Supporting information

Largely-increased length of silver nanowires by controlled oxidative etching process in solvothermal reaction and the application in highly transparent and conductive networks

Xiaomei Xu, Song He, Conghua Zhou*, Xingda Xia, Liao Xu, Hui Chen, Bingchu Yang, Junliang Yang

Hunan Key Laboratory of Super Microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha, Hunan 410083, P. R. China

*Correspondence should be addressed to: chzhou@csu.edu.cn (C.H. Zhou)

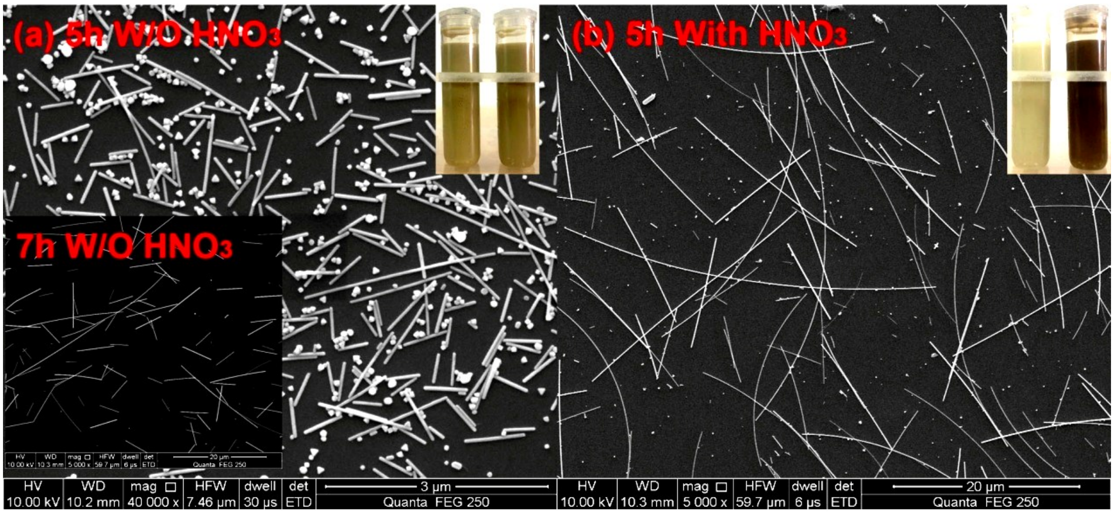

Figure S1. SEM images of AgNWs synthesized by solvothermal reaction: (a) W/O pre-added HNO_3 and reacted at 135°C for of 5h (inset shows 7h reaction W/O HNO_3 pre-added). (b) With pre-added HNO_3 (0.5mL, 0.22mol/L) and reacted at 135°C for of 5h. Photo images in right corner of each figure were: (left) peaked after reaction and (right) mixed with equivalent volume NaOH solution (0.25mol/L).

Photo images at right upper corners depicts indicative experiment to show whether Ag^+ exists in solution. This was done by adding NaOH solution into the as-reacted solution with equivalent volume. Color change was due to reaction between Ag^+ and OH^-, as described by:

$$Ag^+ + OH^- \longrightarrow AgOH \quad (1)$$

$$2AgOH \longrightarrow Ag_2O\downarrow + 2H_2O \quad (2)$$

For sample fetched from reaction W/O addition of HNO_3, the color changed little, thus almost all the Ag^+ ions had been reduced. While for that with HNO_3 pre-added, the color changed from grey white to dark brown, implying that there were concentrated Ag^+ ions left in the solution. This also means, reduction rate of Ag^+ ions was lowered due to pre-added HNO_3, which coincides with the Le Chatelier's principle. And the corresponding SEM morphological properties of AgNWs obtained with or W/O HNO_3 pre-added, AgNWs synthesized at 135°C for 5h showed length less than 3μm (Figure **S1 a**), while that with HNO_3 (0.5mL, 0.22mol/L) added showed length up to ~50μm (Figure **S1** b). Although increasing the reacting period to 7h could make increment of length to ~30μm in the case of W/O HNO_3 pre-added, it was yet far shorter than that synthesized with HNO_3 added (up to 460μm according to Figure 1).

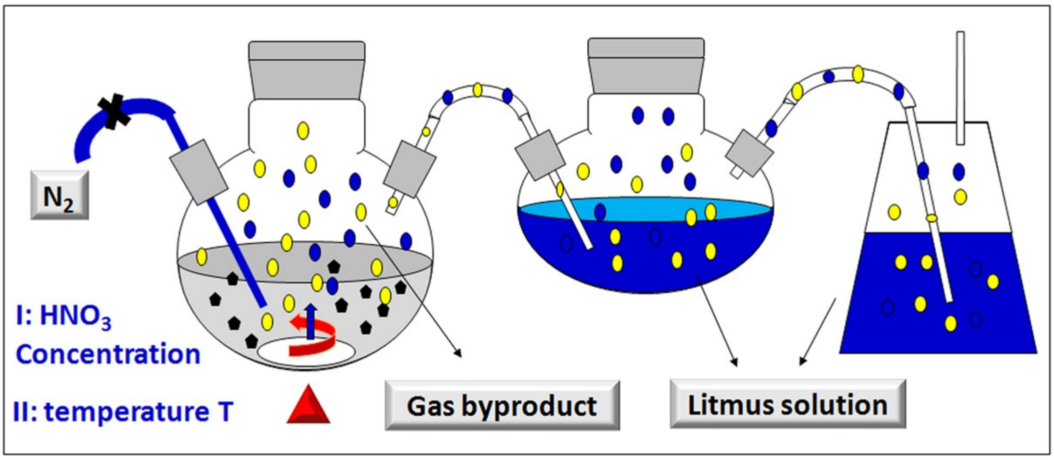

Figure S2. Schematic of indicative experiment. Gas byproduct of the reaction is guided to litmus solution, of which the color could change from blue to red when meeting with acidic substance. Color of litmus solution is monitored in four cases as mixed orthogonally between 1) HNO_3 concentration (N_2 is guided or not to provide low/high concentration) and 2) temperature T (125°C and 170°C). Before reactions take place, air is expelled by N_2 (99.99% in purity) for 20min. All the material (and hence the concentration) used in the reaction is same to that described in the experimental section, except for that no additional HNO_3 is added here.

Table SI Color evolvement of litmus solution in the four indicative experiments

Order	Description	litmus solution color change with time(min)									
		0	20	30	50	70	90	110	120	130	140
No. 1	170 ^{o}C&High[a]							Air imported [c]			
No. 2	170 ^{o}C&Low[b]										
No. 3	125 ^{o}C&High[a]										
No. 4	125 ^{o}C&Low[b]										

[a] N_2 was not conducted, thus HNO_3 accumulates in the container, thus hence provides

background with relative higher concentration.

[b] HNO_3 was guided out by N_2, thus relative low concentration was provided.

[c]Air was imported only in case of No.1 experiment, in all other three experiments, no air was imported, thus the color changes shows HNO_3 was produced.

Figure **S2** depicts the "indicative experiment" used to judge the role of HNO_3 in the low temperature reaction. Litmus solution was used to judge nature of gas byproduct of reaction. That is, if acidic gas was obtained, like HNO_3 or NO_2, the litmus solution should change from its original blue color to the red. Otherwise, it will remain unchanged. Orthogonal experiments were designated with respect to temperature & HNO_3 concentration: for temperature, 170^{o}C and 125^{o}C were chosen; while for concentration, N_2 bubbles (expel the byproduct gas) were used or not so as to provide lower or higher HNO_3 concentrations. Before reactions, air was expelled by N_2 bubbles (purity of 99.99%) for 20min. All experiments were monitored and recorded by a digital video camera, of which the color evolvement with time was collected in Table **SI**. It could be found that, when it was reacted at 170^{o}C & W/O N_2 bubbles (**No. 1**), color of litmus solution remained blue (original color) during the whole reaction; But after air was introduced by fan, it changed quickly to red, indicating that NO had been mainly produced. Such NO could then react with O_2 and led to NO_2. The NO_2 could then reacted with H_2O and obtain HNO_3, which changed litmus color from blue to red. In all other three cases, litmus solution changed gradually from blue to red, showing HNO_3 was produced in major. The indicative experiments thus clearly showed that during the reaction, HNO_3 presented oxidative nature mainly in both higher temperature and higher concentration. Then in the solvothermal reaction used here, oxidative HNO_3 should not conduct in the reaction since the temperature was as low as 125 ^{o}C.

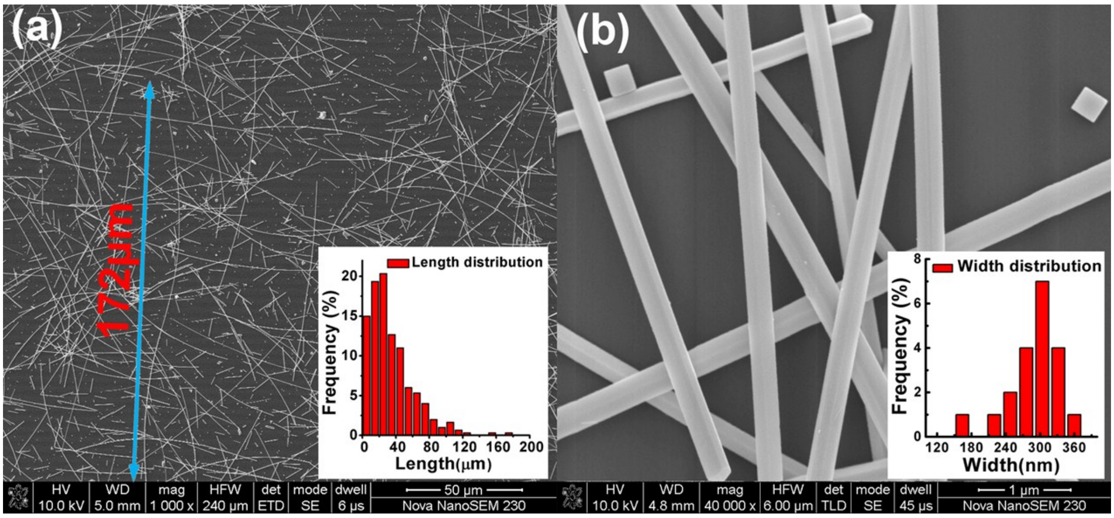

Figure S3. Typical SEM images of AgNWs synthesized by 1-step polyol method 125 ^{o}C and corresponding statistics on both nanowire length (a) and width (b).

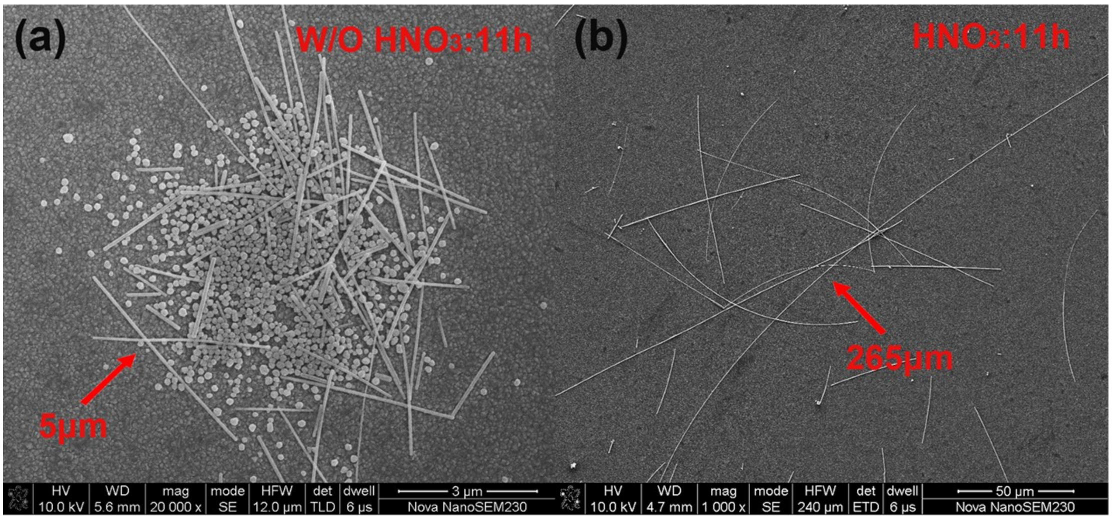

Figure S4. Typical SEM images of AgNWs synthesized by solvothermal reaction at 125 °C: (a) 11h & W/O HNO_3 pre-added, (b) 11h & with HNO_3 pre-added (0.5 mL, 0.22 mol/L).

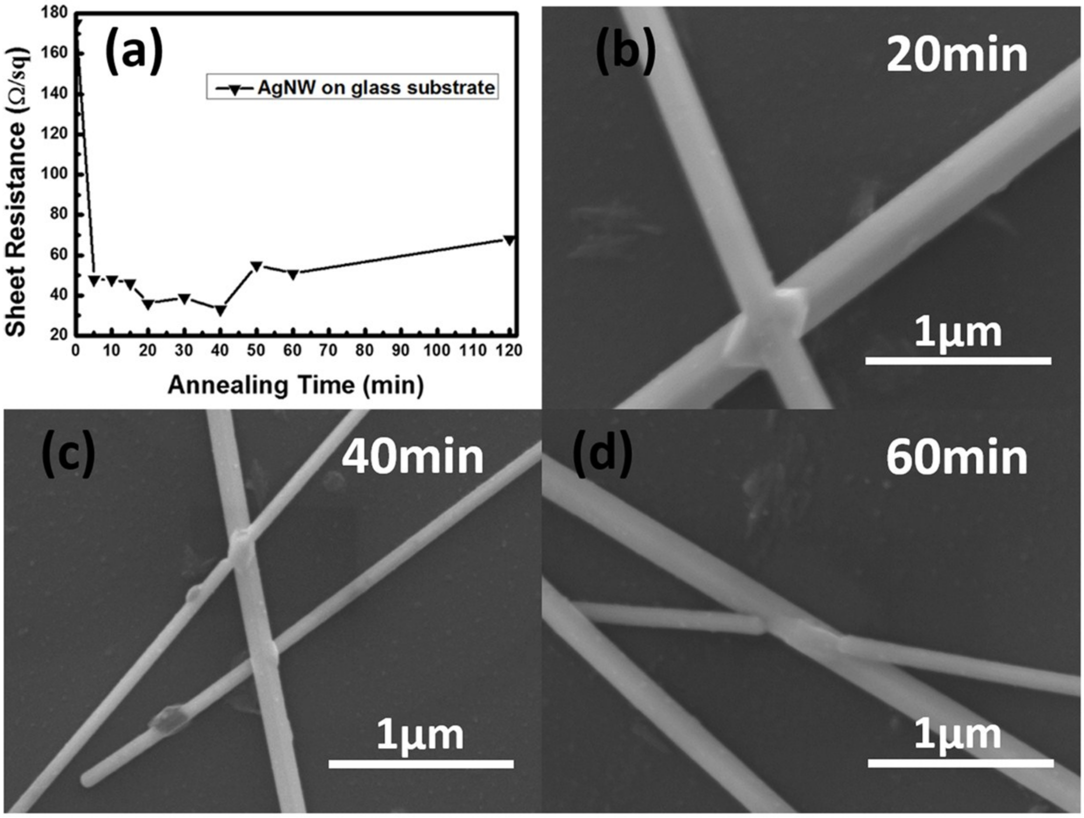

Figure S5. (a) Effect of annealing timeon Sheet resistance of AgNWs TCFs on glass substrate (temperature was 200^{o}C). SEM images of contact point between AgNWs annealed at different period: (b) 20 min, (c) 40 min, (d) 60 min.