Supporting Information

Single Nanoporous Gold Nanowires as a Tunable One-dimension Platform for Plasmon-enhanced Fluorescence

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Materials and Reagents

Polycarbonate (PC) foils (20 μm) were purchased from Bayer company (Germany). Chloroauric acid hydrate ($HAuCl_4 \cdot 4H_2O$, Au content 47.8%) was obtained from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China). Silver bromide (99.9% trace metals basis), aquae hydrogenii dioxidi (30%), (3-aminopropyl)trimethoxysilane (APTMS, 97%) and N,N-dimethylformamide (DMF, amine and water free, 99.9%) were obtained from Alfa Aesar company (Shanghai, China). The DNA sequences were purchased from Sangon Biological Engineering Technology Co., Ltd (Shanghai, China). The Cy5 NHS ester was from Lumiprobe Corporation (USA). Tris-EDTA (TE) buffer solution (100×), sodium chloride (98%), magnesium chloride hexahydrate (99%), tris(2-carboxyethyl) phosphine (TCEP) hydrochloride (98%) were obtained from Sigma-Aldrich. Inc. (USA). 6-mercapto-1-hexanol (MCH, 97%), 3-mercaptopropyltrimethoxysilane (MPTMS, 97%) were from J&K scientific Ltd. (Beijing, China). Concentrated sulfuric acid (95%), concentrated nitric acid (65%), sodium hydroxide (99%), concentrated ammonia water (25%) and dichloromethane (99%) were from Beijing Chemical Works (Beijing, China). Sodium thiosulfate pentahydrate (99%), sodium sulfite anhydrous (99.5%) were obtained from Xilong Chemistry Ltd. (Guangzhou, China).

The single-strand DNA (ssDNA) sequence used in experiments: 5'- Cy5-TTG TTT GTT CCC CTT CTT TCT T-$(CH_2)_3$-SH-3'

Apparatus

The transmission electron microscope (TEM) micrographs and the energy dispersive X-ray (EDX) spectra were obtained from JEM-2010 transmission electron microscope (JEOL Ltd.,

Japan) equipped with Energy Dispersive X-ray Spectrometer (GENESIS, EDAX Inc., USA). The scanning electron microscope (SEM) micrographs and EDX spectra were obtained from JSM7401F scanning electron microscope (JEOL Ltd., Japan) equipped with Energy Dispersive X-ray Spectrometer (X-max, Oxford Inc., USA). Ultraviolet (UV) sensitization of PC films was performed with IntelliRay 400 UV Flood System (Uvitron Inc., USA). The 60 nm Au layer on PC nuclear track membrane was evaporated in L-400EK Anelva Vacuum Evaporation System (Anelva Technix, Japan). Electrochemical deposition and cyclic voltammetry (CV) curves were performed with Source Measure Unit 2401 (Keithley, USA) and CHI660E Work Station (Chenhua Instruments, China). Fluorescence micrographs were gained on Laser Scanning Confocal Microscope X81 (Olympus Ltd., Japan). The fluorescence emission spectrum of Cy5-labeled ssDNA solution was tested on Fluoromax-4 Spectrofluorometer (Horiba Ltd., France). The scattering spectra and dark-field images of nanowires were obtained on Nikon 80i dark-field microscope (Nikon Corporation, Japan) equipped with a CoolSNAP HQ2 charge-coupled Device (CCD) camera (Roper Scientific, USA), a DP72 color CCD camera (Olympus Ltd., Japan) and a 100 W halogen tungsten lamp. The lifetime analysis was carried on Laser Scanning Confocal Microscope X83 (Olympus Ltd., Japan) equipped with LDH-D-C-640 picosecond pulsed laser diode (637 nm, 40 MHz, 84 ps FWHM) (PicoQuant, Germany), PDM series single photon avalanche diode (MPD Corporation, Italy) and PicoHarp 300 time-corrected single photo counting (TCSPC) module (PicoQuant, Germany).

Fabrication of nuclear track membranes (NTMs)

The following fabrication process of PC NTMs is based on the conventional methods.[1,2] PC foils of thickness 20 μm were irradiated at a linear accelerator with Kr^{84} ions (kinetic energy 10 MeV u^{-1}, fluence 2.75×10^{8} ions cm^{-2}) at normal incidence. The ions damaged the polymer

matrix along their trajectories and then latent tracks formed. For the formation of cylindrical pores rather than conical pores, the irradiated PC foils were sensitized by UV light (320~390 nm, 90 mW cm^{-2}) for 1 h from each side to enhance the ratio of track etching rate to bulk etching rate. The sensitized PC foils were then etched in 6.25 M sodium hydroxide aqueous solution at 50 °C after exposure in air for 1 week. The cylindrical pores appeared along the latent tracks (Figure S1,S2). Larger pore diameter can be formed with longer etching time. After etching by sodium hydroxide aqueous solution, the PC NTMs were rinsed by deionized water in an ultrasonic field and then dried at room temperature.

In order to view the cross-section of the membrane, the NTM was irradiatited by UV light (90 mW/cm^2) for 25 h from each side and then embrittled by immersion in liquid nitrogen. Then the membrane could be laniated without elastic deformation. The cross-section micrograph (insert of Figure S1) clearly reveals the straight pores traversing the membrane. Figure S3 shows the linear relationship between the pore diameters (d/nm) and the alkali solution etching time (t/min): $d = 28.58t$ (R^2=0.9970).

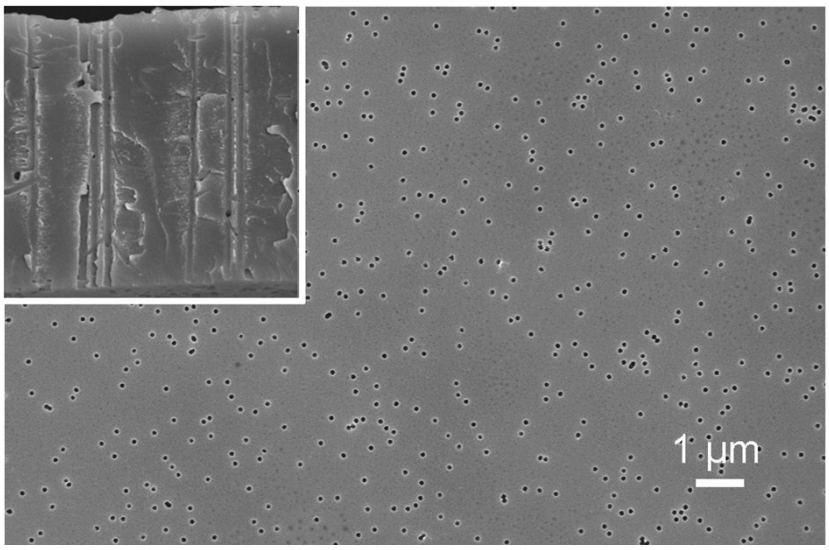

Figure S1. The low magnification SEM image of the PC NTM. The insert is the SEM image of the membrane cross-section.

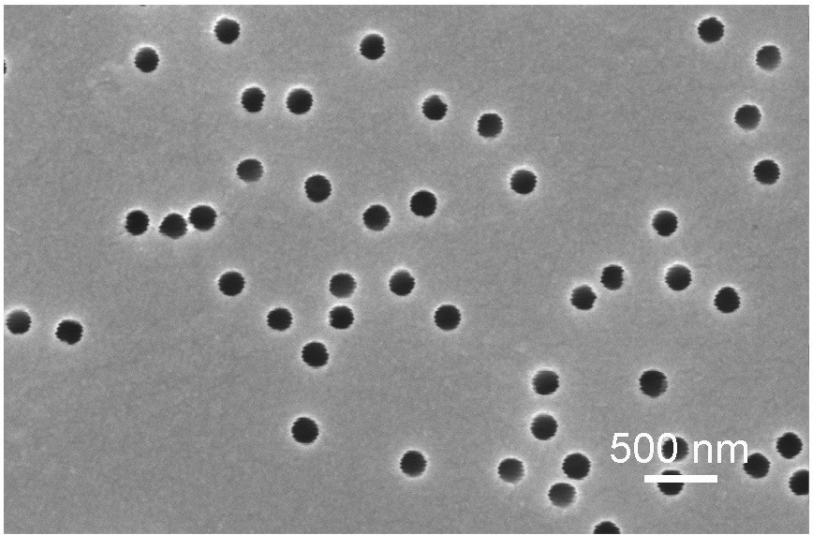

Figure S2. The high magnification SEM image of the PC NTM.

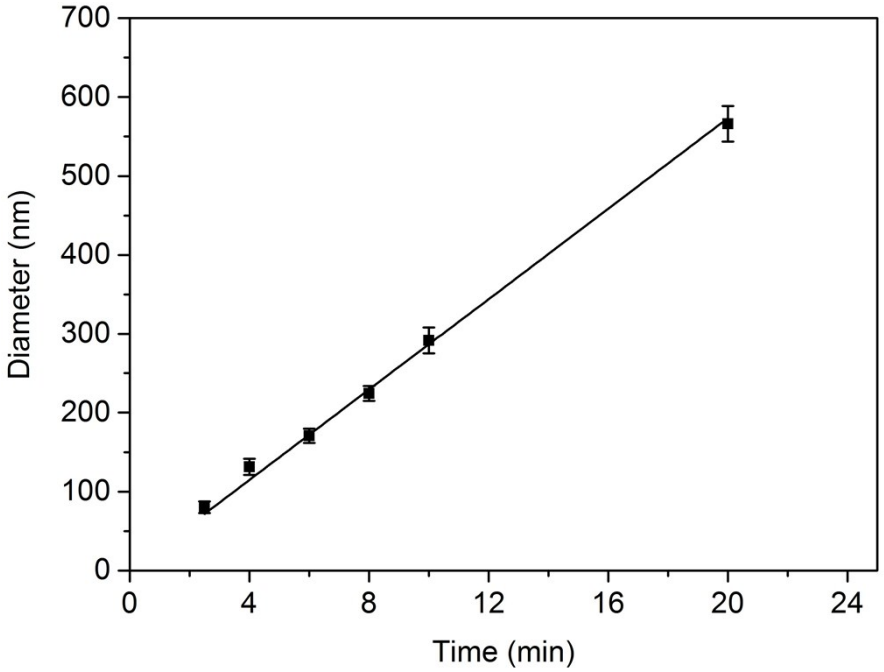

Figure S3. The relationship curve of the pore diameters and the etching time.

Electrodeposition of Au nanowires and Au-Ag alloy nanowires

Prior to electrodeposition, a thin gold layer of thickness ~60 nm was evaporated onto one side of the PC NTMs. Before the evaporation of gold, 5 nm titanium adhere layer was needed. Subsequently, the membrane was inserted into a two-electrode electrolytic cell with the

conductive layer facing an anode of platinum plate. A thick gold layer of ~3 μm thickness was electrodeposited onto the conductive layer with a fixed current density of 1 mA cm^{-2} for the reinforce of the thin gold layer and the block of one end of the pores. The non-cyanide electrolyte was prepared by mixing 10 mM chloroauric acid, 0.42 M sodium thiosulfate and 0.42 M sodium sulfite (pH 7.7).[3] The thick gold layer served as a cathode of the following electrodeposition of nanowires.

To grow Au nanowires (AuNWs) and Au-Ag alloy nanowires (AuAgNWs) in the pores of the PC template, a homemade three-electrode Teflon electrolytic cell (Figure S4) was used for the electrodeposition. The cathode was the thick gold substrate with the polymer template, a Ag/AgCl electrode (saturated KCl solution) acted as a reference electrode and a cone platinum plate served as a counter electrode. The diameter of the cathode was 20 mm. For the growth of AuNWs, the above non-cyanide gold plating solution was used. A solution containing chloroauric acid, silver bromide, 0.42 M sodium thiosulfate and 0.42 M sodium sulfite acted as the electrolyte of AuAgNWs electrodeposition.[4] All of the electrodeposition was operated at 55 °C with continuous stirring. It must be pointed out that the soaking of the template in the electrolyte is helpful for the homogeneous and complete filling of the pores. After deposition for appropriate time, most of the pores could be filled with nanowires.

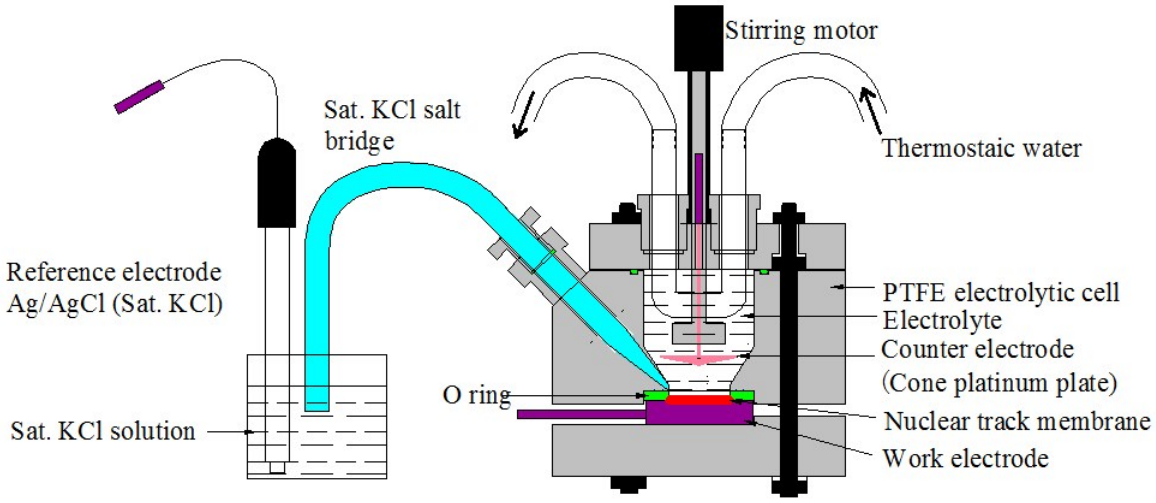

Figure S4. Schematic diagram of the electrolytic cell.

The composition of the alloy nanowires can be tailored by changing the potential and Au^+/Ag^+ molar ratio of the electrolyte. In our experiments, the Au molar ratio in the alloy nanowires increased with the raise of the potential and the Au^+/Ag^+ molar ratio in the electrolyte (Figure S5, S6). Here, we grew AuAgNWs at -320 mV (vs. Ag/AgCl) and 55 °C with an electrolyte containing 5 mM Au^+ and 5 mM Ag^+ (pH 8.1). The EDX spectra of the AuNWs and AuAgNWs are shown in Figure S7, S8. The AuNWs contained only Au element and the Au/Ag molar ratio of the alloy nanowires was 36:64. Elemental mappings show the homogeneous distribution of the Au and Ag atoms in the $Au_{0.36}Ag_{0.64}$ nanowire (Figure S9, S10). Thus, it's possible to prepare nanoporous AuNWs further with the $Au_{0.36}Ag_{0.64}$ nanowires, just as nanowires deposited with conventional cyanide electrolytes.[5-7]

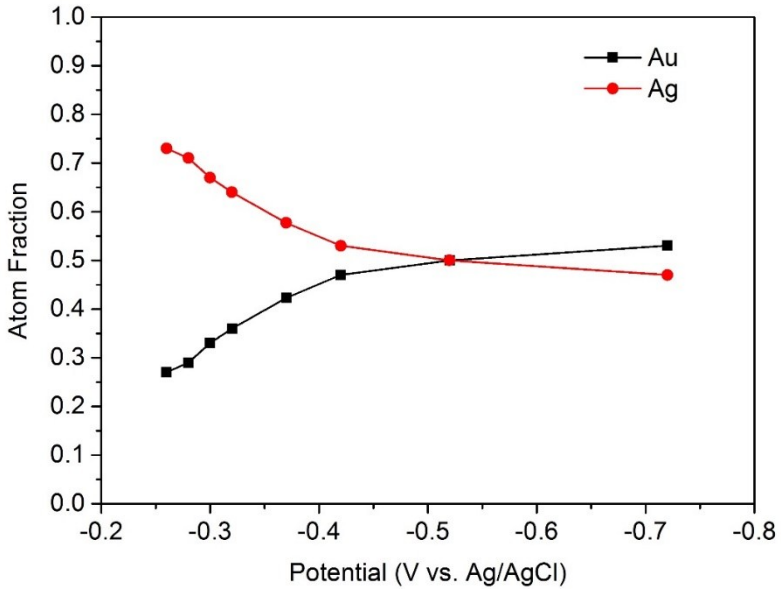

Figure S5. The relationship curves of the Au/Ag atom fraction in the AuAgNWs and the electrodeposition potential. The electrolyte contained 0.42 M sodium thiosulfate, 0.42 M sodium sulfite, 5 mM Au^+ and 5 mM Ag^+. The temperature was 55 °C.

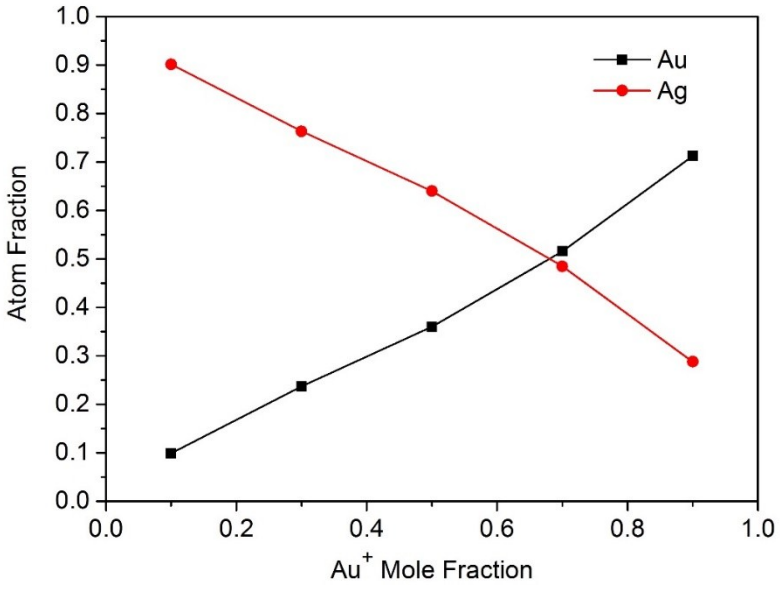

Figure S6. The relationship curves of the Au/Ag atom fraction in the AuAgNWs and Au^+ mole fraction of metal ions (Au^+ and Ag^+) contained in the electrolyte at -320 mV vs. Ag/AgCl (saturated KCl). The electrolyte contained 0.42 M sodium thiosulfate, 0.42 M sodium sulfite, 10 mM metal ions (Au^+ and Ag^+). The temperature was 55 °C.

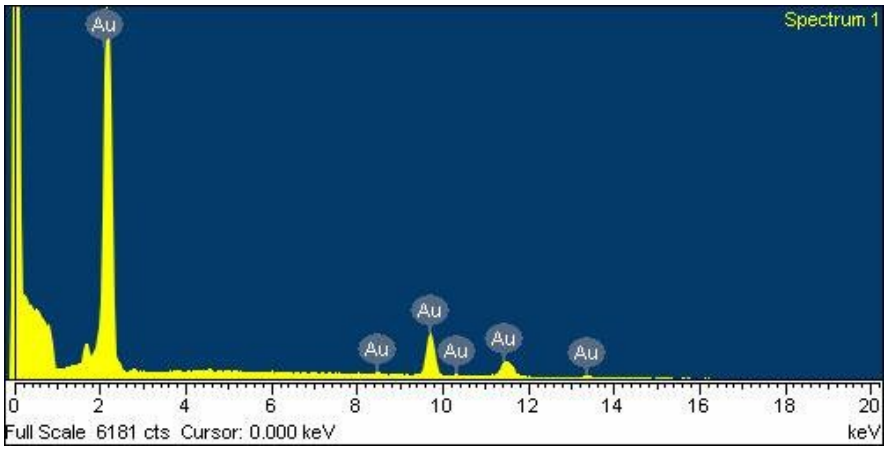

Figure S7. The EDX spectrum of the Au nanowires.

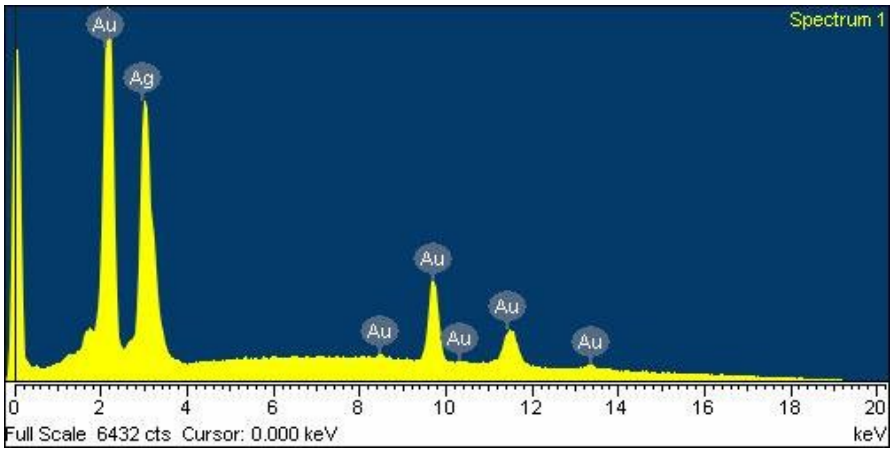

Figure S8. The EDX spectrum of the $Au_{0.36}Ag_{0.64}$ nanowires.

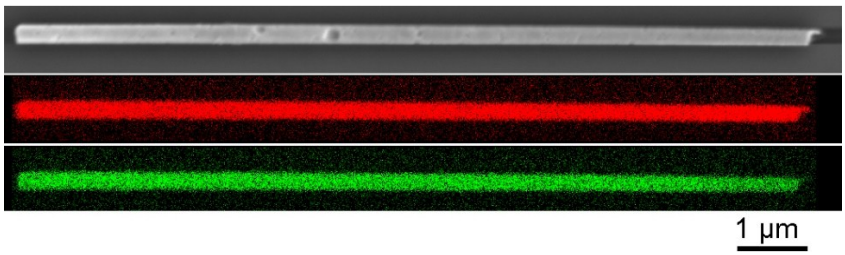

Figure S9. The SEM-EDX elemental mappings of Au (red) and Ag (green) in a $Au_{0.36}Ag_{0.64}$ nanowire.

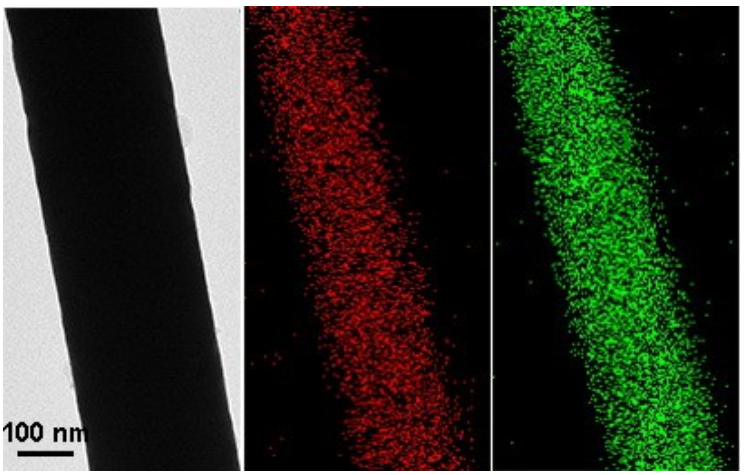

Figure S10. The TEM-EDX elemental mappings of Au (red) and Ag (green) in a $Au_{0.36}Ag_{0.64}$ nanowire.

Figure S11 shows the current curve of the $Au_{0.64}Ag_{0.36}$ nanowires electrodeposition. The curve can be divided into 3 stages, which is the typical characteristic of the template-assistance electrochemical deposition. At stage I, the initial current was relatively large but

declined rapidly, because the formation of Helmholtz electrical double layer at the surface of cathode produced a large charge current. Then the formation of diffusion layer decreased the current. At this stage, the nanowires grew initially, and very short nanorods could be viewed on the gold layer. At stage II, the current was relatively steady. The nanowires grew longer until the nanowires filled the whole nanopores. Then, at stage III, the nanowires grew on the surface of the PC NTM without the restriction of the cylindrical nanopores and small caps formed on the top of the nanowires. Without the concentration gradient of the electrolyte and with the enlargement of the contact area between the cathode and the electrolyte, the current increased rapidly. If the electrochemical deposition continued, the caps would merge together and cover the whole surface of the PC NTM. In our experiment, we stopped the electrodeposition at stage II. The template with nanowires in the pores is shown in Figure S12 and the rounded deep color region contained nanowires.

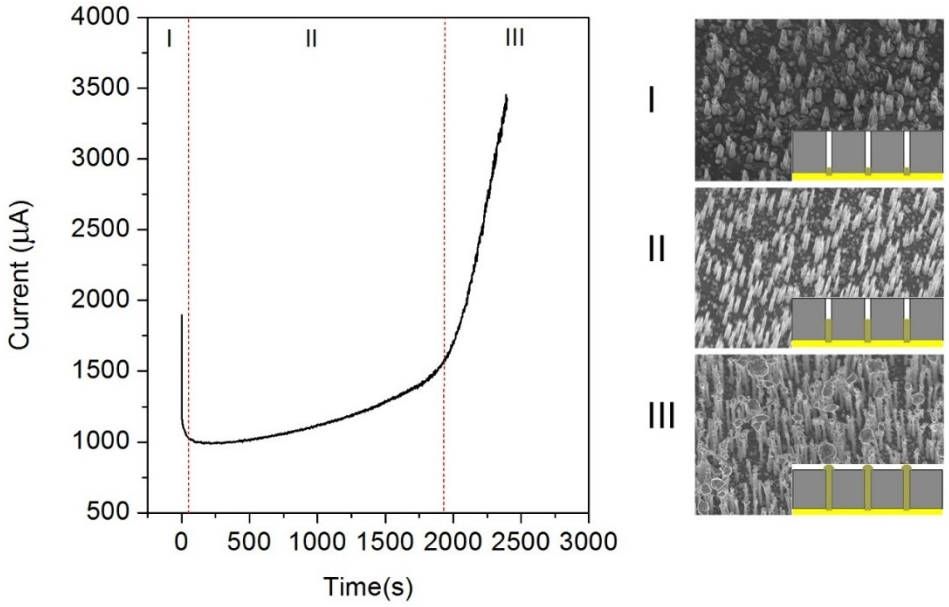

Figure S11. (Left) The current-time curve of the $Au_{0.36}Ag_{0.64}$ nanowires electrodeposition. The electrolyte contained 0.42 M sodium thiosulfate, 0.42 M sodium sulfite, 5 mM Au^{+} and 5 mM Ag^{+}. The temperature was 55 °C. The potential was -320 mV vs. Ag/AgCl (saturated KCl solution). (Right) The SEM images of the nanowires at different electrodeposition stages. The insert is the schematic of the nanowires at these three stages.

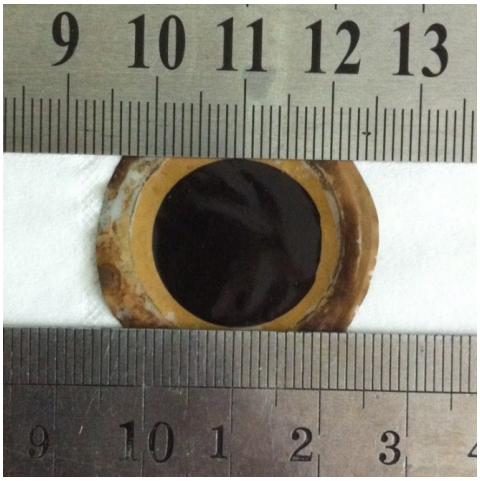

Figure S12. A photograph of PC template with $Au_{0.36}Ag_{0.64}$ nanowires in the pores.

Separation of nanowires from the template

In order to remove the nanowires from the PC template, the Au conductive layer was removed by anodic dissolution in a two-electrode electrolytic cell with a fixed voltage of 4 V at room temperature. The electrolyte consisted of 2 w% thiourea and 0.5 w% sulfuric acid, and the Au conductive layer faced a copper rod cathode. The center of the Au layer was dissolved completely at the first because of the largest current density. Once the Au conductive layer was dissolved, the nanowires were disconnected from the power source and the dissolution of nanowires was avoided.

After the removal of the Au conductive layer, dichloromethane was used to dissolve the PC template. The nanowires were separated by sequential centrifugation, and rinsing with dichloromethane for 5 times.

Fabrication of nanoporous AuNWs

In order to prepare nanoporous AuNWs, dispersed alloy nanowires were immersed in concentrated nitric acid (65-68 w%) at room temperature to remove silver. Then "sponge-like" nanowires comprised almost entirely of Au were obtained. After the dealloying process had proceeded for a desired time, diluent ammonia water was added to the concentrated nitric acid to neutralize it. Then nanoporous AuNWs suspended in water were obtained after sequential filtration and rinsing with deionized water.

Immobilization of nanoporous and smooth AuNWs on glass slides

Glass slides were cleaned by sequential ultrasonic cleaning in acetone, ethanol and deionized water for 15 min and then treated in a piranha solution (98% H_2SO_4 : 30% H_2O_2 solution = 3:1 v/v; Caution: Piranha solution is strongly corrosive and must be performed carefully!) for 2.5 h at 80 °C. After rinsed with deionized water, the cleaned slides were dried under Ar stream and the hydroxylation of glass slide was completed. Subsequently, the slides were immersed in a methanol solution containing 50 mM MPTMS for 2 h at room temperature, then rinsed by methanol and dried under Ar stream. About 30 μL smooth or nanoporous AuNWs dispersion liquid was dropped on one piece of slide, respectively. The slides were sealed in a container for 2 h to prevent the water evaporation. Some of the nanowires were immobilized on the slide by Au-S bond. Then the slides were kept in vacuum overnight to remove the water.

Modification of Cy5-labeled ssDNA on the nanowires

Thiolated oligonucleotide strands were labeled with Cy5 fluorophores and dissolved in TE buffer solution (10 mM Tris-HCl, 1 mM EDTA, pH 8.0) to form a stock solution. Prior to

immobilization on the nanowires, the stock solution was diluted by TE buffer solution to 5 μM. Then sodium chloride (1 M), magnesium chloride hexahydrate (0.1 M), TCEP hydrochloride (1 mM) were added to the solution and the pH was kept at 7.8. The thiols of the oligonucleotides were activated by the reduction effect of TCEP for 1 h at room temperature. Then the nanowires on glass slide were immersed in the oligonucleotide solution for 24 h at room temperature in dark place. After the immersion process, the nanowires were rinsed by TE buffer solution and immersed in MCH solution to remove DNA strands that absorbed on the gold surface via backbones and make the thiol ends tethered DNA strands well-aligned to reduce the fluorescence quenching.[8] Before fluorescence test, the nanowires were stored in TE buffer solution at 4 °C.

Fluorescence test of Cy5 on the nanowires

The fluorescence of Cy5 on the nanowire was tested in 10 mM TE buffer solution using a laser scanning confocal microscope (Olympus X81). A 635 nm laser was used as the excitation light. An oil immersion objective (Olympus, 100×, 1.4 NA) was used to focus the laser to the nanowires. The fluorescence was collected by the same objective and was separated from the excitation laser by an optical grating. A photodiode sensed the fluorescence emission with an integration time of 40 μs/pixel to form an image of 1024×1024 pixels. The fluorescence spectra was scanned with step size of 2 nm and width of 5 nm and then averaged by pixels.

Calculation of fluorescence enhancement factors (EFs) on nanoporous and smooth AuNWs

The fluorescence EFs of smooth AuNWs (E_S) and nanoporous AuNWs (E_N) relative to glass slide can be defined as:

$$E_S=\frac{F_{S,norm}}{F_{G,norm}}\ (1),\ E_N=\frac{F_{N,norm}}{F_{G,norm}}\ (2).$$

$F_{G,norm}$, $F_{S,norm}$, $F_{N,norm}$, refer to dye molecule number normalized fluorescence intensity of Cy5 on glass slide, smooth AuNWs and nanoporous AuNWs, which are defined as follow.

$$F_{G,norm}=\frac{F_G}{N_G}=\frac{F_{G,ave}S_{G,mea}}{D_G S_G}\ (3),\ F_{S,norm}=\frac{F_S}{N_S}=\frac{F_{S,ave}S_{S,mea}}{D_S S_S}\ (4),\ F_{N,norm}=\frac{F_N}{N_N}=\frac{F_{N,ave}S_{N,mea}}{D_N S_N}\ (5)$$

F_G, F_S and F_N refer to the fluorescence intensity of all the Cy5 dye molecules from the detection area on glass, smooth AuNW and nanoporous AuNW. N_G, N_S and N_N mean the total number of Cy5 dye molecule in the detection area. $F_{G,ave}$, $F_{S,ave}$ and $F_{N,ave}$ are the area averaged fluorescence intensity, which can be gained from the peak intensity of the fluorescence spectra given by the instrument. $S_{G,mea}$, $S_{S,mea}$, $S_{N,mea}$ represent the detection area under the microscopy, with which the area averaged fluorescence intensity is obtained (blue lines in Figure S13). D_G, D_S, D_N denote the dye molecule number density on the surface of three substrates, and S_G, S_S, S_N denote the surface area that exposed to the detection area (red lines in Figure S13).

In the experiment, the detection area was a rectangle. As shown in Figure S13, we could get that:

$$S_{G,mea}=d_G l_G\ (6),\ S_{S,mea}=d_S l_S\ (7),\ S_{N,mea}=d_N l_N\ (8)$$

While, the surface shape that exposed to the detection area was different for these three substrate.

For glass, the exposed surface was a rectangle as the same as its detection area:

$$S_G = d_G l_G \quad (9)$$

For smooth nanowire, the exposed surface was a curved surface:

$$S_S = \frac{\pi}{2} d_S l_S \quad (10)$$

For nanoporous nanowire, the exposed surface was an irregular porous surface. According to the literature,[9] in this condition, the exposed surface area could be calculated as follows:

$$S_N = \frac{1}{2} R V_m = R \frac{\pi}{8} \left[{d_N}^2 - \left(d_N - 2h \right)^2 \right] l_N \quad (11)$$

In the formulas, R is the surface-to-volume ratio of nanoporous AuNW and V_m is the volume of the outside layer, which is occupied by one layer pores and ligaments (the zone between the two circular dashed lines of Figure S13 (right)). h is the depth of the nanopores, which can be supposed reasonably equal to the pores width d_p in the main text.[9]

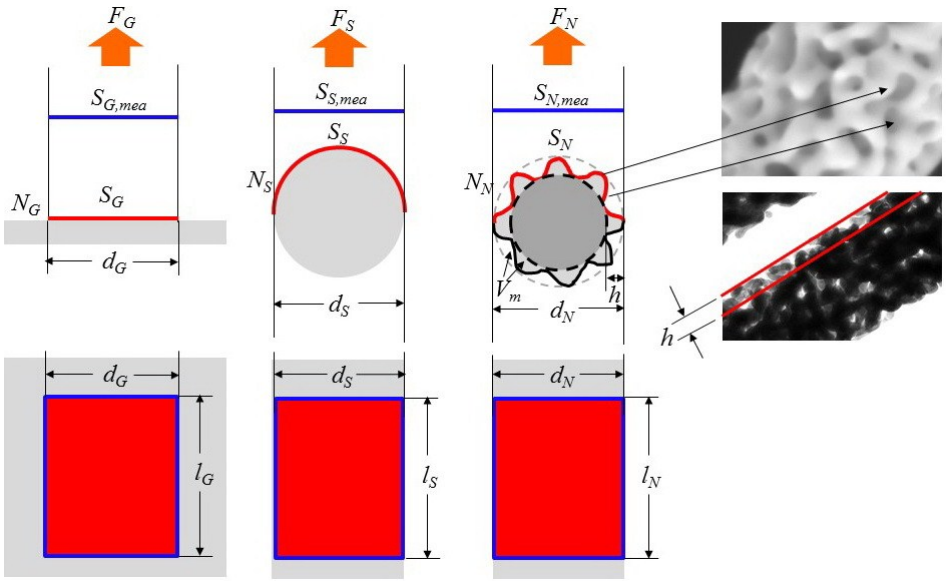

Figure S13. Schematic illustration of the calculation of the dye molecule number normalized fluorescence intensity of Cy5 on glass (left), smooth AuNW (middle) and nanoporous AuNW (right).

Plug equation (6) (9) into (3), equation (7) (10) into (4), equation (8) (11) into (5).

$$F_{G,norm}=\frac{F_G}{N_G}=\frac{F_{G,ave}S_{G,mea}}{D_G S_G}=\frac{F_{G,ave}d_G l_G}{D_G d_G l_G}=\frac{F_{G,ave}}{D_G} \quad (12)$$

$$F_{S,norm}=\frac{F_S}{N_S}=\frac{F_{S,ave}S_{S,mea}}{D_S S_S}=\frac{F_{S,ave}d_S l_S}{D_S \frac{\pi}{2} d_S l_S}=\frac{F_{S,ave}}{D_S}\frac{2}{\pi} \quad (13)$$

$$F_{N,norm}=\frac{F_N}{N_N}=\frac{F_{N,ave}S_{N,mea}}{D_N S_N}=\frac{F_{N,ave}d_N l_N}{D_N \frac{1}{2} R \frac{\pi}{4}\left[{d_N}^2-\left(d_N-2h\right)^2\right] l_N}=\frac{F_{N,ave}d_N}{D_N R \frac{1}{4}\left[{d_N}^2-\left(d_N-2h\right)^2\right]}\frac{2}{\pi} \quad (14)$$

Plug equation (12) (13) into (1), we could get the fluorescence EFs of smooth AuNWs relative to glass:

$$E_S=\frac{F_{S,norm}}{F_{G,norm}}=\frac{\frac{F_{S,ave}}{D_S}\frac{2}{\pi}}{\frac{F_{G,ave}}{D_G}}=\frac{2}{\pi}\frac{F_{S,ave}}{F_{G,ave}}\frac{D_G}{D_S} \quad (15)$$

$F_{G,ave}$ and $F_{S,ave}$ are the area averaged fluorescence intensity, which can be gained from the peak intensity of the fluorescence spectra given by the instrument. D_G and D_S denote the dye molecule number density on the substrates surface and could be calculated by a adsorption method below.

The fluorescence EFs of nanoporous AuNWs relative to glass:

$$E_N = \frac{F_{N,norm}}{F_{G,norm}} = \frac{F_{N,norm}}{F_{S,norm}} \frac{F_{S,norm}}{F_{G,norm}} = E_S \frac{F_{N,norm}}{F_{S,norm}} = E_S \frac{\frac{F_{N,ave} d_N}{D_N R \frac{1}{4}\left[{d_N}^2 - \left(d_N - 2h\right)^2 \right]} \frac{2}{\pi}}{\frac{F_{S,ave}}{D_S} \frac{2}{\pi}}$$

$$= 4E_S \frac{\frac{F_{N,ave} d_N}{D_N R \left[{d_N}^2 - \left(d_N - 2h\right)^2 \right]}}{\frac{F_{S,ave}}{D_S}} = 4E_S \frac{D_S}{D_N} \frac{1}{R} \frac{F_{N,ave}}{F_{S,ave}} \frac{d_N}{{d_N}^2 - \left(d_N - 2h\right)^2} \quad (16)$$

The surface-to-volume ratio R can be calculated by $R = S_{N,single} / V_{N,single}$, in which $S_{N,single}$ is the entire surface area of single nanoporous AuNW, including the surface inside the nanoporous AuNW and $V_{N,single}$ is the volume of the single nanoporous AuNW, including the nanopores and ligaments of the nanowire.

$$E_N = 4E_S \frac{D_S}{D_N} \frac{1}{R} \frac{F_{N,ave}}{F_{S,ave}} \frac{d_N}{{d_N}^2 - \left(d_N - 2h\right)^2} = 4E_S \frac{D_S}{D_N} \frac{V_{N,single}}{S_{N,single}} \frac{F_{N,ave}}{F_{S,ave}} \frac{d_N}{{d_N}^2 - \left(d_N - 2h\right)^2}$$

$$= 4E_S \frac{D_S S_{S,single}}{D_N S_{N,single}} \frac{V_{N,single}}{S_{S,single}} \frac{F_{N,ave}}{F_{S,ave}} \frac{d_N}{{d_N}^2 - \left(d_N - 2h\right)^2} = 4E_S \frac{D_S S_{S,single}}{D_N S_{N,single}} \frac{\frac{1}{4}\pi {d_N}^2 l_{N,single}}{\pi d_S l_{S,single}} \frac{F_{N,ave}}{F_{S,ave}} \frac{d_N}{{d_N}^2 - \left(d_N - 2h\right)^2}$$

$$= E_S \frac{D_S S_{S,single}}{D_N S_{N,single}} \frac{F_{N,ave}}{F_{S,ave}} \frac{{d_N}^2}{d_S} \frac{d_N}{{d_N}^2 - \left(d_N - 2h\right)^2} = E_S \frac{N_{S,single}}{N_{N,single}} \frac{F_{N,ave}}{F_{S,ave}} \frac{{d_N}^2}{d_S} \frac{d_N}{{d_N}^2 - \left(d_N - 2h\right)^2} \quad (17)$$

$N_{S,single}$ (equal to $D_S S_{S,single}$) and $N_{N,single}$ (equal to $D_N S_{N,single}$) are the total number of Cy5 dyes on single smooth AuNW and single nanoporous AuNW, which could be calculated by the adsorption method below. $F_{S,ave}$ and $F_{N,ave}$ are the area averaged fluorescence intensity, which can be gained from the peak intensity of the fluorescence spectra given by the instrument. d_S and d_N are the diameter of smooth AuNW and nanoporous AuNW. h is the depth of the nanopores, which can be supposed reasonably equal to the pores width.[9] d_S, d_N

and h could be measured by SEM or TEM images. E_S is the fluorescence EFs of smooth AuNWs relative to glass. In the calculation, the bottom surface of the cylinder is negligible, because the nanowires have large length-diameter ratio and dyes on the bottom surface were not measured in the experiments.

Adsorption method:

1) In order to estimate the adsorbing capacities of a smooth AuNW ($N_{S,single}$) and a nanoporous AuNW ($N_{N,single}$), we removed the PC template by dichloromethane after the electrochemical deposition of Au and $Au_{0.36}Ag_{0.64}$ nanowires without the removal of gold substrate. Then we immersed the $Au_{0.36}Ag_{0.64}$ nanowires array in concentrated nitric acid for different time to prepare nanoporous AuNWs array on gold substrate and rinsed the arrays with deionized water. Subsequently we immersed the smooth AuNWs and nanoporous AuNWs arrays in TE buffer containing the same components as the Cy5 modification process in above by the same modification time, then MCH solution was used by the same process. Part of the ssDNA molecules adsorbed on the nanowires array, then we diluted the solution containing remaining ssDNA. The concentration of the remaining ssDNA can be measured by spectrofluorometer. After the measurement, we can obtained the dye molecule number density on smooth AuNW (D_S), adsorbing capacities of a smooth AuNW ($N_{S,single}$) and a nanoporous AuNW ($N_{N,single}$).

2) In order to measure the Cy5 fluorescence intensity on flat glass slide, we first completed the hydroxylation process with the same method above. Then we immersed the glass slide in methanol solution containing 50 mM APTMS for 18 h, rinsed the slide with methanol and dried it under Ar stream. NHS-ester Cy5 was dissolved in DMF (amine and water free) to prepare stock solution. 20 μL sodium bicarbonate aqueous solution (0.1 M, pH 8.4) containing 2 μM NHS-ester Cy5 (stock solution dissolved in sodium bicarbonate solution)

was dropped onto the slide carefully to ensure the liquid drop rounded. The slide was kept in a tiny and inclosed container overnight at room temperature. After reaction, the slide with 20 μL solution was rinsed with bicarbonate solution and the solution was diluted to 10 mL. After the measure by spectrofluorometer, we can calculate the Cy5 molecular density (D_G) on glass. The fluorescence intensity ($F_{G,ave}$) of Cy5 immobilized on glass was estimated by laser scanning confocal microscope and the background emission of bare glass slide was eliminated.

After the experiment, the fluorescence EFs of smooth AuNW and nanoporous AuNW of different dealloying time relative to glass can be obtained (Table S1).

Table S1. The fluorescence EFs of smooth AuNW and nanoporous AuNW of different dealloying time relative to glass

Dealloying time	Cy5 molecule number corrected EF (relative to glass)
Smooth AuNW	7.5 ± 4.2
5 min	9.6 ± 1.9
15 min	15.6 ± 3.7
1 h	22.2 ± 4.7
3 h	29.9 ± 5.1
6 h	61.5 ± 12.5
11 h	61.7 ± 8.2

In addition, if we assume the dye molecule number density on smooth AuNW (D_S) and nanoporous AuNW (D_N) is equal, we can obtain the surface-to-volume ratio and detected Cy5 molecule number density ratio (relative to smooth AuNWs) of nanoporous AuNWs of different dealloying time (Table S2), which is close to the report [9], in which the surface-to-volume ratio of nanoporous Au film was measured by quantitative electron tomography.

Table S2. The surface-to-volume ratio and the detected Cy5 molecule number density ratio (relative to smooth AuNWs) of nanoporous AuNWs of different dealloying time.

Dealloying time	Surface-to-volume ratio [0.01 nm^2 nm^{-3}]	Detected Cy5 molecule number density ratio
5 min	18.55 ± 0.45	1.69 ± 0.04

15 min	13.43 ± 2.14	1.93 ± 0.31
1 h	10.97 ± 1.05	2.16 ± 0.21
3 h	8.94 ± 1.01	2.51 ± 0.28
6 h	7.47 ± 1.46	2.37 ± 0.46
11 h	4.79 ± 0.87	1.68 ± 0.30

TCSPC fluorescence lifetime analysis

The lifetime of Cy5 on flat glass slide, smooth AuNWs and nanoporous AuNWs of 6 h dealloying time and in TE buffer solution was measured on laser scanning confocal microscope (Olympus X83) with TCSPC system. The instrument response function was measured before the experiments. The decay curves were fitted by: $I(\mathrm{t})=\sum_i A_i \exp(-t/\tau_i)$ and the averaged lifetime was calculated by: $\bar{\tau}=\frac{\sum_i A_i\tau_i^2}{\sum_j A_j\tau_j}$.

Following are the TCSPC intensity decay curves.

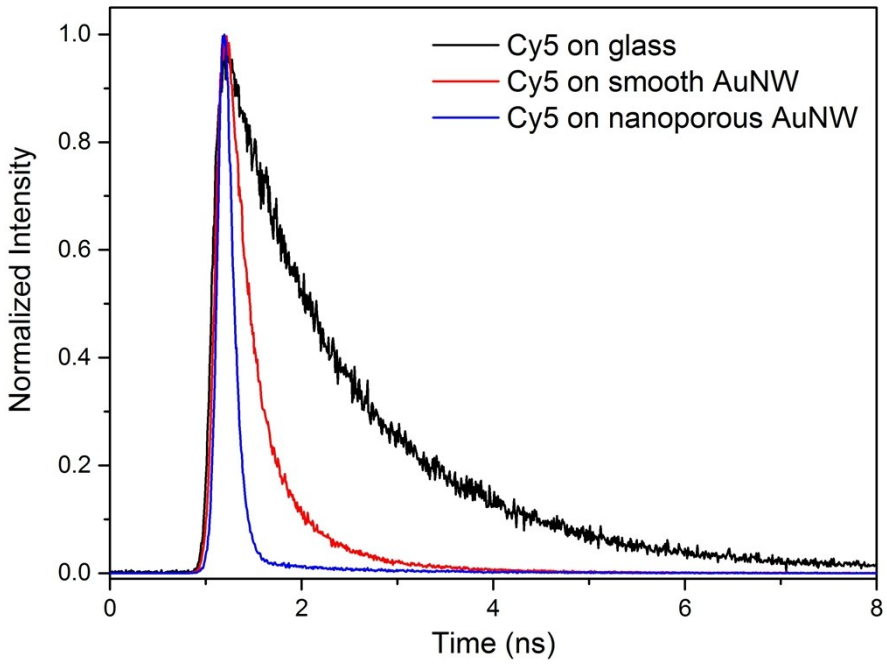

Figure S14. Typical TCSPC intensity decay curves of Cy5 on nanoporous AuNW, smooth AuNW and flat glass slide.

From the intensity decay curves shown in Figure S13, the lifetimes of Cy5 on nanoporous AuNWs and smooth AuNWs can be obtained by double exponential fitting analysis, the former is 0.19 ns and the latter is 0.43 ns. Both are shorter than 1.44 ns on glass slide, which is obtained by mono-exponential fitting.

Dark-field spectra test and dark-field images of nanowires acquirement

The dark-field images of smooth AuNWs and nanoporous AuNWs were acquired in 10 mM TE buffer solution. The upright dark-field microscope was equipped with a 60× plan fluor oil immersion objective with iris and an NA = 1.20–1.43 oil immersion dark-field condenser. The dark-field condenser produced hollow cone of light focused on the nanowires and only the scattered light can be collected by CCD camera after passing through the objective.

As shown in the supplementary Figures of another report[10] adopting the same method to measure the LSPR spectra of nanorods, the dark-field scattering light of a nanowire (smooth or nanoporous) was splitted by transmission grating beam splitter, then the zero- and first-order images of the nanowire can be obtained from a CCD camera (CoolSNAP HQ2). Typical spectral images of a smooth and nanoporous Au nanowires are shown in Figure S15. On the right side of the zero-order image, a first-order image formed by Bragg diffraction can be seen, which was then analyzed using ImageJ software to acquire the scattering spectra. Before the spectra analysis, calibration of the set-up was needed.[10]

The color images (inserts of Figure 3b) of nanowires were acquired from color CCD (DP72).

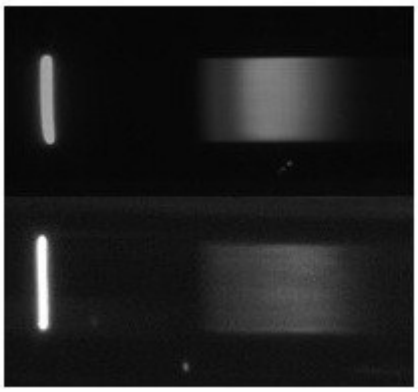

Figure S15. Typical spectral images of a smooth (up) and nanoporous (down) Au nanowire

Background emission of nanowires

The background emission of nanoporous AuNWs and smooth AuNWs without any Cy5 modification were tested on the laser scanning confocal microscope (Olympus X81) with the same parameters as the fluorescence spectra test in above. Typical background emission spectra and the influence on detected Cy5 spectra are shown in Figure S16 and S17.

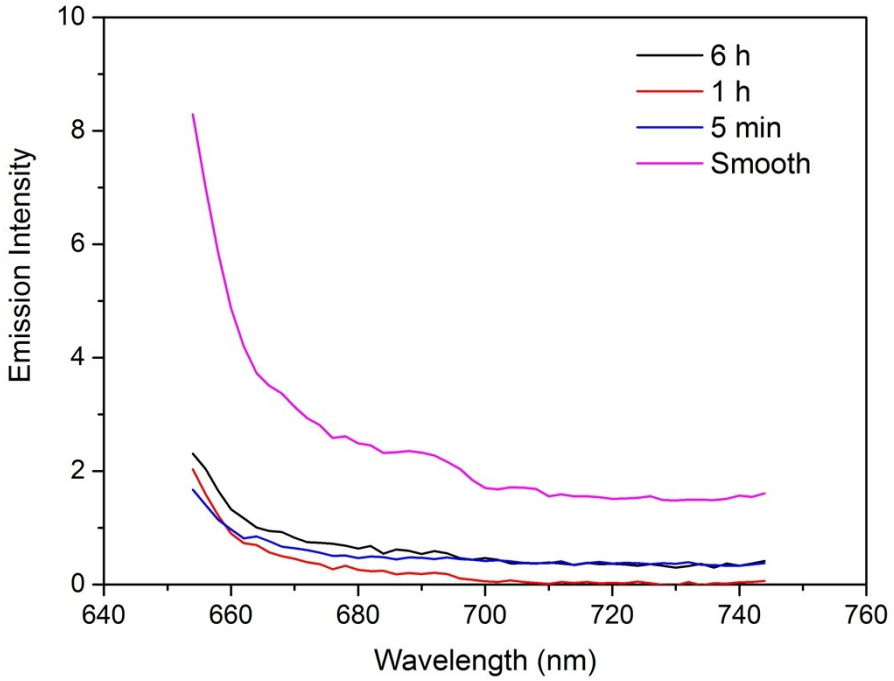

Figure S16. The background emission spectra from nanoporous AuNWs (6 h, 1 h and 5 min dealloying time) and smooth AuNWs.

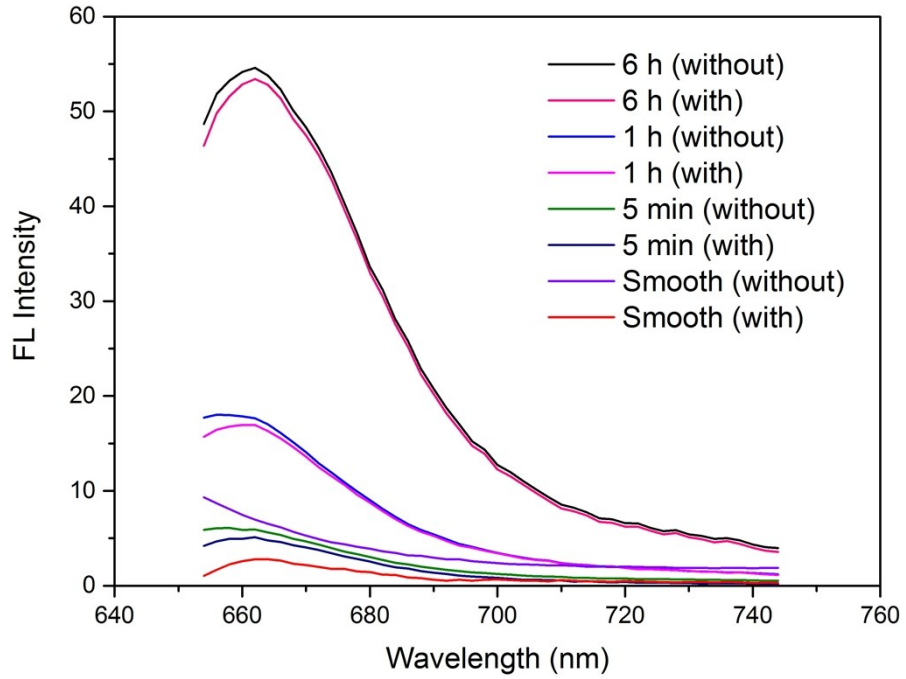

Figure S17. The fluorescence spectra of Cy5 on nanoporous AuNWs (6 h, 1 h and 5 min dealloying time) and smooth AuNWs without and with the elimination of background emission.

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