Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2015

Electronic Supplementary Information

Organic-free synthesis of ultrathin gold nanowires as effective SERS substrates

Man Zhou, [a] Ming Lin,[b] Yongzheng Wang,[a] Xiangke Guo,[a] Luming Peng,[a] Weiping Ding[a] and Xuefeng Guo*[a]

*[a] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

E-mail: guoxf@nju.edu.cn; Fax: +86 25-83317761.

[b] Institute of Materials Research & Engineering, A*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602, Singapore

1. Experimental details

1.1 Chemicals

$HAuCl_4 \cdot 4\ H_2O$ (99%) was obtained from Nanjing Chemical Reagent Co. Ltd (China). 0.6 mm thick Cu sheets (99.5% metal basis) were purchased from Aladdin Chemicals. Medium speed filter papers were purchased from Hangzhou Whatman-Xinhua Filter Paper Co., Ltd (China). All of the chemicals were used without further purification. Millipore purified water was used in all the experiment.

1.2 Characterizations

TEM images were recorded with a JEM-1011 Electron Microscope (JEOL) at an accelerating voltage of 100 kV. HRTEM was performed with a JEOL JEM-2010 instrument at an acceleration voltage of 200 kV. Raman spectra were recorded in a Bruker Multi RAM FT-Raman spectrometer. (Laser source: 633 nm light of He-Ne laser). Rhodamine 6G (R6G) in ethanol was employed as the analyte. Different concentrations (10^{-5} M, 10^{-6} M and 10^{-7} M) were carried out to test the detection limit of R6G on the substrates. 10 μL analyte was carefully dropped on the substrates placed on slide (25 mm × 25 mm) and dried under ambient conditions for each measurement. The spectra recorded sequentially in experiments with the same instrumental settings were compared.

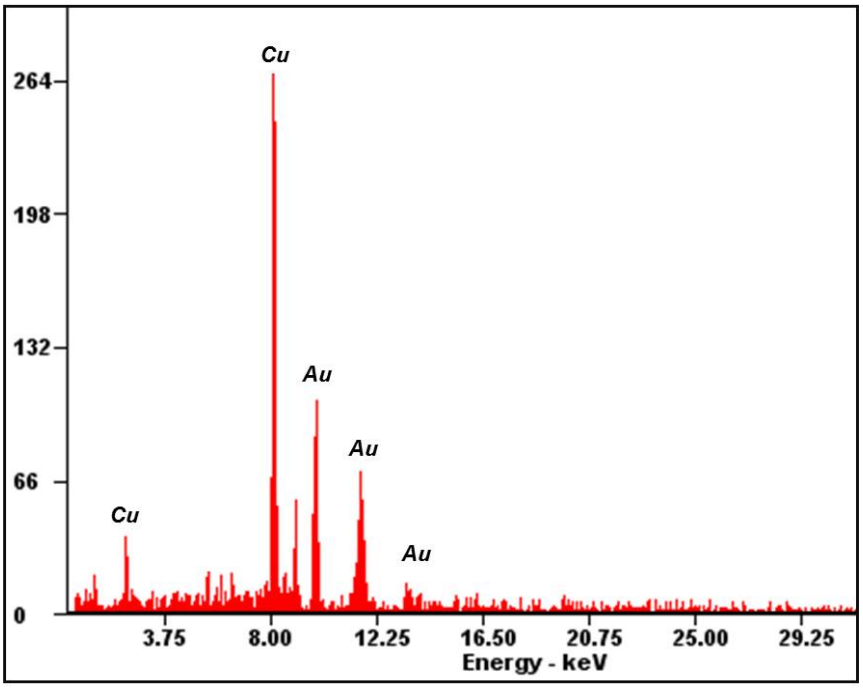

Figure S1. EDX spectrum recorded from a bundle of ultrathin Au NWs.

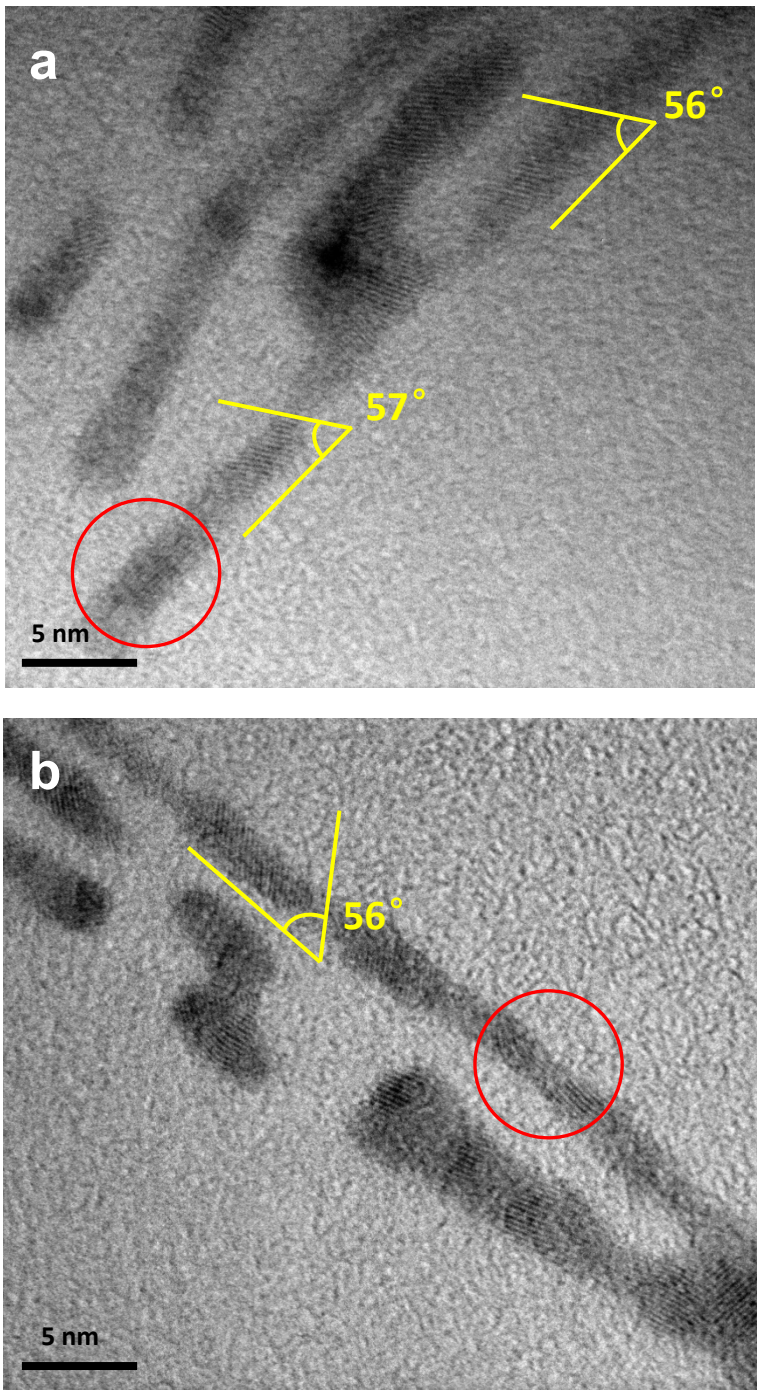

Figure S2. HRTEM image recorded from a bundle of ultrathin Au NWs. Red circle showed the lattice fringe parallel to the growth direction; yellow notes showed about 56° deviation from the lattice fringe to the growth direction.

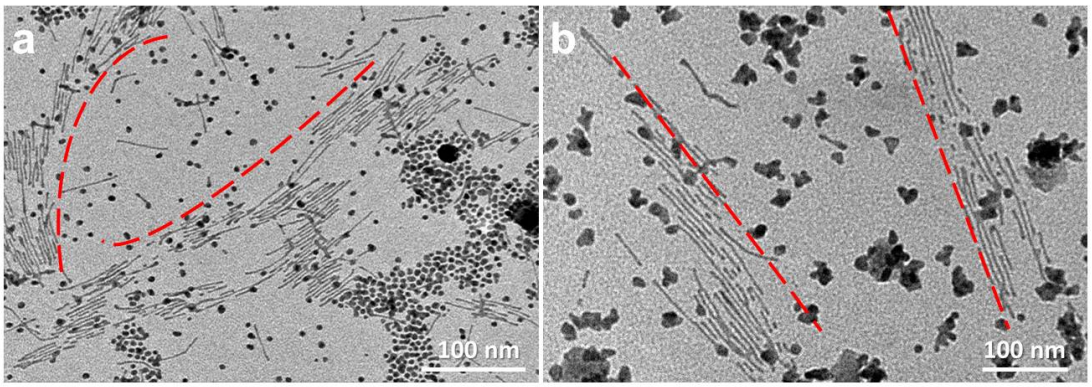

Figure S3. (a, b) TEM images of short Au NWs arrays after adding three droplets to carbon-coated Cu grid placed with an oblique angle to the horizontal plane. Red lines indicated the directions of Au NWs arrays which might be consistent with the diffusion effect.

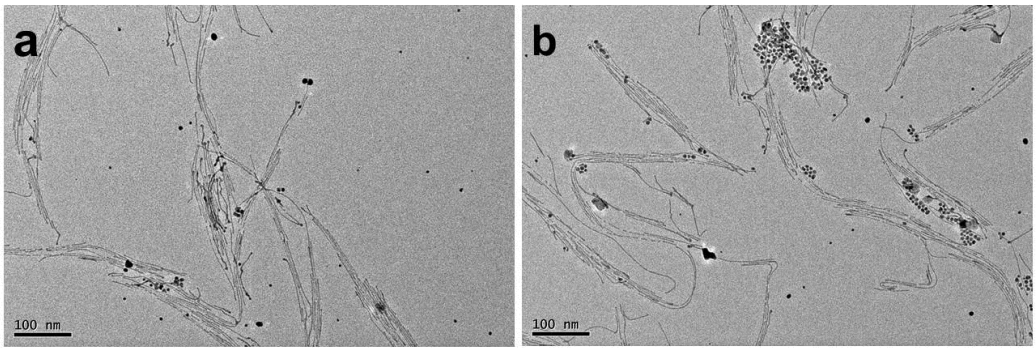

Figure S4. TEM images of ultrathin Au NWs on carbon-coated Cu grid (a) before and (b) after a week.

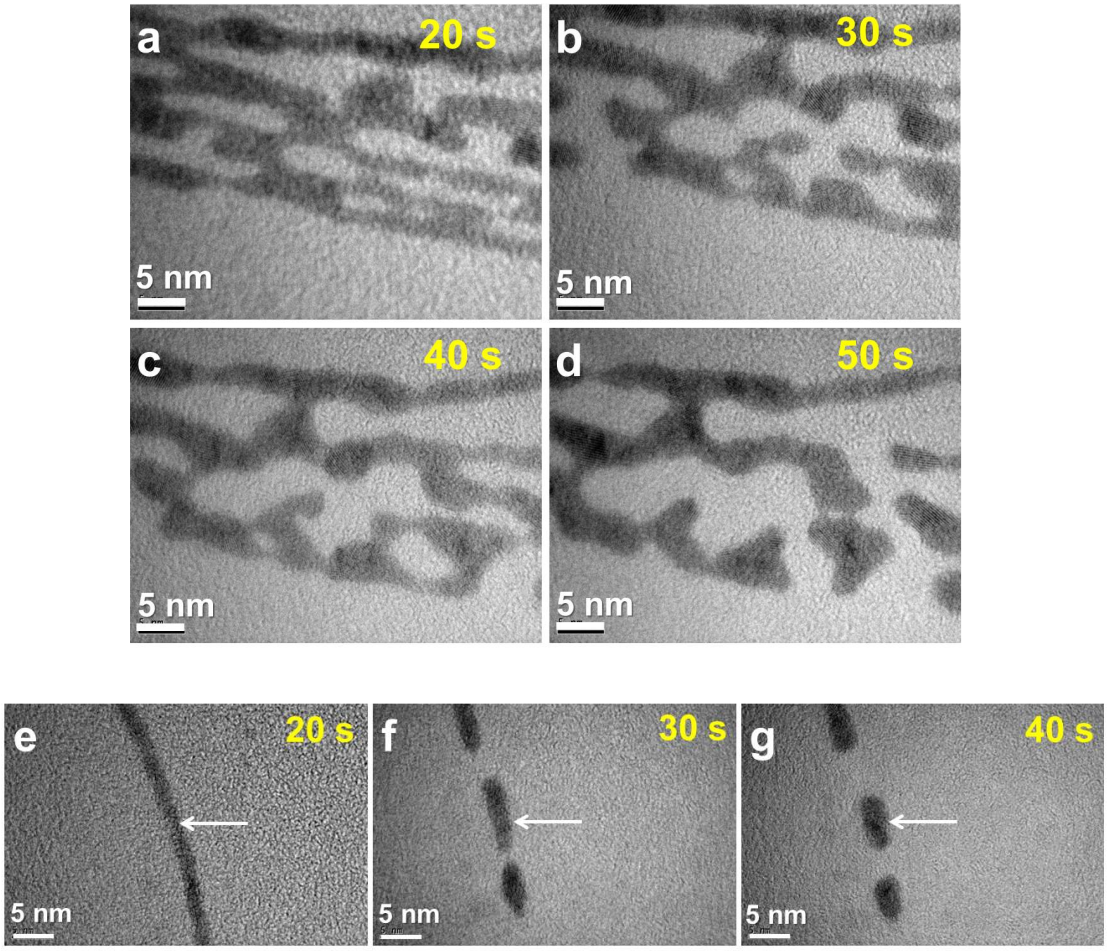

Figure S5. TEM images showing ultrathin Au NWs degradation upon long exposure to the high-energy electron beam during HRTEM analysis. (a-d) a bunch of ultrathin Au nanowires; (e-g) a single ultrathin Au nanowire.

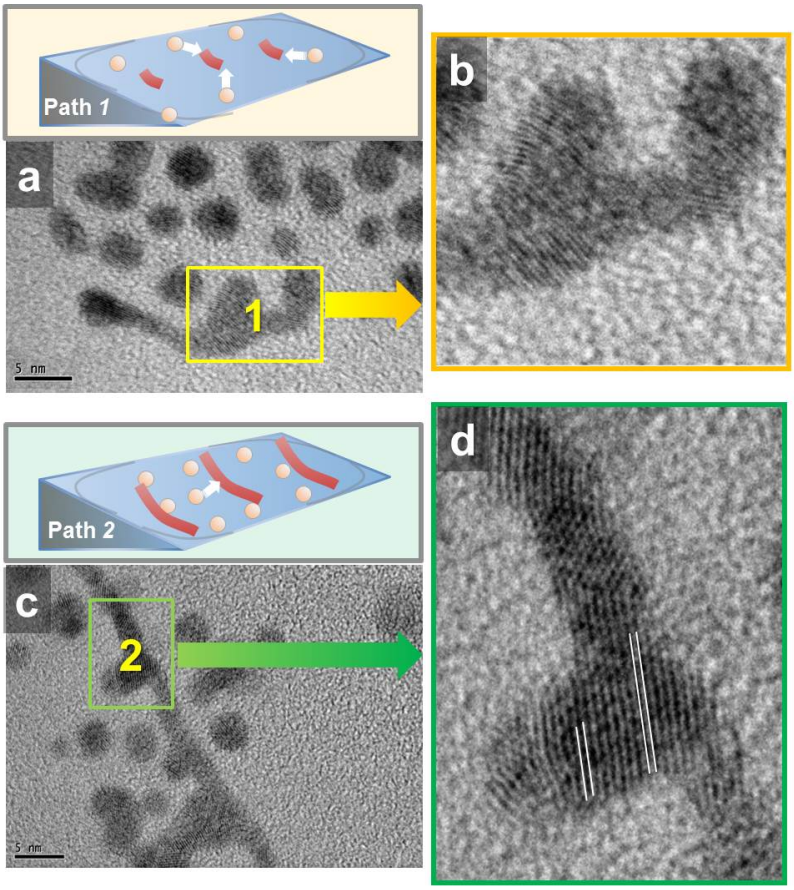

Figure S6. HRTEM images during the growth of ultrathin Au NWs on substrate. (a, b) Au nanoseeds connected at the ends of short Au nanorods; (c, d) Au nanoseeds connected in the middle of short Au nanorods.

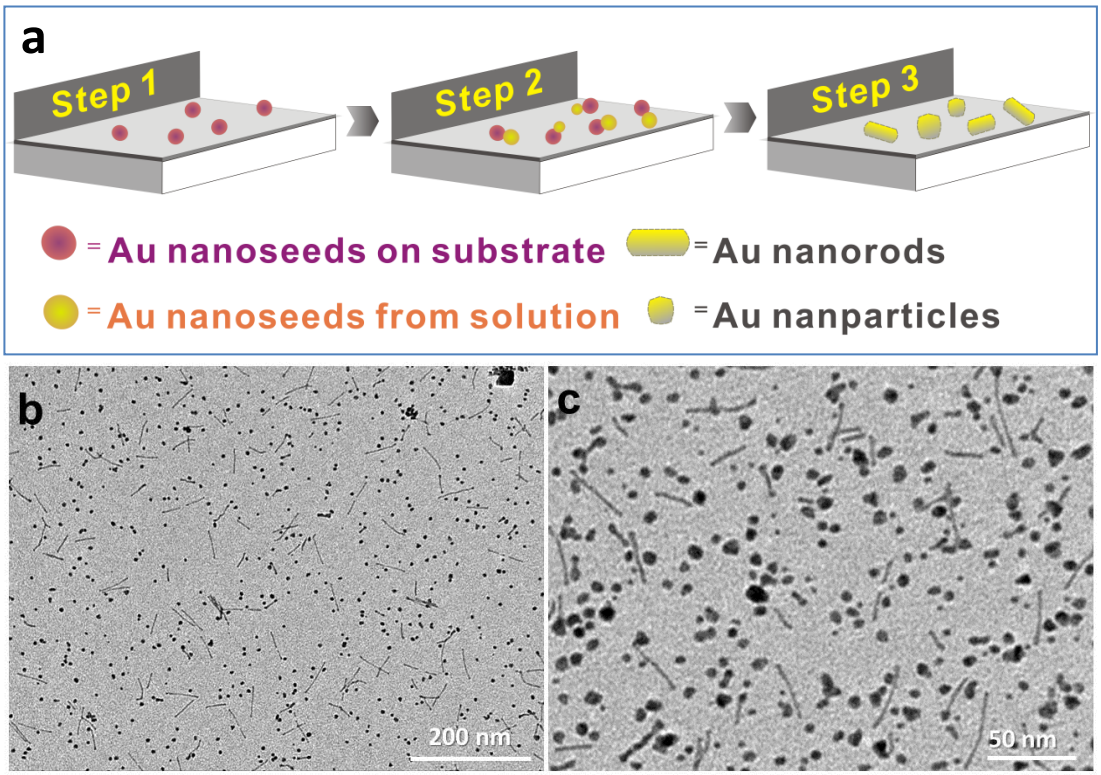

Figure S7. (a) Illustration of the final products on horizontally placed Cu grid; (b-c) TEM images of short Au nanorods and particles after adding four droplets to horizontally placed Cu grid.

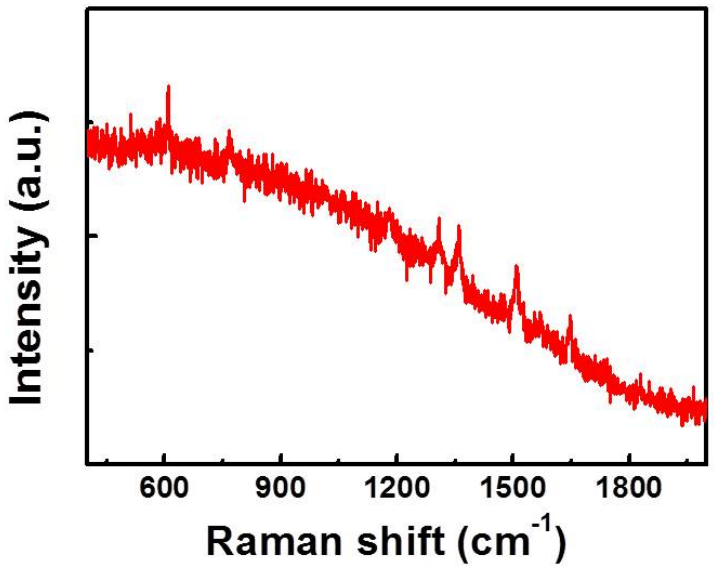

Figure S8. Eight times enlarged the SERS signals of 0.1 μM R6G on Cu grid supported Au NWs in Fig. 5(a).

Table S1. Assignment of selected Raman peaks of R6G.

NRS (cm^{-1}) [a]	SERS (cm^{-1}) [b]	Assignment
613	609	In plane xanthenes ring deformation
775	770	Out of plane C-H bending
1184	1180	In plane xanthenes ring deformation, C-H bending, N-H bending
1312	1309	In plane xanthenes ring breathing, N-H bending, CH_2 waggling
1364	1358	Xanthenes ring stretching, in plane C-H bending
1512	1507	Xanthenes ring stretching, C-H stretching, C-H bending, N-H bending
1577	1572	Xanthenes ring stretching, in plane N-H bending
1651	1645	Xanthenes ring stretching, in plane C-H bending

(a) Calculated data: Jensen, L.; Schatz, G. C. Resonance Raman scattering of rhodamine 6G as calculated using time-dependent density functional theory. *J. Phys. Chem. A*. 2006, **110**, 5973-5977.

(b) Experimental data.

AEF Calculation example of ultrathin Au NWs on Cu grid in **Figure 5a** is listed as follows.

$AEF = (I_{SERS}/C_{SERS}) / (I_{RS}/C_{RS})$

Calculation for the peak at 1358 cm^{-1};

I_{SERS} = 183 counts, $C_{SERS} = 1\times10^{-5}$ M

I_{RS} = 334 counts, $C_{RS} = 1\times10^{-1}$ M

$AEF = (I_{SERS}/C_{SERS})/(I_{RS}/C_{RS}) = (183/10^{-5}) / (334/10^{-1}) =$ **0.54×10^4**

Calculation for the peak at 1507 cm^{-1};

I_{SERS} = 180 counts, $C_{SERS} = 1\times10^{-5}$ M

I_{RS} = 411 counts, $C_{RS} = 1\times10^{-1}$ M

$AEF = (I_{SERS}/C_{SERS})/(I_{RS}/C_{RS}) = (180/10^{-5}) / (411/10^{-1}) =$ **0.43×10^4**

Average AFE value = $(0.54+0.43)\times10^4/ 2 =$ **4.9×10^3**