

Supporting Information

Simple and Rapid Synthesis of Ultrathin Gold Nanowires, Their Self-Assembly and Application in Surface-Enhanced Raman Scattering

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Materials and General methods:

Chemicals: Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was purchased from Alfa Aesar. Oleylamine (OA) was obtained from Fluka. Triisopropylsilane (TIPS) was provided from Sinopharm. Hexane was purchased from Tedia. All chemicals were purchased and used without further treatments. All the other starting materials were obtained from Sigma or Aldrich. Commercially available reagents were used without further purification, unless noted otherwise. All chemicals were analytical grade or better.

Instruments: Fourier transform infrared spectra (FTIR) were recorded on a Shimadzu IRprestige-21 FTIR spectrophotometer. The morphologies and compositions of ultrathin Gold nanowires (AuNWs) were characterized using a transmission electron microscope (JEOL 2000 EX TEM operating at 120kV) and a high-resolution transmission electron microscope (JEOL JEM 2100 TEM operating at 200 kV, combined with energy disperse X-ray spectroscopy (EDX) detection). X-ray diffraction (XRD) pattern was measured from a Bruker D8 Advanced diffractometer using $\text{Cu K}\alpha$ radiation. Surface-Enhanced Raman Scattering (SERS) experiments were performed using a confocal Raman microscope (WITec CRM200) with a 100 \times objective lens (numerical aperture = 0.95). The incident laser has a wavelength of 532 nm and spot size of \sim 500 nm. The laser power was attenuated to 0.05mW to avoid photodecomposition of the SERS reporter.

Preparation of ultrathin AuNWs: OA was used as stabilizer and one-dimensional growth template. TIPS was used as highly effectively reducing agent. The synthesis was carried out as follows. 100 μL

OA and 3 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were added into 2.5 ml hexane to form a yellow solution. Then 150 μL TIPS was added to the solution, and kept standing at room temperature for 4-5 hours. The ultrathin AuNWs solution was added into 8 ml ethanol, centrifuged at 4500 rpm for 15 min, the supernatant discarded and the dark-red precipitate redispersed in 2.5 ml hexane for two times to remove the excess of oleylamine. The final ultrathin AuNWs were dispersed in 2.5 ml hexane.

Surface-Enhanced Raman Scattering (SERS) Measurements: For the preparation of SERS substrates, 20 μL of AuNWs solution was dropped on the silicon wafer and left to dry in air. For SERS measurement, 4-mercaptobenzoic acid (MBA) was diluted to different concentrations from 10^{-1} M to 10^{-4} M with methanol, then 20 μL of MBA solution was dropped onto the SERS substrate, and left to dry in air. As comparison, other positions of the same sample were also measured where no AuNWs were found and only dry MBA was adsorbed there. For each measurement, 5 different points were selected to detect the MBA probes, and the average value was used as the final result.

Control experiments: Control experiments in the absence of TIPS and higher temperature were also investigated. The photographic images of the results were shown in Figure S1. At the beginning of the reaction, the solutions were yellow color, indicating that Au (III) were the dominant species. After 5 hours reaction at 25°C , the solution with TIPS changed from yellow to dark-red, showing ultrathin AuNWs had been produced. However, in the control experiment at room temperature without TIPS, the color of solution still remained yellow (Figure S1(C)) and no any expected AuNWs product was formed after 5 hours reaction. At a higher temperature of 80°C , the color of solution changed into colorless after 5 hours reaction, indicating that Au (III) ions had been converted to Au (I) ions.^{1,2} But no nanowires are produced until the reaction time is over 24 hours at this temperature.

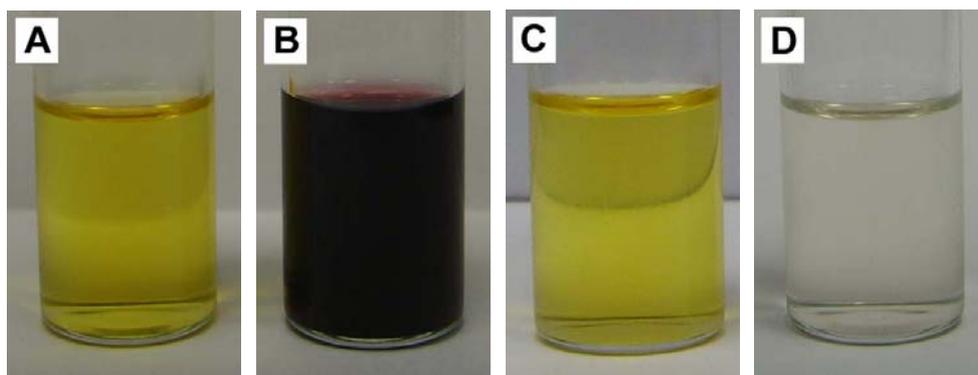


Figure S1. Photographic images of the reaction mixture with TIPS: (A) at the initial stage of mixing (0 min), (B) 5 hours reaction at room temperature; (C) 5 hours room temperature reaction without TIPS, (D) 5 hours reaction at 80°C in the absence of TIPS.

Large-scale experiment: The rapid synthesis of ultrathin gold nanowires was also conducted by using the same approach in large quantity. In a typical experiment, 1.5 mL OA and 44 mg HAuCl_4 were added into 40 ml hexane to form a yellow solution. Then 2.1 mL TIPS was added to the solution, and

kept standing at room temperature for 4-5 hours. The final dark-red AuNWs were centrifuged at 4500 rpm for 15 min, washed by ethanol and finally redispersed in 40 ml hexane. The photographic images of the results are shown in Figure S2.

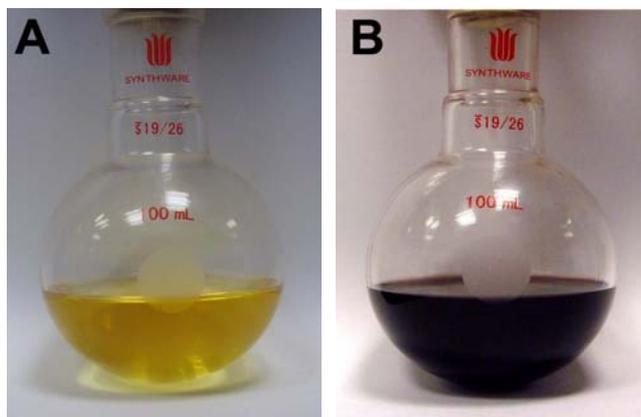


Figure S2. Photographic images of the preparation of ultrathin AuNWs with TIPS in large quantity: (A) at the initial stage of mixing (0 min) and (B) after 5 hours reaction at room temperature.

The whole process of large-scale preparation of ultrathin AuNWs was also monitored by TEM images of samples at different reaction time. The TEM results showed that the quality of AuNWs prepared in a large scale was the same as prepared in a smaller scale.

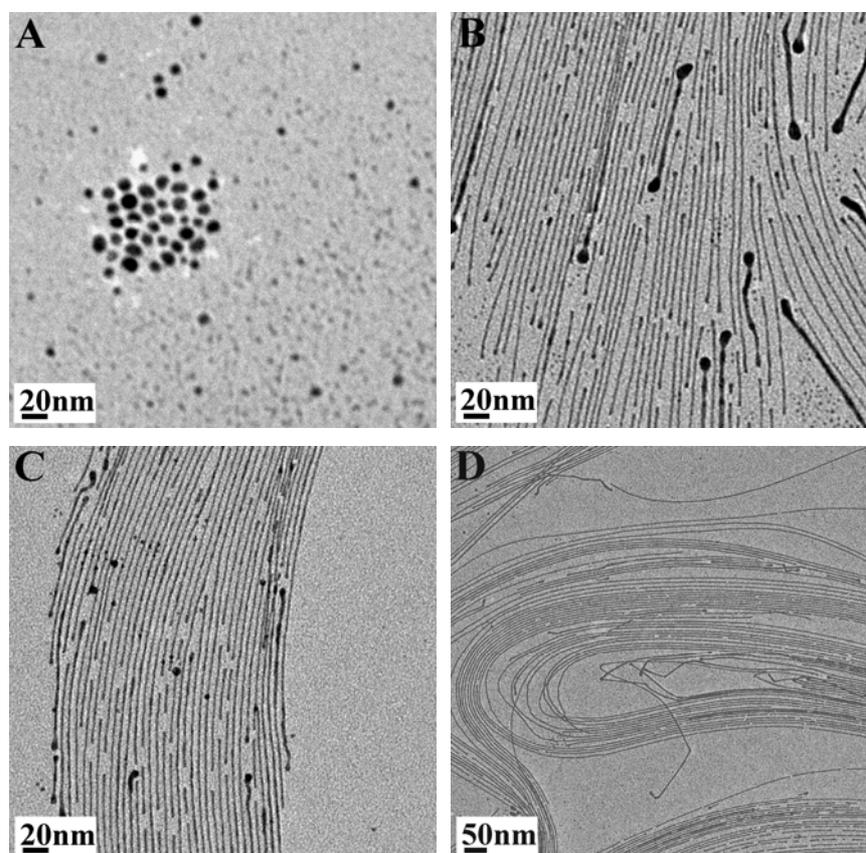


Figure S3. TEM images of the intermediate products at the different reaction time in the large-scale preparation of ultrathin AuNWs. (A) 30 min; (B) 90 min; (C) 180 min; (D) 240 min.

Characterization of Ultrathin AuNWs:

EDX spectrum: EDX analysis of ultrathin AuNWs indicated that the nanowires were composed of pure gold. The Cu peaks were from the TEM copper grid. The very weak peaks at 5.4 KeV, 6.4 KeV and 6.9 KeV could be assigned to Fe, Cr, or Co elements. These small peaks may appear randomly in the process of EDX measurements. Two typical EDX spectra without and with these peaks were presented in Fig. S4. We suppose that these weak peaks were introduced by the impurities from the copper grid, TEM system or the preparation procedure. EDX spectra of ultrathin AuNWs with similar weak peaks can also be observed in recent publications.⁴

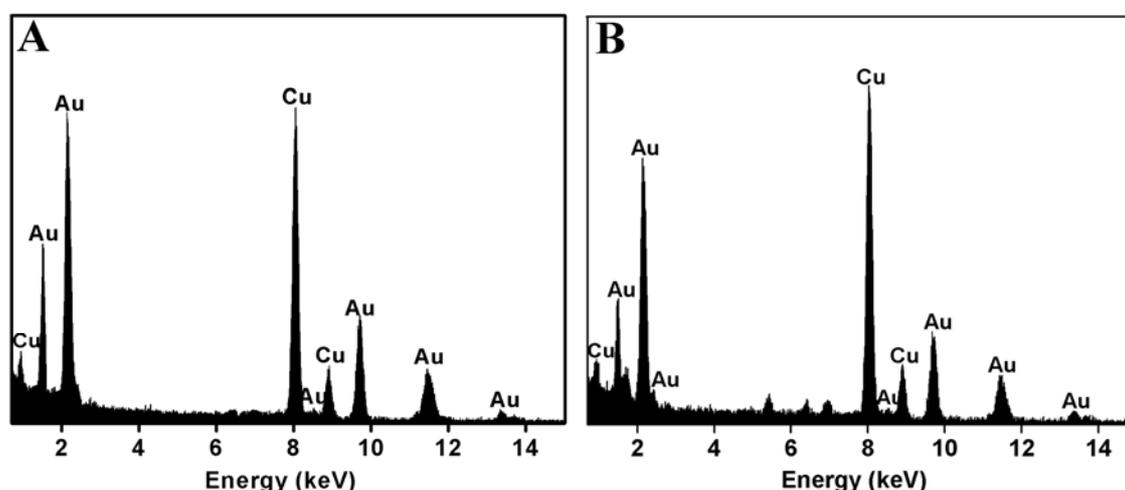


Figure S4. EDX spectra of ultrathin AuNWs. (A) and (B) are two typical EDX spectra with or without peaks at 5.4 KeV, 6.4 KeV and 6.9 KeV.

High resolution TEM images of ultrathin AuNWs: Crystalline structures of ultrathin AuNWs were investigated by high resolution TEM. Ultrathin AuNWs showed high-quality single crystalline structures with the diameter of ~ 1.8 nm. Bundles of parallel single crystalline AuNWs and their overlap could be clearly observed with high resolution TEM. AuNWs were highly sensitive to the electron beam of high resolution TEM because of their ultrathin diameter. It could be observed that, within a few seconds exposure, nanowires were melted by the heating of electron beam. The single crystalline structures at the broken positions were usually turned to polycrystalline structure.³

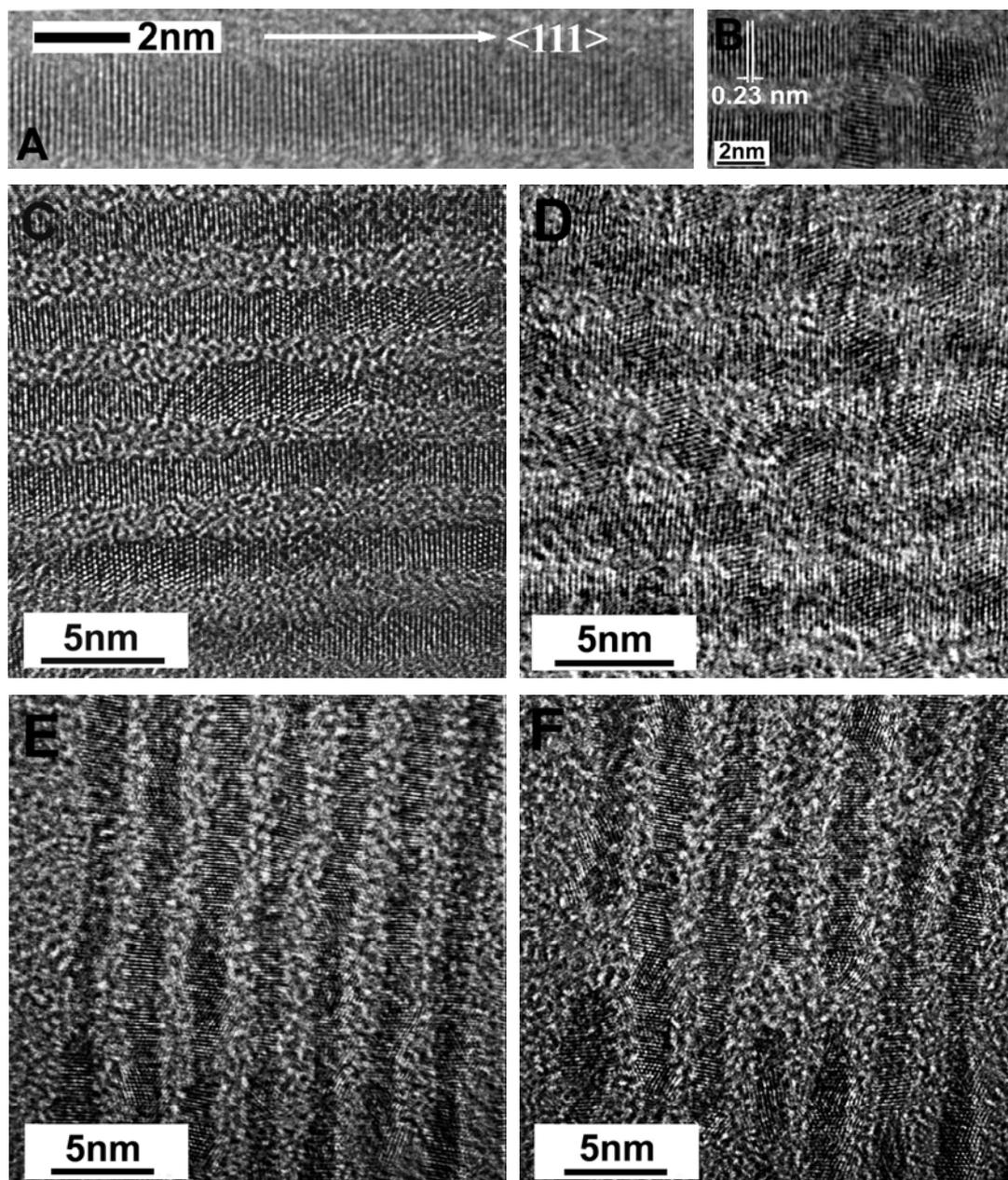


Figure S5. High resolution TEM images of ultrathin AuNWs: (A) an individual single crystalline ultrathin AuNW and the {111} lattice planes; (B) overlap between differently oriented ultrathin AuNWs; (C) bundles of parallel ultrathin AuNWs; (D) overlap of ultrathin AuNWs; (E, F) melting of ultrathin AuNWs observed at the same position under electron beam heating.

Raman spectra: The enhancement of Raman signals was influenced by the concentrations of dropped MBA solution onto the substrate. As showed in Fig. S6, the SERS signals decreased greatly with the decrease of concentrations from 10^{-3} M to 10^{-4} M. Obvious SERS enhancement can be observed at 10^{-3}

M of MBA. When the concentration of MBA was low to 10^{-4} M, the SERS enhancement of MBA would be masked by the background and no obvious signals could be identified.

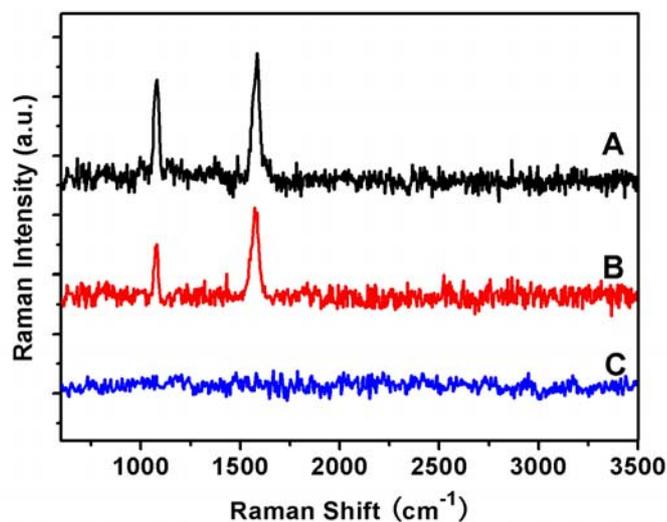


Figure S6. Raman spectra of MBA adsorbed on the assembled AuNWs prepared by dropping different concentration of MBA solution: (A) 1×10^{-3} M; (B) 5×10^{-4} M; (C) 1×10^{-4} M.

References:

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