"Hot spots" Growth on Single Nanowire Controlled by Electric Charge

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Table of Contents

SI.1. Materials and Characterizations.

All commercial materials were used as received unless specified. The nanostructure and composition of silver nanowires was characterized by TEM, STEM, HRTEM (200kV, Tecnai G2 F20 S-TWIN; FEI), and SEM (Quanta 400 FEG; FEI), EDX (EDAS) at CAS-Platform for Characterization & Test in Suzhou Institute of Nano-tech and Nano-bionics. Image analyses were done using home-written SCILAB codes

SI.2. Characterizations of Ag Nanowires Before and After GRR.

The as-synthesized Ag nanowires were characterized by TEM, SEM in Figure S1. The TEM and SEM images in Figure S1A-B shows that the Ag nanowires are of tens nm diameter and very long length. Figure S1C-D shows that the diameter and the length of Ag nanowires are 50.1±8.5 nm and 6.3±3.6 μm.

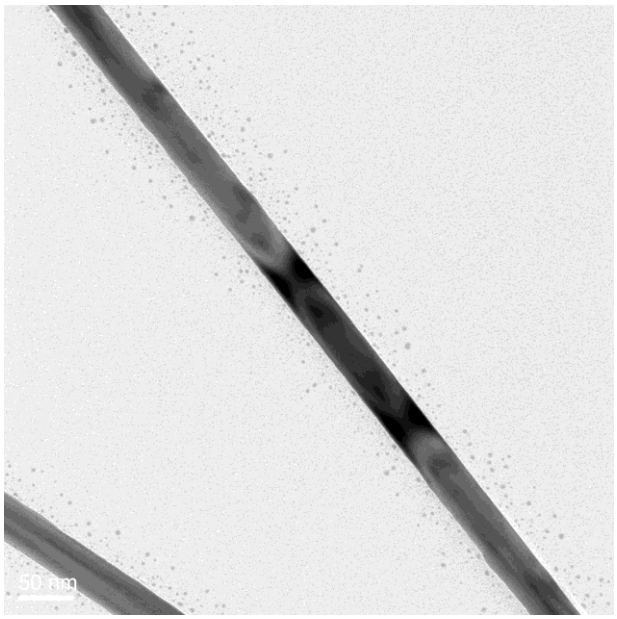

Figure S1. TEM image of as synthesized Ag nanowires.

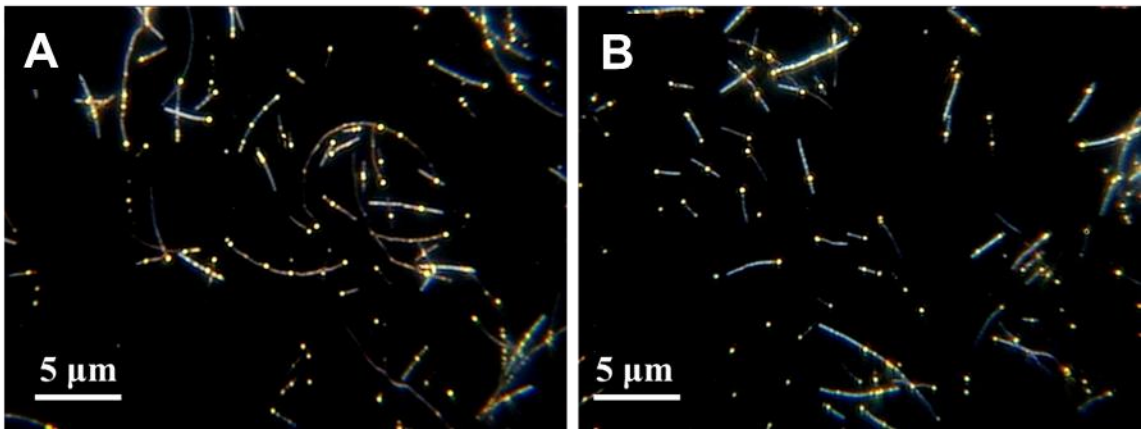

Figure S 2. Dark-field image of well dispersed single Ag nanowires taken by color camera after 2.4 ks GRR at 0.02 mM [$HAuCl_4$].

SI.3. Directly correlate the DFM image and SEM images after GRR

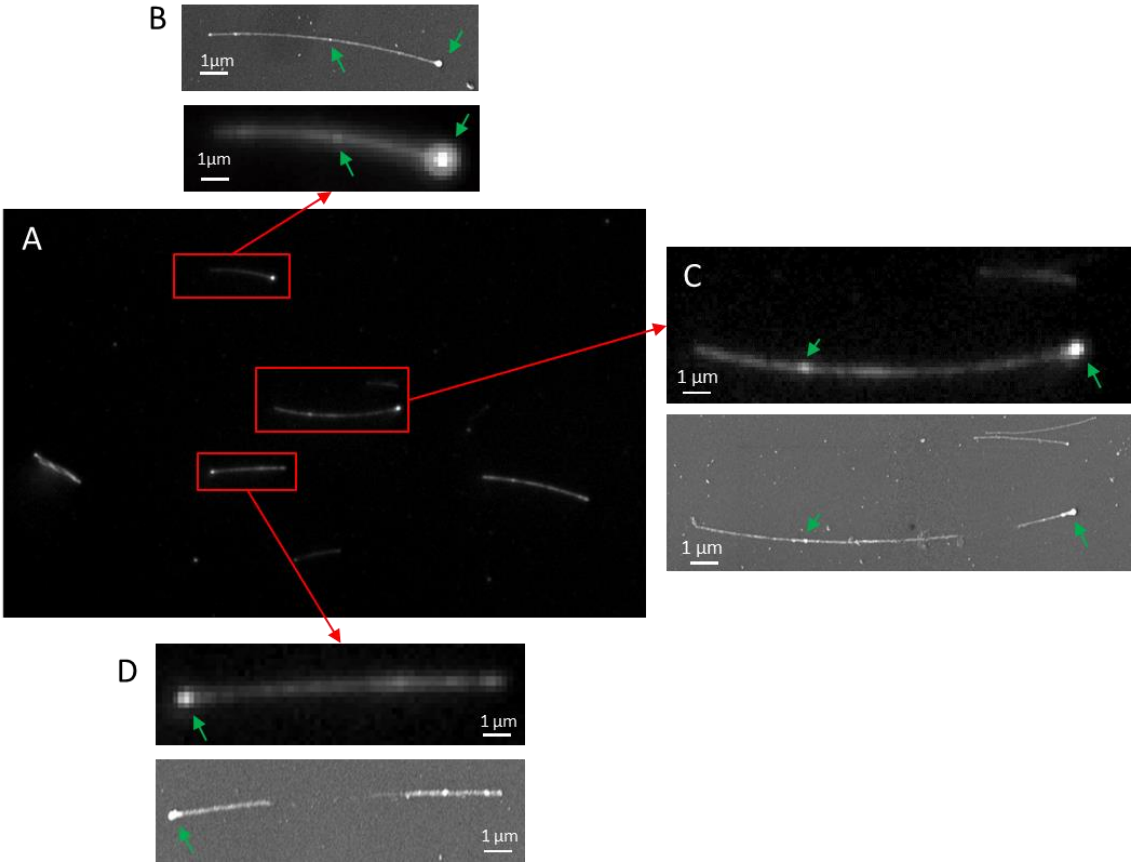

Figure S 3. Directly correlate the DFM image and SEM images on the same sample after GRR for ~2400 s. (A) DFM image. (B)-(D) Examples for the direct correlation of the DFM image and SEM images SEM image.

SI.4. EDX measurement of hot spots

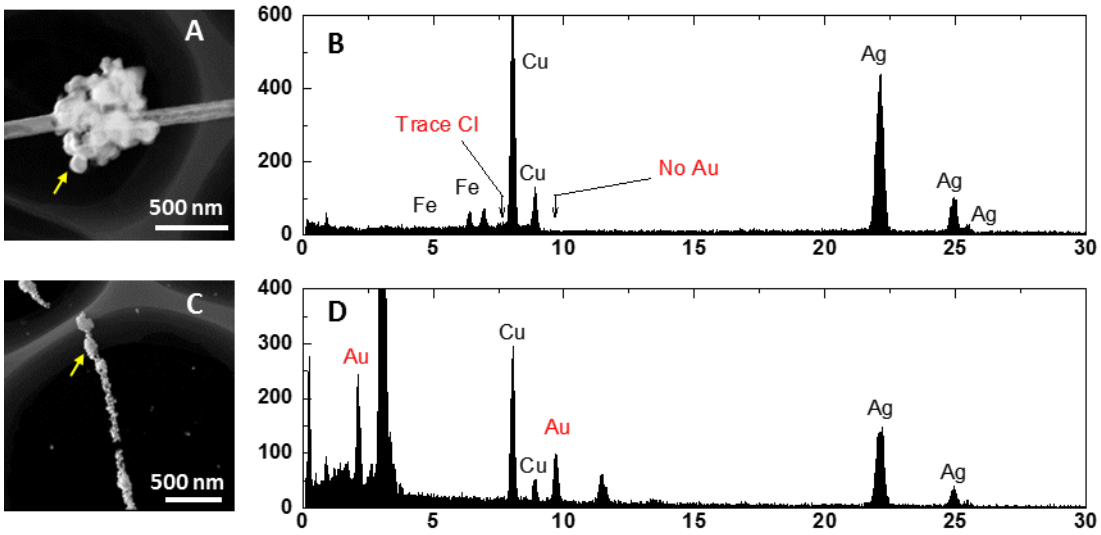

Figure S 4. TEM and EDX measurement of hot spots. (A) TEM of hot spots generated at 0.02 mM $HAuCl_4$. (B) EDX of hot spots generated at 0.02 mM $HAuCl_4$. (C) TEM of hot spots generated at 0.50 mM $HAuCl_4$. (D) EDX of hot spots generated at 0.50 mM $HAuCl_4$.

SI.5. STEM and EDX for the body of Ag nanowire reacted with $HAuCl_4$

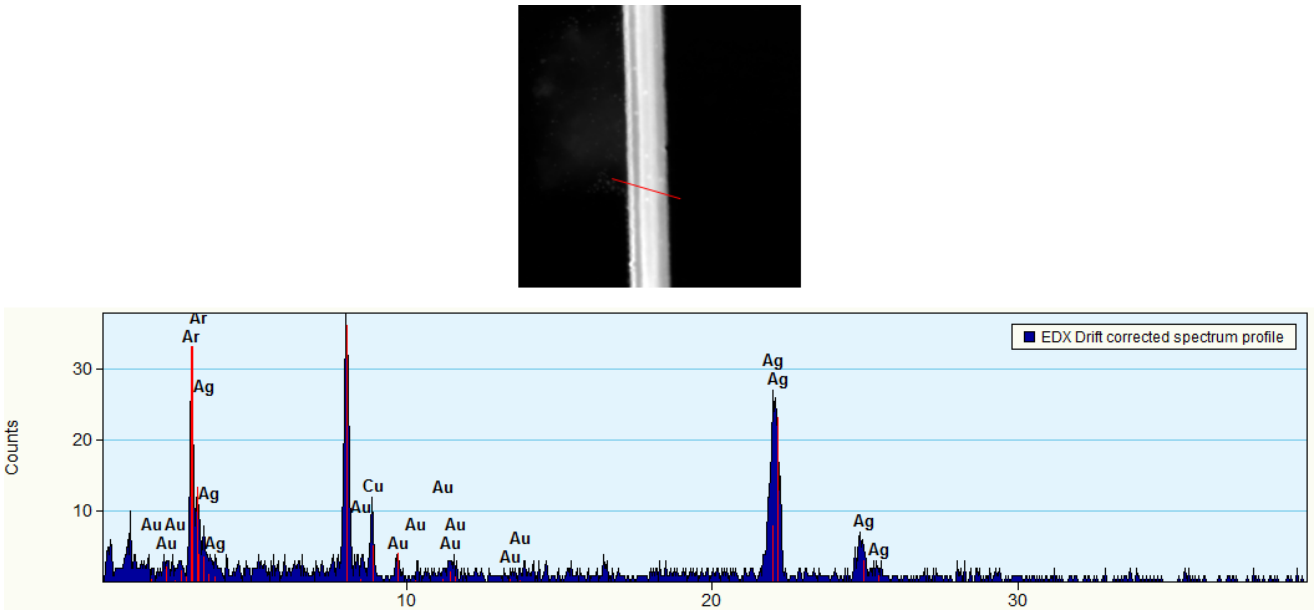

Figure S 5. STEM and EDX for the body of Ag nanowire reacted with 0.02 mM $HAuCl_4$ reacted for about 1200 s.

SI.6. Electrochemical Potential Measurements of Ag Nanowires during the GRR.

All experiments were done at room temperature under ambient conditions.[1] All electrochemical potential measurements were done at open circuit condition in CS350 Potentiostat/galvanostat (Wuhan CORRTEST Instruments CO., LTD) with a three-electrode cell. The reference electrode is the Ag/AgCl/sat KCl reference electrode. All the potentials were quoted with respect to RHE reference electrode for the convenience of comparison. The counter electrode was a large area Pt plane. The working electrode is a bare Au electrode (Diameter is 2 mm. CH Instruments, Inc), which was polished with the slurry of 0.05 μm alumina powders (CH Instruments, Inc) and was sonicated in water.

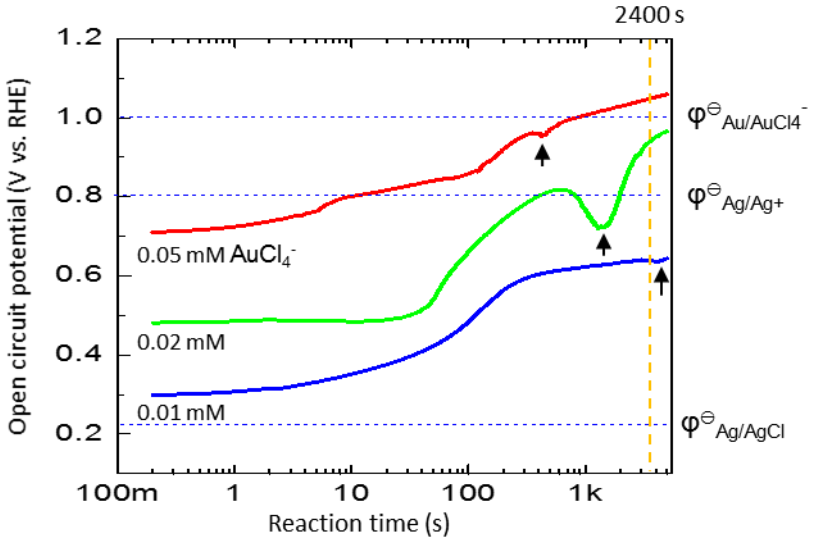

Figure S 6. Electrochemical potential trajectories at different [$HAuCl_4$]s during GRR. The yellow dash line indicates the point corresponding to 2400 s in the OCP results.

SI.7. Energy Loss for Different Distance Distribution of Neighbored Hot Spots

a. Energy loss in one unit

In order to support the growth of hot spots, electrons need to transfer from some parts of the Ag nanowire to the hot spots. We can extract one unit between two neighbored hot spots as shown in Figure S 7. Assume the electrons from this segment equally support these two hot spots, then the place where I = 0 is in the middle. If the ability of generating electron is uniform along this segment, the current function between the zero point to hot spot 2 is,

$$i(x) = k_1 x \qquad \text{(Eq.S 1)}$$

Where k_1 (A m^{-1}) is the ability of generating electron of unit length. While the resistance of the wire is also proportional to the length

$$dR = \frac{\rho}{S} dx = \rho' dx \qquad \text{(Eq.S 2)}$$

Where ρ (Ω·m) is the resistivity, S (m^2) is the cross sectional area, ρ' (Ω·m^{-1}) is the resistivity per unit length (the diameter of Ag nanowires in this paper is D = 50.1±8.5 nm). ρ' equals 8.37×10^6 Ω·m^{-1}. Therefore the energy loss by Joule heat on the right side can be expressed as

$$\mathrm{P_r} = \int_0^{l/2} i(x)^2 dR = \int_0^{l/2} k_1^2 x^2 \rho' dx = \frac{k_1^2 \rho'}{24} l^3 \qquad \text{(Eq.S 3)}$$

So the total energy loss by Joule heat on both left and right side is

$$P = P_r + P_l = \frac{k_1^2 \rho'}{12} l^3 \qquad \text{(Eq.S 4)}$$

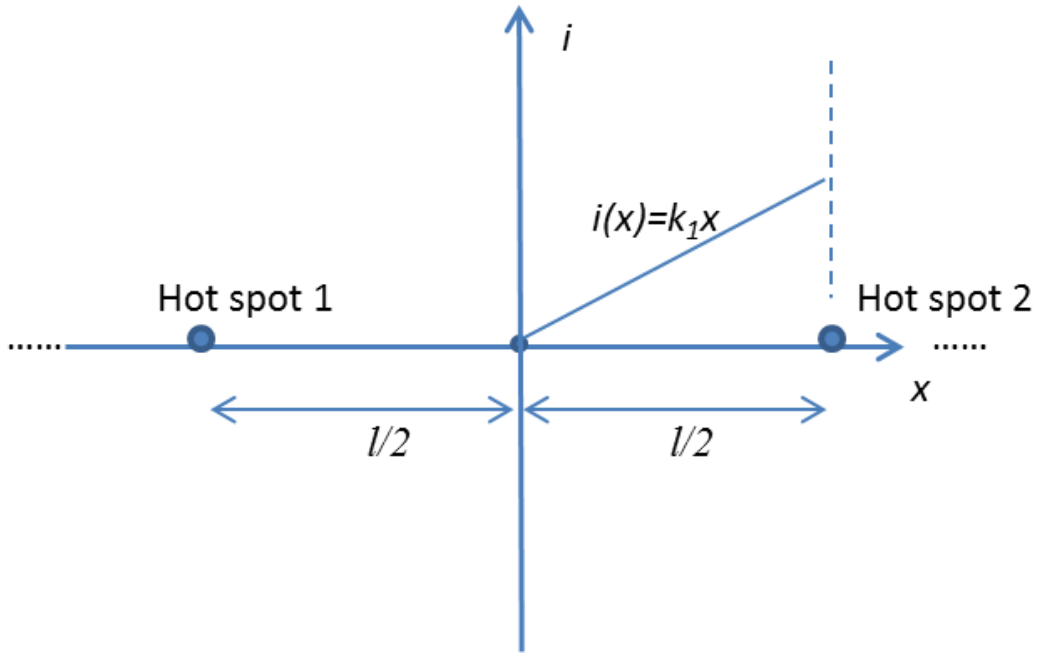

Figure S 7. Model of energy loss for one unit with the length of *l*.

The diameter of Ag nanowires in this paper are D = 50.1±8.5 nm. According to Figure 2A, the quick reaction on each location of the Ag nanowire can finish in Δt=~50 s. The ability of generating electron of unit length is

$$k_1 = \frac{\rho_{Ag}\pi(D/2)^2 F}{M_{Ag}\Delta t} = 3.70\times10^{-7}\ (\mathrm{A\ m^{-1}}) \qquad \text{(Eq.S 5)}$$

Where ρ_{Ag} is the density of silver, F is the Faraday constant, M_{Ag} is the molar mass of Ag. So the total energy loss by Joule heat is

$$P = \frac{k_1^{\,2}\rho'}{12} l^3 = 9.55\times10^{-8} l^3 \quad \text{(W)} \qquad \text{(Eq.S 6)}$$

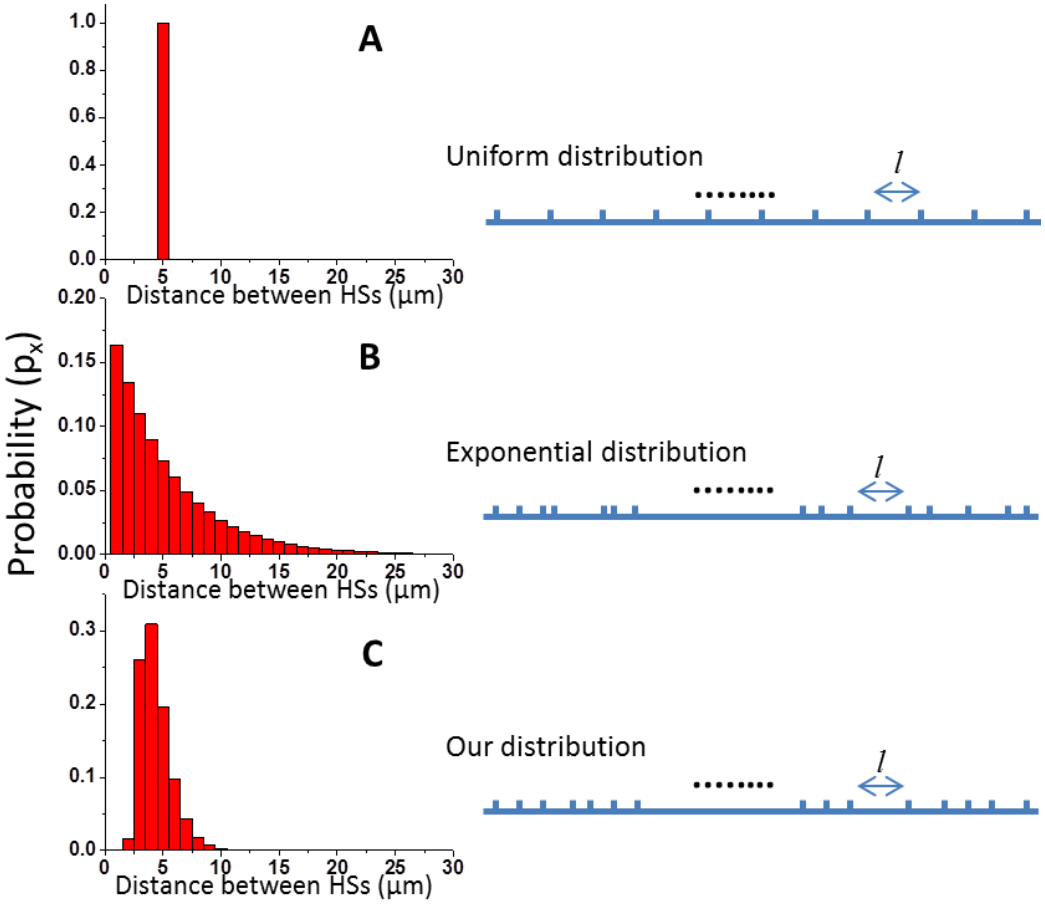

Figure S 8. Three distributions of the distance between HSs. (A) Uniform distribution. (B) Exponential distribution. (C) The distribution in our research.

b. Energy loss for uniform distribution

For a nanowire with the length of L μm, the length of each segment at uniform distribution in Figure S 8A is,

$$l = L / N \qquad \text{(Eq.S 7)}$$

N is the total number of segments. Then the energy loss per unit length is,

$$P_U = \frac{NP}{L} = \frac{N}{12L} k_1^2 \rho (\frac{L}{N})^3 = \frac{1}{12} k_1^2 \rho \frac{L^2}{N^2} \qquad (\text{W m}^{-1}) \qquad \text{(Eq.S 8)}$$

Since $\frac{k_1^2 \rho}{12}$ equals 9.55×10^{-8}, so

$$P_U = 9.55\times10^{-8} \frac{L^2}{N^2} \qquad (\text{W m}^{-1}) \qquad \text{(Eq.S 9)}$$

Let $< l >$ = L/N, $< l >$ is the average length of each segment, then

$$P_U = 9.55\times10^{-8} < l >^2 (\text{W m}^{-1}) \qquad \text{(Eq.S 10)}$$

c. Energy loss for exponential distribution

If the hot spots randomly appear on the nanowire, the distribution of the distance between two neighbored hot spots should be an exponential function,

$$p_x = k_2 e^{-k_2 x} \qquad \text{(Eq.S 11)}$$

Where

$$\int_0^\infty x p_x dx = \int_0^\infty k_2 x e^{-k_2 x} dx = 1/k_2 = L/N \qquad \text{(Eq.S 12)}$$

$$k_2 = N/L \qquad \text{(Eq.S 13)}$$

So the energy loss per unit length is

$$P_{\text{exp}} = \frac{1}{L} \int_0^\infty \frac{1}{12} k_1^2 \rho x^3 g N k_2 e^{-k_2 x} dx = \frac{k_1^2 \rho N}{2 k_2^3 L} = \frac{k_1^2 \rho}{2} \frac{L^2}{N^2} \qquad (\text{W m}^{-1}) \qquad \text{(Eq.S 14)}$$

So

$$P_{\exp} = 5.73e-7\frac{L^2}{N^2} = 5.73\times10^{-7}< l >^2 \quad (\mathrm{W\ m^{-1}}) \qquad \text{(Eq.S 15)}$$

d. Energy loss for the distribution controlled by electric field in this paper

The distribution of the distance in our research is

$$p_x = \frac{1}{n_0}\exp(\frac{MQ^2}{Tx} - \frac{1}{n_0}x\exp(\frac{MQ^2}{Tx})); (M = \frac{e^2}{4\pi k\varepsilon_0}) \qquad \text{(Eq.S 16)}$$

In order to normalize the function, a constant k_3 is added,

$$\int_0^\infty k_3 p_x dx = \int_0^\infty k_3 \frac{1}{n_0}\exp(\frac{MQ^2}{Tx} - \frac{1}{n_0}x\exp(\frac{MQ^2}{Tx}))dx = 1 \qquad \text{(Eq.S 17)}$$

And the mathematical expectation is,

$$\int_0^\infty k_3 x p_x dx = \int_0^\infty k_3 \frac{1}{n_0}x\exp(\frac{MQ^2}{Tx} - \frac{1}{n_0}x\exp(\frac{MQ^2}{Tx}))dx = L/N \qquad \text{(Eq.S 18)}$$

The total energy loss by Joule heat on the whole nanowire is

$$P_{our} = \frac{N}{L}\int_0^\infty \frac{1}{12}k_1^2\rho x^3 g k_3 \frac{1}{n_0}\exp(\frac{MQ^2}{Tx} - \frac{1}{n_0}x\exp(\frac{MQ^2}{Tx}))dx \quad (\mathrm{W\ m^{-1}}) \qquad \text{(Eq.S 19)}$$

$$P_{our} = \frac{k_1^2 k_3 \rho N}{12Ln_0}\int_0^\infty x^3\exp(\frac{MQ^2}{Tx} - \frac{1}{n_0}x\exp(\frac{MQ^2}{Tx}))dx \ (\mathrm{W\ m^{-1}}) \qquad \text{(Eq.S 20)}$$

When plot Eq.S25, Eq.S30 and Eq.S35 in Figure 5, we can get the energy loss for these three different distribution types. Energy loss for the distribution controlled by electric field in this paper shows much lower level than that for random distribution.

Table 1. Table of parameters

Name of parameters	Symbol	value	Note
Ion mobility of Ag^+($m^2\ s^{-1}\ V^{-1}$)	μ_{Ag^+}	6.42×10^{-8}	[2]
Ion mobility of $AuCl_4^-$ ($m^2\ s^{-1}\ V^{-1}$)	μ_{AuCl^-}	7.05×10^{-8}	[2]Ion mobility of ClO_4^-
Diffusion coefficient of Ag^+(m^2/s)	D_{Ag^+}	1.648×10^{-9}	[2]
Diffusion coefficient of $AuCl_4^-$ (m^2/s)	D_{AuCl^-}	9.59×10^{-10}	[2]
Vacuum permeability (F/ m)	ε_0	8.85×10^{-12}	[2]
Dielectric constant of solution	ε	87	[2]
Electron charge (C)	e	1.60×10^{-19}	[2]
Boltzmann constant (J/K)	k	1.38×10^{-23}	[2]
Resistivity ($\Omega\cdot m$)	ρ	1.65×10^{-8}	[2]For Ag
Resistivity per unit length ($\Omega\cdot m^{-1}$)	ρ'	8.37×10^{6}	For Ag nanowire with 50.1 nm diameter
Number of electrons	Q	counts	
Temperature (K)	T	293	
Electric field in y direction ($V\ m^{-1}$)	$E_y(x)$	-	Variable
Distance to nanowire (m)	H	-	Variable
Charge density at the position x (m^{-1})	$\sigma(x)$	-	Variable
Concentration of Ag^+ ($mol\ m^{-3}$)	c_{Ag^+}	-	Variable
Concentration of $AuCl_4^-$ ($mol\ m^{-3}$)	$c_{AuCl_4^-}$	-	Variable

References:

1. Griffiths DJ, Li Y, Charge density on a conducting needle. *Am. J. Phys.*, 1996; 64; 706-714.

2. Lide DR, Ed. CRC Handbook of Chemistry and Physics; 76th ed., CRC Press, Inc., 1995.