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Elaborately Programmed Nanowires Fabricated by Tapered Push-Pull Nozzle System

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Experimental Section

Preparation of tapered push-pull nozzle system

All the reagents were of reagent grade, were purchased from Sigma Aldrich (USA), and were used without further purification. Deionized (DI) water was used in all experiments. Tollens reagent (5 mM silver nitrate, 10 M ammonia) was prepared from a silver nitrate solution (5 mM) and ammonia water (10 M). The glucose solution (0.01 wt%) was used to reduce the silver ions to form elemental silver. Calcium carbonate was formed by the reaction of sodium carbonate (5 mM) with calcium nitrate solutions (10 mM). Poly (sodium 4-styrenesulfonate: PSS) (mW ~100,000, 0.05 wt%) and hexadimethrine bromide (HDB 0.02 wt%) were used for the preparation of p-HB:PSS polymer.

Different inner diameter glass capillary nozzles(Fig. S2) were fabricated by a capillary stretching technique with a heat puller (PB-7, NARISHIGE, Tokyo Japan). The manual XYZ stage (Sigma KOKI Co., Ltd., Tokyo Japan) served as the nozzle holder (Insert caption in scheme.1 (a)). Throughout the experiments, the position of the nozzle was maintained constant, while the substrate fixed on XY stage was moved by an Opt Mike Controller (OMEC-2BF, Sigma KOKI Co., Ltd., Tokyo Japan). We used the Opt Mike Controller and a personal computer (Panasonic, CF-R4, Tokyo, Japan) with BASIC software to move the XY stage. By moving in the X- and Y-directions, any desired pattern could be obtained. The XY stage was installed on the inverted microscope (Olympus IX71). The flow speed of the solution in nozzle was controlled by the springs pump (NE-1000-SPR, USA) for both injection and aspiration.

The cyclic voltammetry was carried out with a Versa STAT3 (AMETEK) and 0.01 mM Potassium ferric cyanide was used. The scan speed was 5 mV/S.

Preparation of silver wires by different inner diameter TPPNS

Here the Tollens reagent (5 mM) and glucose solution (10 mM) were injected while systematically making the ratio QA, QI (QA=300 μL h^{-1} and QI=10 μL h^{-1}) and the gap constant (gap=30 μm), and the chemical pen was then moved along the X axes by MCS. Silver wires were fabricated by a silver mirror reaction between Tollens reagent and a glucose solution underneath the mesa of nozzle (id.100, 75, 50 and 25μm). Deionized water was used as the surrounding medium. In order to firmly fix the silver wires to the surface of the glass, the glass substrate was immersed beforehand in a saturated aqueous solution of tin chloride for surface treatment. A thin layer of tin ions is formed on the glass surface and was used to fix the silver wire.

Preparation of silver wires by different Qa/Qi and gap

Here we used a 25 μm nozzle and the Tollens reagent (5 mM) and glucose solutions (10 mM) were injected while systematically varying the QA/QI ratio and the gap. Here, the injection rate is maintained constant, QI=10 μm h^{-1}, and only the QA and gap were varied. The effects of different gaps and QA/QI values were investigated. The gap and QA/QI rates jointly determine the width of the silver wires.

Preparation of calcium carbonate nanowire arrays wires by TPPNS

The experimental conditions for calcium carbonate were nozzle inner diameter=25 μm, QA=300 μm h^{-1}, QI=10 μm h^{-1}, gap=30 μm. The injection solutions were calcium nitrate (5 mM) and sodium carbonate (5 mM).

Preparation of P-HB-PSS nanowire arrays wires by TPPNS

The experimental conditions for the p-HB:PSS polymer were nozzle inner diameter=25 μm, QA=300 μm h^{-1}, QI=10 μm h^{-1}, gap=30 mm. The injection solutions were Poly (sodium 4-styrenesulfonate) (mW ~100,000，0.05 wt%) and hexadimethrine bromide (mW ~50,000 0.02 wt%).

Simulation by Comsol Multiphysics software

Considering the accuracy of the Comsol software, we selected a relatively small gap, QA and QI in the simulation experiment, since the Péclet numbers can be relatively smaller and the diffusion larger under these conditions. Thus the width of silver wires could be satisfied the precision of software. Gap=10 μm, QA=10 μL h^{-1} and QI=1 μL h^{-1} are determined. We used nozzles with inner diameters of 25 μm, 50 μm, 75 μm and 100 μm to construct the 3D models (Fig. S4). The Tollens reagent (1 mM) and the glucose solution (2 mM) were configured as two individual injections.

Comsol Multiphysics 4.3b software (Comsol, Stockholm, Sweden) was used to carry out 3-dimentional simulations on a six-core, 64-bit computer (Dell, Texas, USA) with 32 GB of RAM. The Navier-Stokes equation and the convection-diffusion equations were coupled in the simulation. Each of the two injection solutions was assumed to be water with a density of 999.7 kg m^3 and a viscosity of 0.001 Pa·s. The diffusion coefficients for silver ion and glucose were 2.65×10^{-11} m^2 s^{-1} and 1.36×10^{-11} m^2 s^{-1}, respectively. The simulations were run under steady state S2 conditions with the flow boundary conditions at the edges of the nozzle end perimeter sides set as open boundaries (equal to atmospheric pressure).

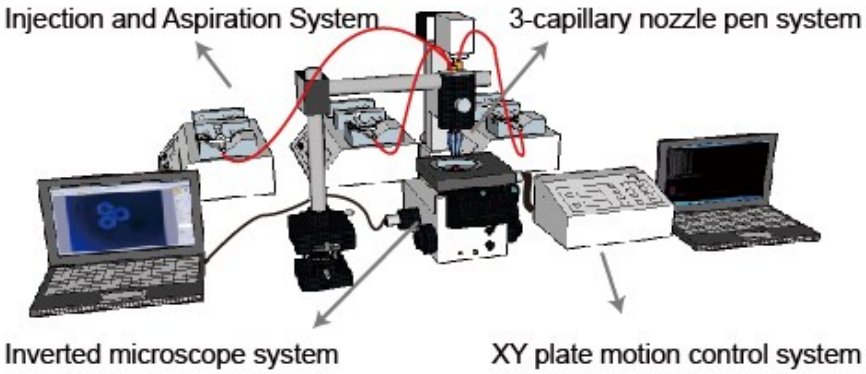
Material physical characterization

SEM images were performed on a scanning electron microscope (SEM, LEO 6510, JEOL, Tokyo, Japan) operating at 5 KV. Samples were prepared by fabricting nanowires on glass surface. HRTEM images and the SAED patterns were obtained on a JEOL-JEM-3200FS microscopy (Tokyo, Japan) with a accelerating voltage of 300 KV. Sample grids were prepared by fabracting nanowires on carbon-coated holey film supported on a copper grid.

Silver wire resistance

we designed a wire with 20 μm on the two sides and 300 nm in the middle on the ITO glass to measure the resistance of the silver nanowires. The two sides of the silver wires were conncected to the current amplifier. In order to prevent the rupture of silver nanowires by heating, we immersed the device in ethanol.

Construction of TPPNS



Scheme S1. The construction scheme of the Tapered Push-Pull Nozzle System.

The TPPNS consists of a reagent injection and aspiration system (IAS), a closely attached tapered 3-capillary nozzle pen system (3-CNPS), an inverted microscope system (IMS) and an XY motion control system (MCS) (Scheme S1). The IAS consists of three syringe pumps with gas tight syringes (10.0 mL SYR, HAMILTON, USA). The tips of 3-capillary nozzles are set close to the glass substrate at the top of the inverted microscope by the manual XYZ motion stage, which can be used to adjust the height of the glass capillary with a 1 μm accuracy. Here, the glass substrate in a petri dish is fixed on the electromotive XY stage, the movement of which can be controlled arbitrarily by the BASIC program through a RS232C interface. The inverted microscope is used to observe both the bottom of the glass capillary and the surface of the glass substrate.

The manufacture of TPPNS

The output of the syringe was connecting to the peek tube (I.D.500 μm, O.D.750 μm) with connecter respectively. And then the top sides (I.D.500 μm，O.D. 1000 μm) of tapered 3-capillaries nozzle pen are hermetically connected with peek tubes by using fused silica capillaries (I.D. 250 μm，O.D. 350 μm) and hot-melt glue (Fig. S1).

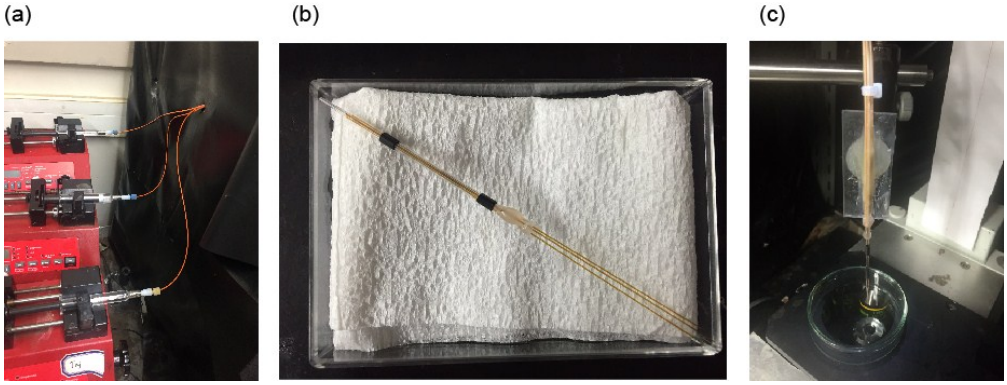


Fig. S1 a) Connection between syringe and peek tube b) Connection between the silica capillary and nozzle c) Connection between peek tube and nozzle pen

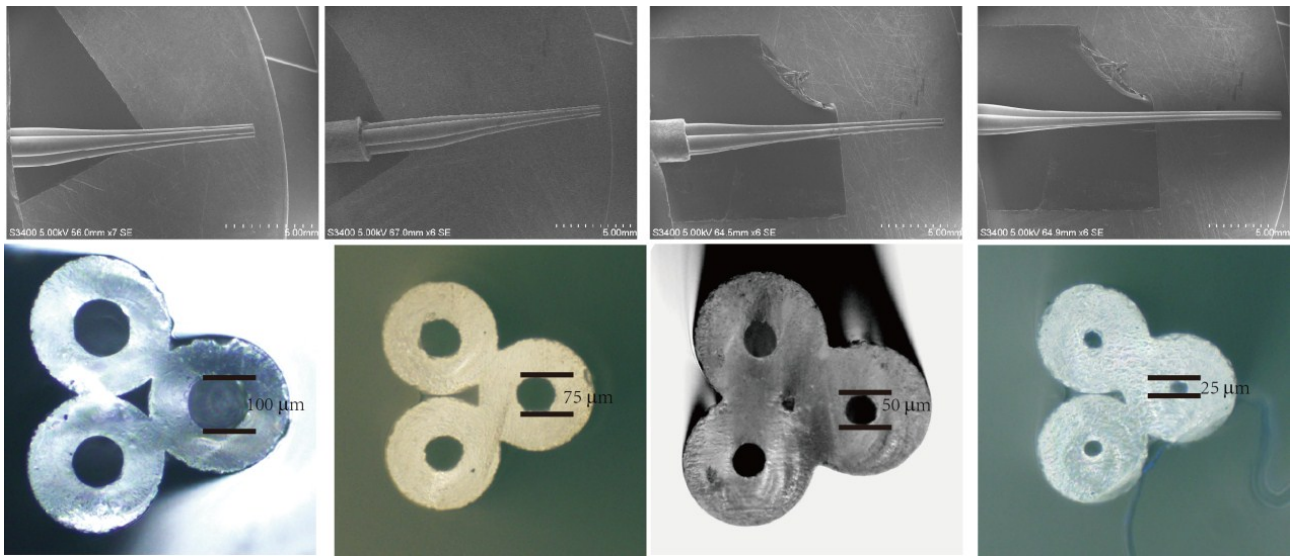


Fig. S2 Different inner diameter nozzle pens.

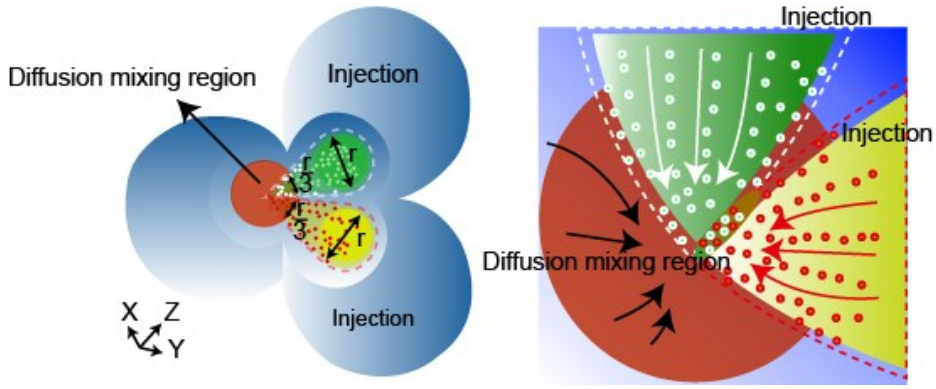


Fig. S3 Illustration of bottom view of 3-capillary nozzle pen.

The Reynolds number is an important dimensionless quantity in fluid mechanics that is used to predict the transition from a laminar to a turbulent flow and is defined as

$$\mathrm{Re} = \frac{2R_H \rho \upsilon}{\eta} \quad (1)$$

where R_H is the hydraulic radius, ρ is the density of the liquid, υ is the average flow speed and η is the dynamic viscosity, respectively. The value Re 2000 is the empirical limit between laminar flow (Re<2000) and turbulent flow (Re>2000).The Péclet number (Pe) is a measure of the convective versus diffusive transport and permits one to evaluate whether diffusion broadens the hydrodynamically confined micro flow stream. The ratio of diffusive transport decreases and the ratio of convective transport arise with decrease of Pe.

$$Pe = \frac{2R_H \upsilon}{D_n} \quad (2)$$

where Dn is the diffusion constant of the solute; the lower the flow speed, the larger the broadening of the flow stream. The hydraulic radius is defined as R_H=2A/P, where A is the cross-section area of the channel at the aspiration and injection nozzles and P is the perimeter. Here the cross-section area A of the channel between the nozzle and substrate takes the value of the circular perimeter circular, so A is equal to 2πrG. P is corresponding to the perimeter of the circle on the substrate and on the mesa of injection and aspiration nozzles, so P is equal to 2×2πr. We find R_H is equal to Gap. In addition, the injection and aspiration rate is defined as Q= υπr^2.
Finally Reynolds and Péclet number equations are reduced to

$$Re = \frac{2\rho G Q}{\pi r^2 \eta} \quad (3)$$

$$Pe = \frac{2GQ}{\pi r^2 D_n} \quad (4)$$

where G is the gap between the end of micro nozzle and substrate surface, Q is the injection and aspiration rate, r is the inner diameter of micro nozzle. Here we also found that the Péclet numbers are inversely proportional to the square of the nozzle inner diameter r and linearly related to the Q and the gap. As a result, the solution diffusion mixing region can be changed by changing these parameters.

In our case, the injection liquid is Tollens reagent and glucose solution separately. The parameters for Tollens solution is ρ= 1.03×10^3 kg m^{-3}, η= 1.02 cp and Dn= 2.65×10^{-11} m^2 s^{-1}. The parameters for the glucose solution are ρ= 1.05×10^3 kg m^{-3}, η= 1.12 cp and Dn= 1.36×10^{-11} m^2 s^{-1}. The injection rate QI is controlled among 1.0 to 10 μL h^{-1} and the aspiration rate is controlled during 5 to 500 μL h^{-1} by a spring pump; the gap G is precisely controlled by the XYZ stage during 5 to 50 μm (Scheme 1c, Table S1, S2).

Reynolds numbers for injection and aspiration are calculated under the condition of G 50 μm, QA 5 μL h^{-1}, QI 1 μL h^{-1} and inner diameter of micro nozzle 25 μm. The corresponding Reynolds numbers are Re_{I1}=0.020, Re_{I2}=0.020 and Re_A=0.102 at the injection and aspiration nozzles respectively. These results corroborate the experimental observations of laminar-flow conditions.

Péclet number are Pe_{I1}=769, Pe_{I2}=1498 and Pe_A=5095 at the injection and aspiration nozzles respectively. The connective transport is more than 100 times larger than the diffusive transport, which therefore does not markedly enlarge the micro nozzle.

Table S1 Reynolds numbers and Péclet number for 3-capillary nozzle pen

D/μm	Q_{I1}/ μL h^{-1}	Q_{I2}/ μL h^{-1}	Gap/μm	Re	Pe
25	1	***	50	0.051	19.6
25	***	1	50	0.047	37.5
25	10	***	50	0.51	196
25	***	10	50	0.47	375
D/μm	Q_A/ L h^{-1}		Gap/μm	Re	Pe
8.3	5	***	50	0.233	88.9
8.3	***	5	50	0.233	169.9

8.3	50	***	50	2.333	889
8.3	***	50	50	2.333	1699

Table S2 Péclet number for different I.D. nozzle

D/ µm	Q_A/ µL h^{-1}	Gap/µm	Pe
25	300	30	3461
50	300	30	865.2
75	300	30	384.5
100	300	30	216.3

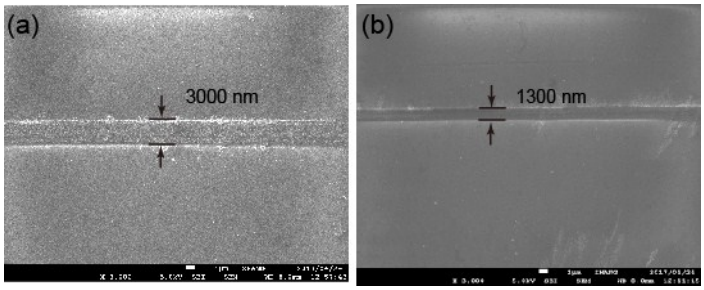


Fig. S4 SEM images of sliver wires prepared using different I.D. nozzles under same parameters condition (a) Nozzle I.D. 100 μm (b) Nozzle I.D. 75 μm

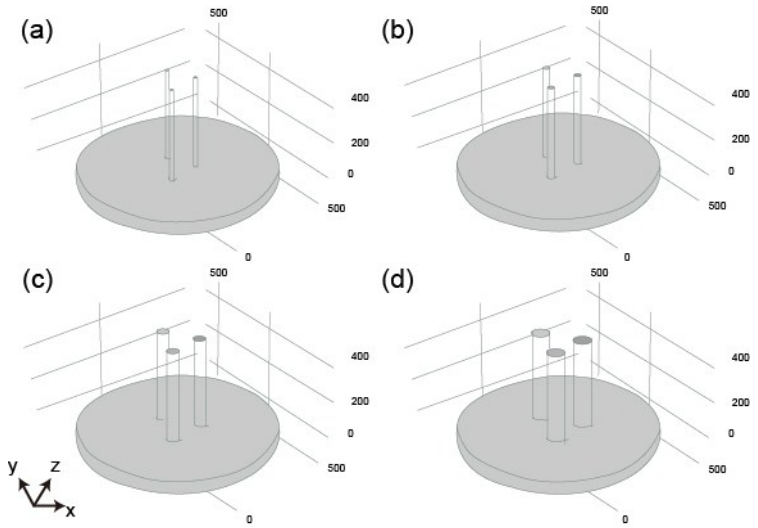


Fig. S5 3D model of different inner diameter nozzle a)25 μm b)50 μm c) 75 μm d) 100 μm

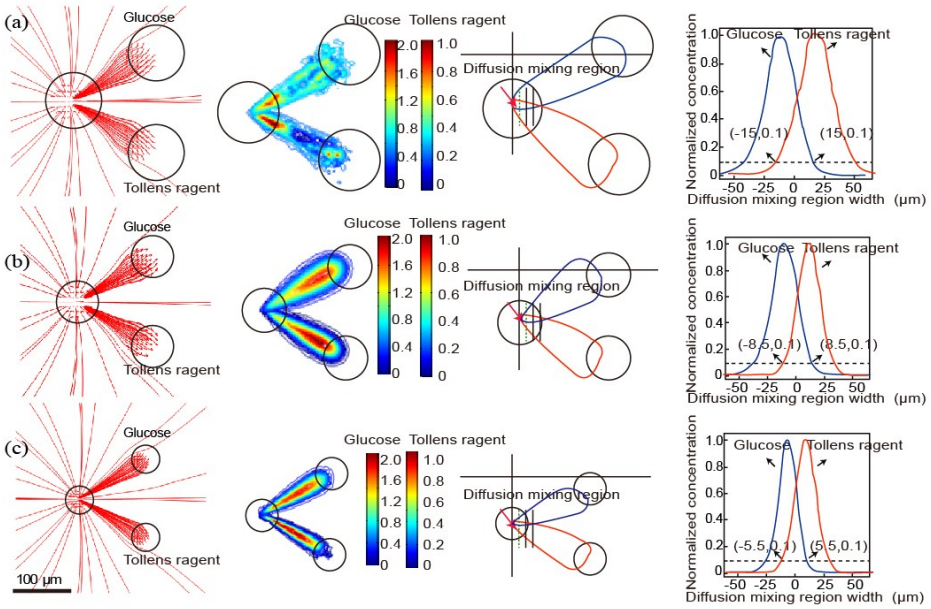


Fig. S6 The diffusion mixing region of nozzle pen (a) I.D. 100 μm (b) I.D. 75 μm (c) I.D. 50 μm.

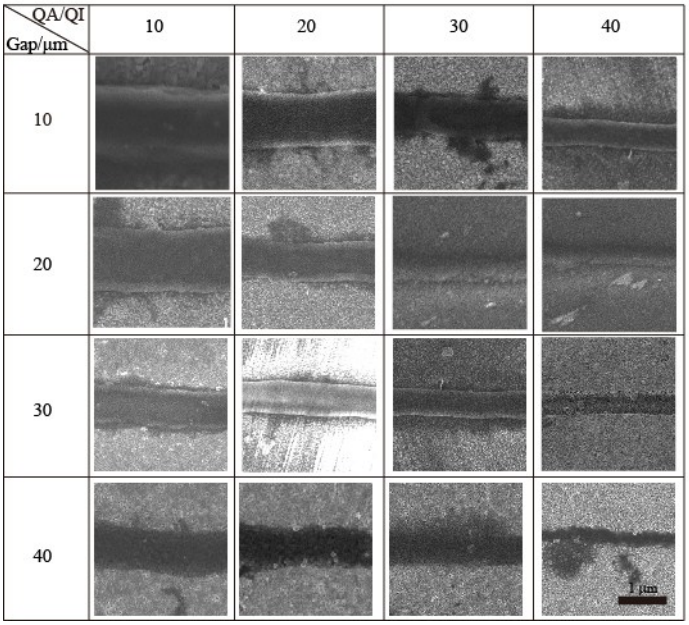


Fig. S7 SEM images of Silver wires fabricated under different gap and QA/QI.

These results show that the width of the silver wire is directly related to the diffusion mixing region. The experiments verify one certain condition (the I.D. of the nozzle, the QA/QI ratio and gap) correspond to one width of the silver wire. Thus, the width of the patterns could be adjusted within a large range (from 3000 nm to 100 nm).

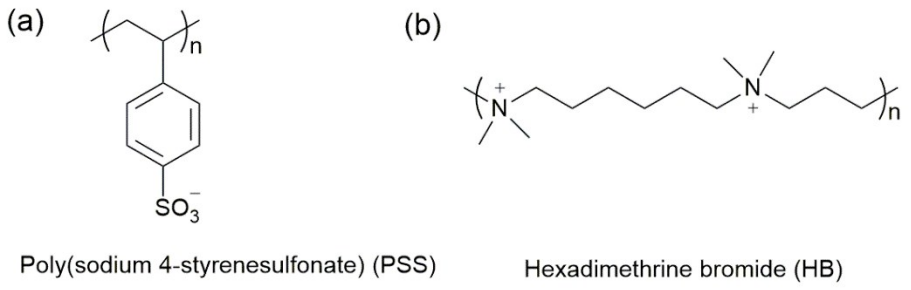


Fig. S8. (a) The molecular formula of ply(sodium 4-styrenesulfonate) (PSS).
(b) The molecular formula of Hexadimethrine bromide (HB).

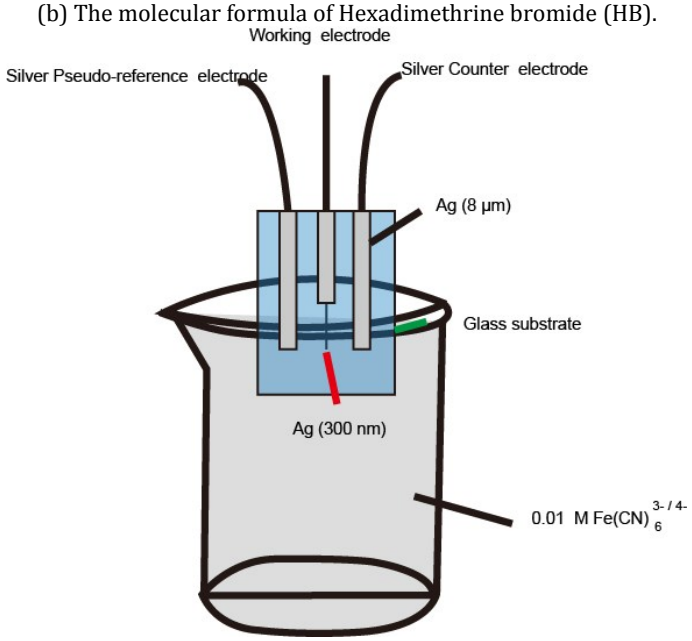


Fig. S9 The instrument for the cyclic voltammetry determination of potassium ferric cyanide with a nano three electrode device

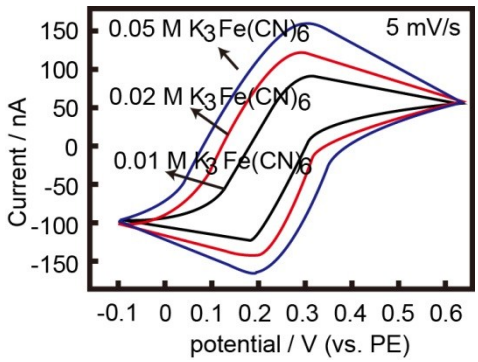


Fig. S10 The Cyclic voltammetry of silver three electrode system. in different $K_3Fe(CN)_6$ solution.

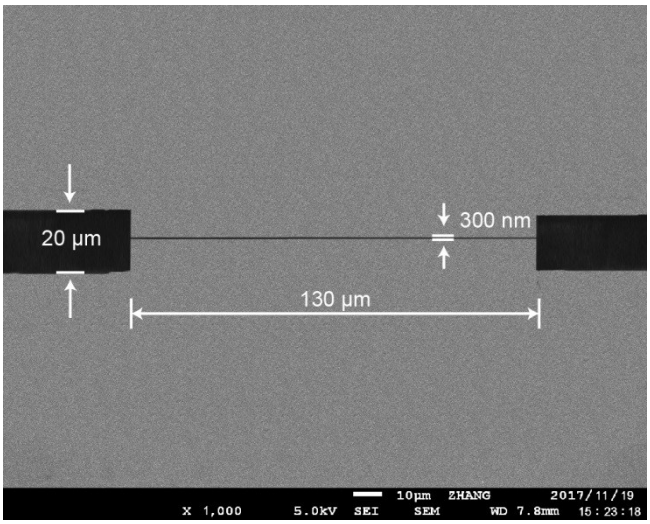


Fig. S11 SEM image of silver wire for resistance test.

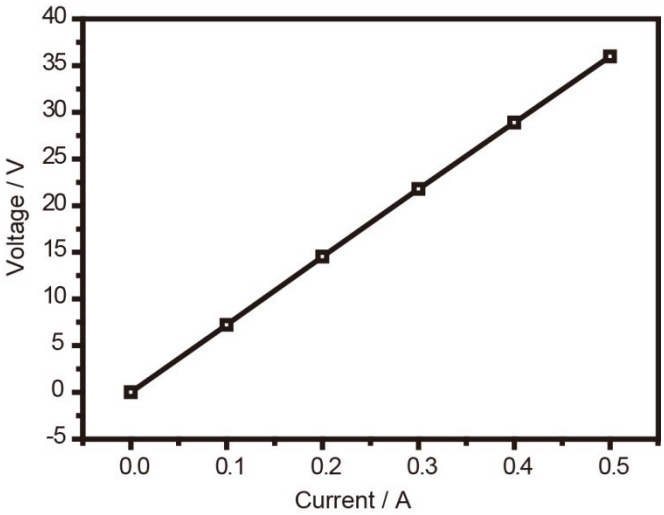


Fig. S12 The Current v.s.voltage curve for silver nano wire by using current amplifier.