Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Growth of Non-branching Ag Nanowires via Ion Migrational - Transport Controlled 3D Electrodeposition

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Experimental procedure

Only two ingredients are required in this protocol: silver electrodes and water or silver nitrate aqueous solution. Two parallel electrodes of silver plate (99.995%) with dimension 50×10×0.5 mm separated by a distance of 10 mm were immerged in the electrolyte solution. The deposition process was performed in various concentrations of $AgNO_3$ with a strong direct current (DC) potential of 1-30 V. After finishing the deposition process, the product is transferred to a SiO_2 substrate. Then the product was washed with ethanol and distilled water, and dried at ambient temperature. The morphology and surface structure of the nanowires were characterized by scanning electron microscopy (SEM, JSM-7000F) and transmission electron microscopy (TEM, JEM-2100). The samples used for TEM observations were prepared by directly taking some products onto a copper grid and evaporated in air at room temperature.

Details of simulation parameter and the calculated results

We have performed numerical simulations of the electric field distributions in the vicinity of the electrodes using a finite element partial differential equations solver (FlexPDE).[1] FlexPDE can numerically solve systems of first- or second order partial differential equations in one-, two- or three- dimensional geometry based on the finite element method. The basic equation is the Poisson and Planck-Nernst equation. Left and right boundary conditions both are Neumann conditions. For all other boundaries (top, bottom, and wire shape), Dirichlet conditions were used.

We have simulated the steady-state Ag+ current by solving the Poisson and Planck-Nernst equation:

Poisson:

$$\Delta(\varepsilon(\vec{r})\Delta\phi(\vec{r})) - \xi \cdot q_{Ag^+} c_{Ag^+} - \xi \cdot q_{NO_3^-} c_{NO_3^-} = 0$$

Nernst-Planck:

$$\Delta(D_{Ag^+}\Delta c_{Ag^+} + \xi \cdot \mu_{Ag^+} c_{Ag^+}\Delta\phi) = 0$$

$$\Delta(D_{NO_3^-}\Delta c_{NO_3^-} + \xi \cdot \mu_{NO_3^-} c_{NO_3^-}\Delta\phi) = 0$$

With the electrical potential ϕ, the concentration c, the charge q, the diffusion constant D and the mobility $\mu = qD / k_B T$.

The steady state provides $-\Delta j_i = \partial c_i / \partial t \equiv 0$ (continuity equation).

The ion currents are the sums of the diffusion current and drift current:

$$\vec{j}_{Ag^+}(\vec{r}) = -D\Delta c_{Ag^+} - \mu_{Ag^+} c_{Ag^+} \Delta\phi$$

$$\vec{j}_{NO_3^-}(\vec{r}) = -D\Delta c_{NO_3^-} - \mu_{NO_3^-} c_{NO_3^-} \Delta\phi$$

The simulation was performed $\xi = 1$

Parameters:

$$c'^{\,bulk}_{Ag^+} = c'^{\,bulk}_{NO_3^-} = 1E-6 \text{ (molar)}$$

$$D_{Ag^+} = D_{NO_3^-} = 1.65E-9 \,(\text{m}^2/\text{s})$$

Boundary conditions:

Top: $\phi_{bot} = 0;\ c_{Ag^+} = c'_{Ag^+} * 1000 * N_A(m^{-3});\quad c_{NO_3^-} = c'_{NO_3^-} * 1000 * N_A(m^{-3});$

Left and right: $\partial\phi / \partial n = 0$

Bottom: $\phi_{low} = -50V;\quad c_{Ag^+} = 0;\quad \partial c_{NO_3^-} / \partial n = 0$

Geometry:

Height of simulation space $A = 3\mu m$

Wire width w=100 nm

Distance between wires $L =$ 100 nm, 200 nm, 400 nm, 800 nm, 1000 nm

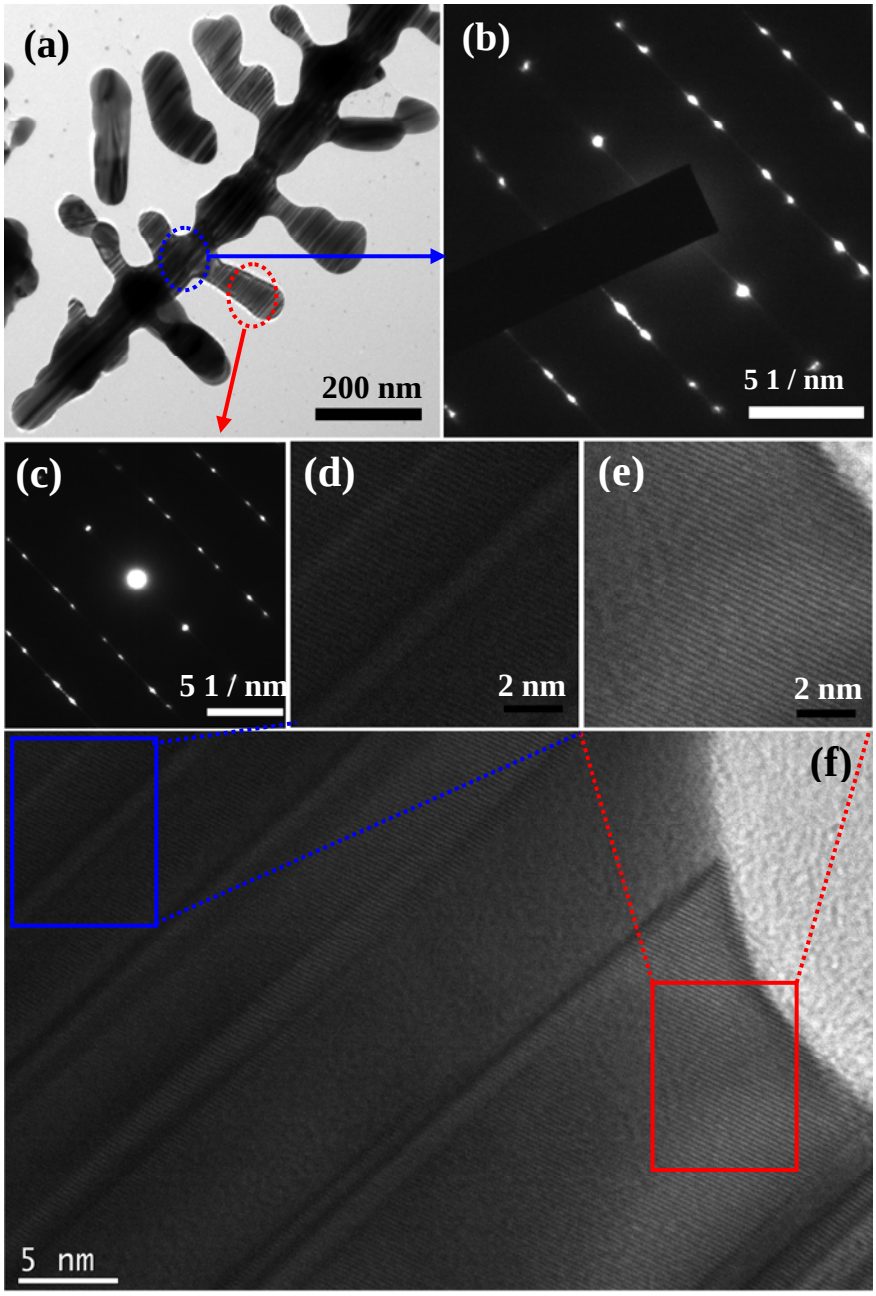

Fig. S1 TEM images of silver dendrites, (a) A magnified image of one dendrite with several branchings. A SAED pattern of the corresponding backbone is shown in (b). (c) the SEAD pattern of one branch, (d) and (e) are the magnified HREAM images from the two rectangular regions of (f), (f) a HREAM image of the dendritic crotch. The spacing of the observed lattice planes is 2.265 Å and 2.366 Å for the backbone (blue region) and the crotch (red region) of nanowires, respectively.

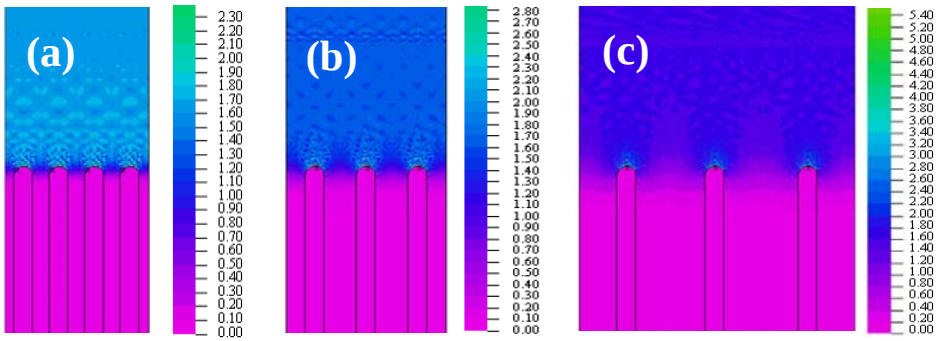

Fig. S2 (a) - (c) interspaces dependent - ion currents for interspaces of nanowires array of 100 nm, 200 nm and 400 nm, respectively.

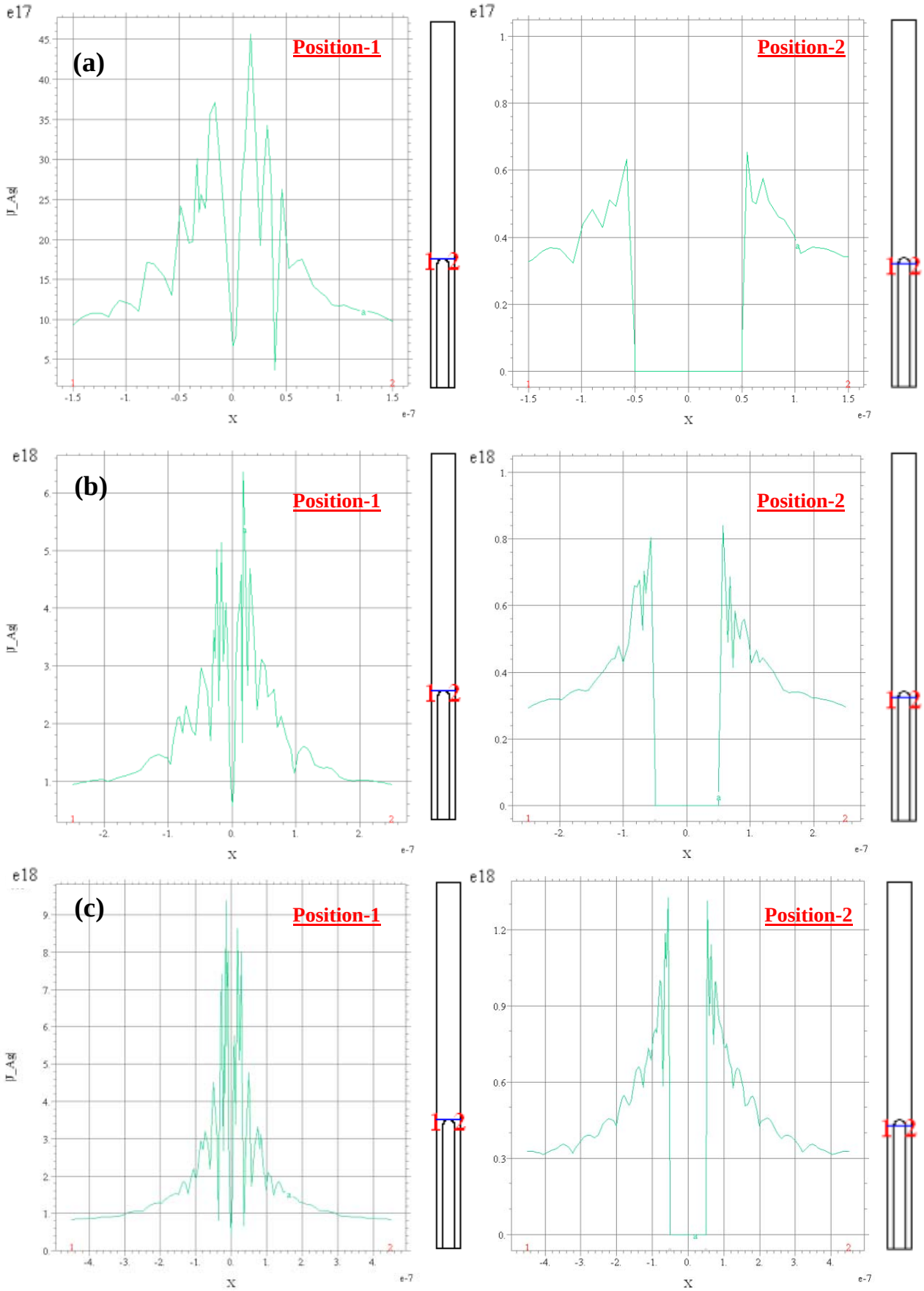

Fig. S3 Intensity of Ag ion flux for various interspaces of Ag nanorods at position 1 (tip of Ag nanorod), and position 2 (50 nm below of Ag tip) as shown by the blue line，indicating a Ag ion flux for (a) 200 nm, 0.6:25, (b) 400 nm, 0.8:3, and (c) 800 nm, 1.3:4.

1 R. D. Coalson and M. G. Kurnikova, *IEEE Transactions on Nanobioscience* 2005, **4**, 81.