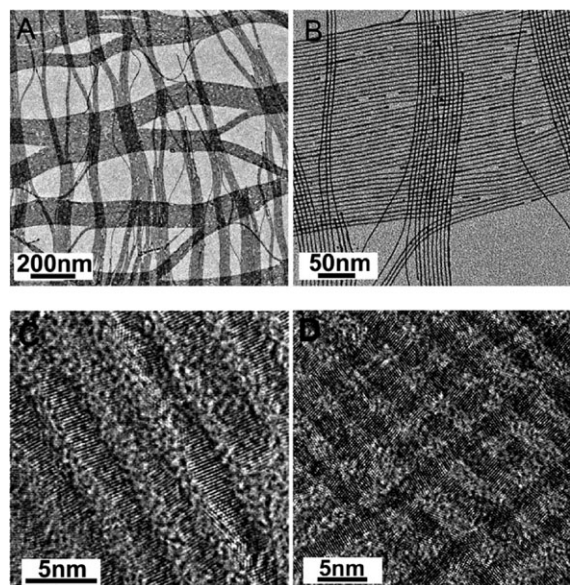


Fig. 2 (A) TEM image of self-assembled ultrathin AuNWs network structures; (B) TEM image of bundles composed of differently oriented AuNWs; (C) and (D) high-resolution TEM image of ultrathin AuNWs.

able to self-assemble into closely packed two-dimensional network structures at a uniform distance of ~ 2 nm between two adjacent nanowires. High-resolution TEM images of ultrathin nanowires clearly displayed the parallel structure and the overlap between differently oriented ultrathin AuNWs (Fig. 2, S5, ESI[†]). Each of the AuNWs was single crystalline and the interfringe distances were 0.23 nm, corresponding to {111} lattice spacing of the face centered cubic (fcc) Au nanocrystals, which was consistent with the results reported

recently.^{7–10} The (fcc) structure of AuNWs was also confirmed by the X-ray diffraction (XRD) pattern in Fig. 1(A). The XRD peaks of ultrathin nanowires at 38.2° , 44.4° , 64.6° and 77.6° could be assigned as (111), (200), (220) and (311) reflection lines, respectively, which were in agreement with the diffraction standard of Au (JCPDS 04-0784).

FTIR spectra of TIPS, OA and OA-capped ultrathin AuNWs were also investigated (Fig. 1(B)). The absorption peak at 2091 cm^{-1} of TIPS corresponded to the stretching mode of Si–H and 802 cm^{-1} to the stretching mode of Si–C. However, these two characteristic peaks disappeared in the FTIR spectrum of ultrathin AuNWs, indicating that TIPS could be simply removed after preparation of the ultrathin nanowires. The N–H stretching vibration at 3381 cm^{-1} of OA was increased noticeably and shifted to 3339 cm^{-1} in OA-capped ultrathin AuNWs. This could be attributed to the coordination of ultrathin AuNWs with OA. The C–N stretching vibration at 1070 cm^{-1} of OA was also increased in intensity and shifted to 1050 cm^{-1} because of the proximity to the gold surface. The bands in the range of $2850\text{--}2960\text{ cm}^{-1}$ were typical C–H stretching vibrations.^{10a,12}

The possible growth mechanism of ultrathin AuNWs was monitored by taking samples out of the reaction mixture at different time intervals. Fig. 3(A) showed the initial stage of the synthesis at 30 min, when only spherical Au nanoparticles

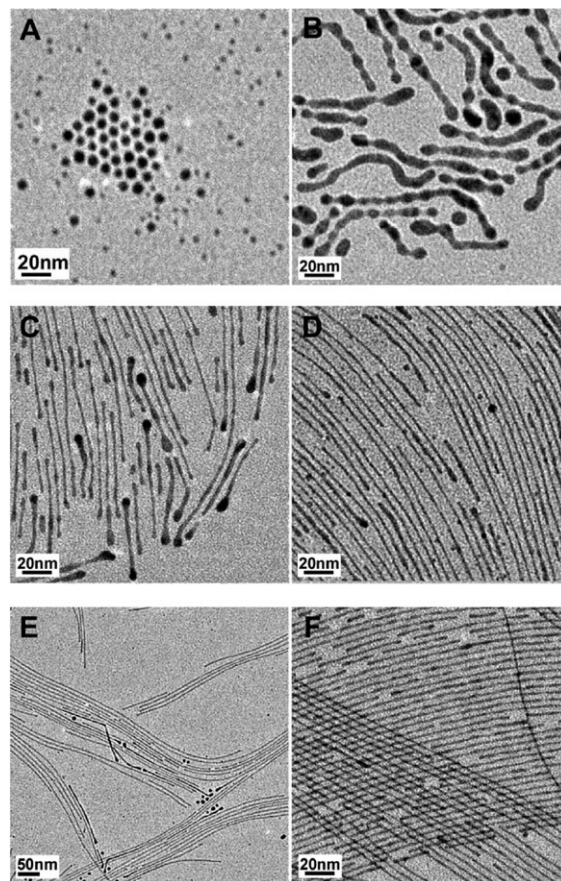


Fig. 3 TEM images of the intermediate products at different time intervals in the process of ultrathin AuNWs preparation: (A) 30 min; (B) 60 min; (C) 90 min; (D) 180 min; (E) 240 min; (F) self-assembled ultrathin AuNWs at 240 min.

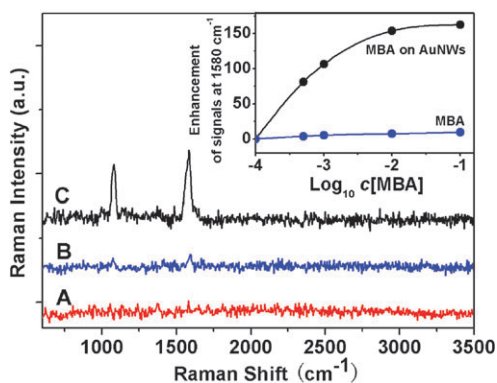


Fig. 4 Raman spectra of (A) AuNWs, (B) MBA and (C) MBA adsorbed on the assembled AuNWs; 10^{-3} M MBA solution was dropped on the substrates in (B) and (C). The inset image reflects the enhancement of SERS signal at 1580 cm^{-1} with the concentration of MBA.

with diameters of 3–8 nm could be detected, indicating the rapid reduction of HAuCl_4 by TIPS. After 60 min reaction, two or more Au nanoparticles were fused together to form irregularly chain-like intermediates through an oriented-attachment process (Fig. 3(B)).¹³ The alternative convex and concave regions of the chain-like nanoparticles exhibited the different chemical potentials and thus resulted in a smoothing extension of interconnected nanoparticles by diffusion. This neck-growing process created elongated chain-like nanoparticles along the $\{111\}$ direction and eventually led to the formation of gold nanowires with one or two enlarged spherical ends, as the structure showed in Fig. 3C.^{10a,14} After the solution was aged for 180 min, the diameter of AuNWs became thinner (~ 1.8 nm) and the spherical ends of AuNWs became smaller or even disappeared (Fig. 3(D)). As the aging extended to 240 min, ultrathin nanowires with a diameter of 1.8 nm and large aspect ratios (with length up to 2 μm) were formed (Fig. 3(E)). These ultrathin AuNWs were sensitive to the electron beam of the high-resolution TEM, and could be melted within a few seconds exposure. (Fig. S5, ESI[†]). The as-synthesized nanowires usually tended to form bundles of parallel AuNWs and then self-assembled into two-dimensional network structures on the substrate (Fig. 3(F)).

The self-assembled networks of single crystalline ultrathin AuNWs with a gap dimension (~ 2 nm) could easily trap the analyte molecules and automatically position them in the interstices between the closely packed parallel AuNWs, which are very suitable as substrates for SERS studies because of their large localized electromagnetic (EM) fields.¹⁵ To this end, we performed SERS measurements by choosing a commonly used Raman active reporter, 4-mercaptobenzoic acid (MBA)^{15b} and assembled AuNWs networks as substrates. MBA was adsorbed onto assembled AuNWs. The SERS response was investigated with a 532 nm laser excitation. As shown in Fig. 4(A), no Raman signals were observed in the AuNWs substrate in the absence of MBA. Fig. 4(B) showed the Raman spectrum of MBA onto the silicon wafer. The intensities of the characteristic bands of MBA at 1580 and 1074 cm^{-1} were very weak. A significant increase in intensity

was detected from the sample in which MBA was adsorbed onto the surface of AuNWs (Fig. 4(C)). This indicated a strong Raman enhancement induced by the assembled AuNWs. The SERS signal was found to be concentration dependent and was no longer altered after the adsorption of MBA reached saturation (Fig. 4, inset).

In summary, this paper presents a very simple and highly effective approach for the rapid synthesis of single-crystal ultrathin AuNWs with a diameter of 1.8 nm at room temperature within a few hours. The as-synthesized ultrathin AuNWs could easily self-assemble into two-dimensional networks with closely packed parallel nanowires when deposited onto substrates. The networks were found to serve as a well-defined SERS-active system, indicating that such assembled ultrathin nanowires have important implications as specific devices for molecular recognition and signal amplification. This newly developed method may also be applicable to the synthesis of other ultrathin metals or semiconductor nanowires.

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