

**ESI (Electronic supporting information)**

**Silver nanowires growth via branch fragmentation of electrochemically grown silver dendrites<sup>§</sup>**

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**Fig. S1** FE-SEM images of branch breaking process

**Fig. S2** UV-vis absorption spectra of different relaxation time

**Fig. S3** XRD patterns of as-prepared NWs

**Fig. S4** TEM image of Ag nanostructures electrodeposited at 10 mM, 2 V, and 120 s, then relaxed at 10 mM for 5h

**Fig. S5** SEM image of Ag nanostructures electrodeposited at (a): 0.001 mM, 30 V, and 60min; (b) 500 mM, 30 V, and 30s.

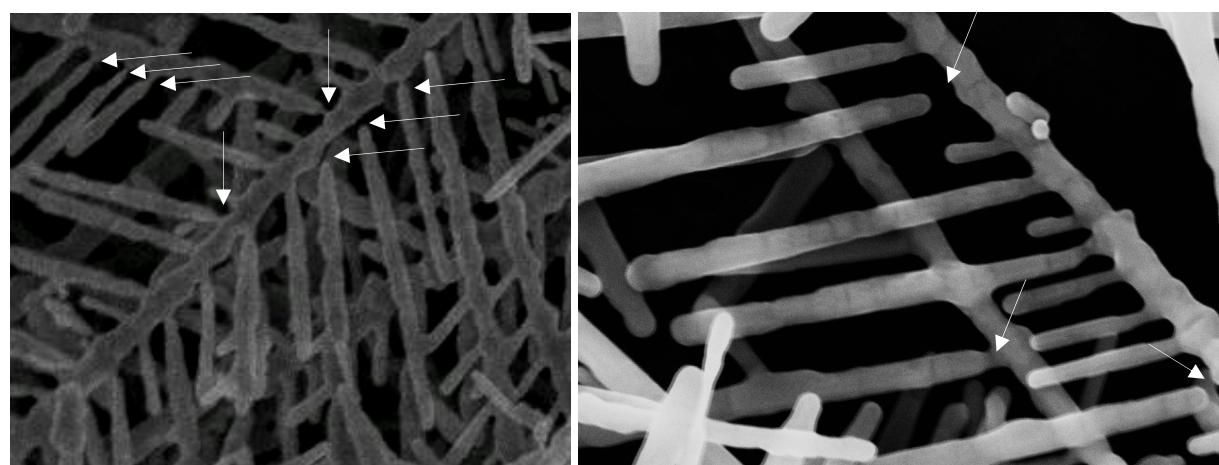


Fig. S1 FE-SEM images of branch breaking process. The white arrows represent the breaking regions.

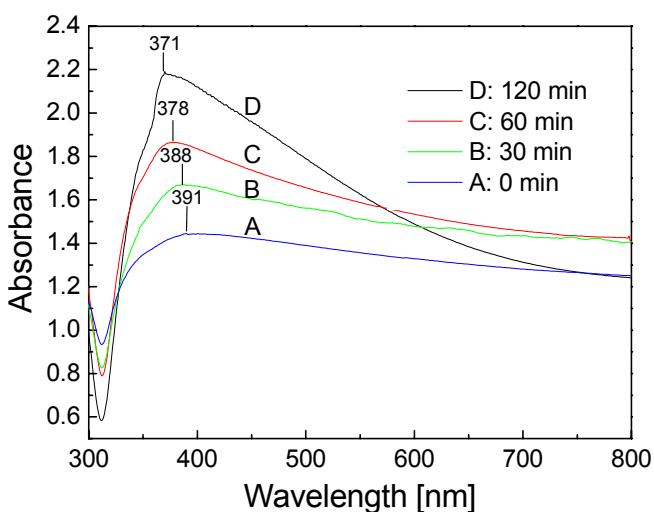


Fig. S2 UV-vis absorption spectra of different relaxation time: (A) 0 min, (B) 30 min, (C) 60 min, and (D) 120 min, following the electrodeposition at the same conditions as Fig. 2.

Fig. S2 represents the UV-vis spectra taken from the ethanol suspensions of the different specimens that were investigated by electron microscopy in Fig. 2(a)-(c). The relaxation time ( $t$ )-dependent change in optical features observed in these spectra correlates well with the SEM images. At  $t = 0$  min, the surface plasmon resonance (SPR) of silver dendrites displays a weak plasmon peak at about 391 nm (curve-A). The intensity of the plasmon peak increases as prolonging  $t$  to 30 min in curve-B and  $t = 60$  min in curve-C. In the meantime, the maximum of the plasmon peaks for the two curves exhibits a blue-shift from  $\sim 390$  to  $\sim 380$  nm which was always described as the transverse mode of Ag NWs or nanorods. This could be considered as the optical signature of formation of silver nanowires in the current reaction system by a branch breaking mechanism as shown in Fig. 2(b). Moreover, with fragmentation of rod-like branches, the trunks of silver dendrites can convert into long NWs, which would support a blue-shift optical style of the plasmon peak. These results are consistent with the theoretical predictions: with increasing the aspect ratio, the transverse SPR band shifts slightly to the blue side.<sup>[1]</sup> As the breaking process further proceeds, the plasmon peak shifts to  $\sim 371$  nm at  $t = 120$

min (curve - D), and the plasmon band becomes relatively narrow. Thus the conversion of Ag nanostructures into the single NWs can be formed as demonstrated in Fig. 2(c) and Fig. 3(a).

[1] Y. G. Sun, Y. D. Yin, B. T. Mayers, T. Herricks and Y. N. Xia, Chem. Mater. 2002, **14**, 4736.

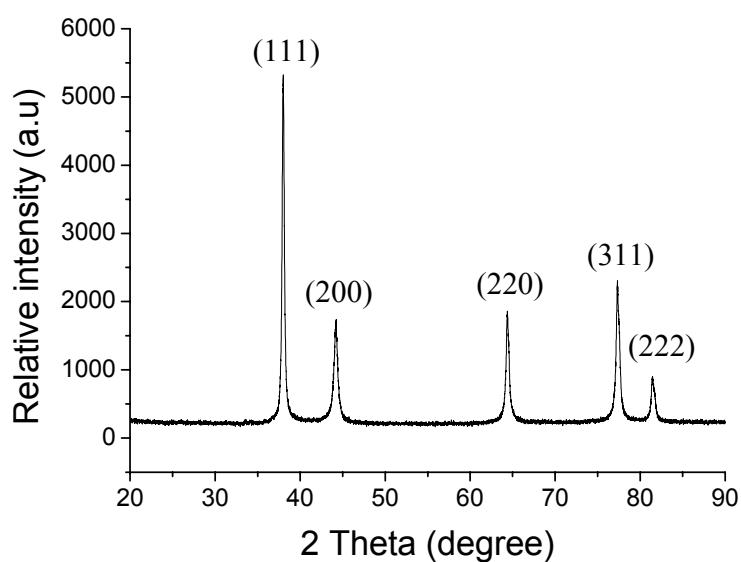


Fig. S3 XRD patterns of as-prepared NWs under the same experimental conditions as in Fig. 2

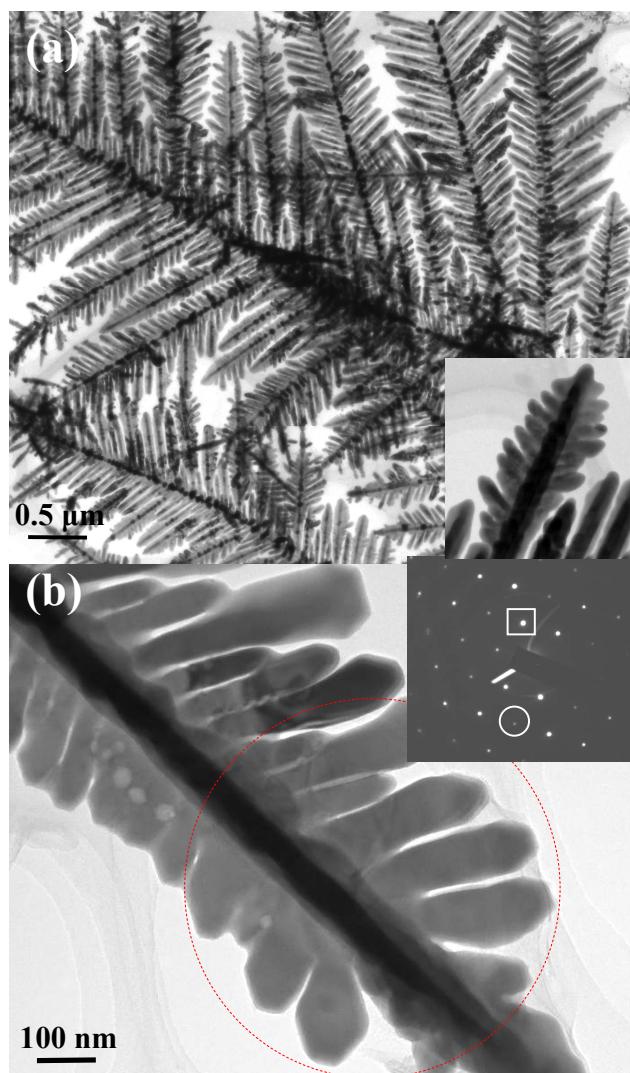


Fig.S4 (a) TEM image of electrodeposited Ag nanostructures with silver ions concentration  $[\text{Ag}^+]$ , applied potential [V] and reaction time [t]: (a) 10 mM, 2 V, 120 s, respectively; (b) Relaxed structure of Figure 6a at the silver ions concentration and relaxed time, 10 mM and 5h, respectively. The SAED pattern of circled area indicates a perfect single crystalline structure.

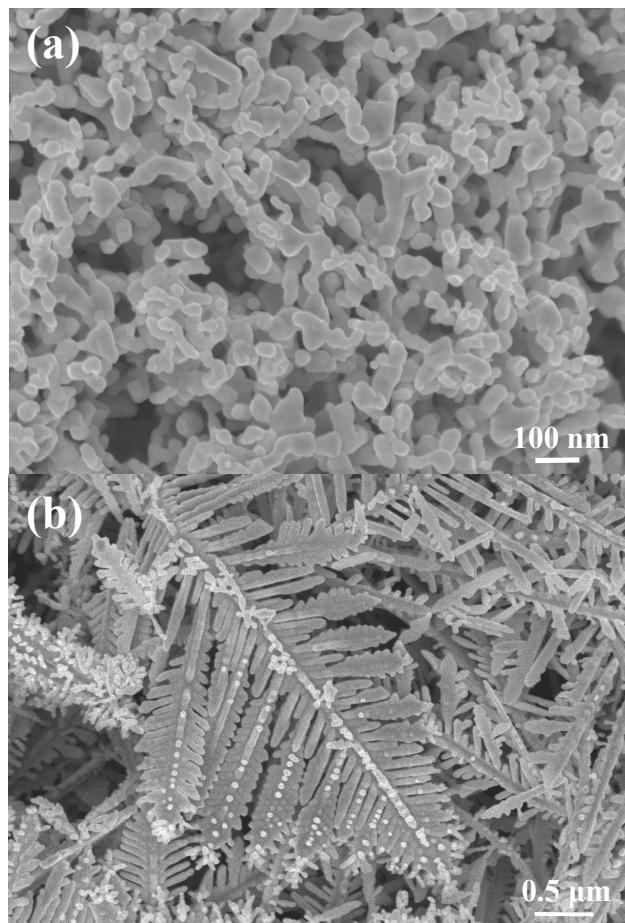


Fig. S5 SEM image of Ag nanostructures electrodeposited at the silver ions concentration, applied potential and reaction time, (a): 0.001 mM, 30 V, and 60min; (b) 500 mM, 30 V, and 30s.