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

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Hang Yuan,[a] Yuexiang Lu,*[a] Zhe Wang,[a] Zhonghua Ren,[a] Yulan Wang,[a] Sichun Zhang,[b] Xinrong Zhang,[b] and Jing Chen*[a]

We introduce individual nanoporous Au nanowires (AuNWs) as a tunable one-dimension platform for plasmon-enhanced fluorescence, with an enhancement factor of 62, ~8-fold higher than smooth AuNWs. Besides, nanoporous AuNWs have much lower background emission than smooth nanowires. These results indicated that nanoporous AuNW is an excellent optical sensing platform.

Plasmon-enhanced fluorescence (PEF) or metal-enhanced fluorescence (MEF) has increasingly attracted scientists' attention, as it could increase the fluorescence emission intensity leading to improved signal-to-noise ratio, detection sensitivity and imaging quality.[1] Although many plasmonic nanostructures have been developed for PEF, such as nanoparticles,[2] nanorods,[3] bowtie nanoantennas,[4] Au/Ag island films[5] and porous Au/Ag films,[6] the research of PEF on single plasmonic nanowires is very rare. Compared to 'zero-dimension' (0D) nanoparitlces and 'two-dimension' (2D) films, one-dimension (1D) nanowires, with nanometer-scale transverse dimension and micrometer-scale longitudinal dimension, provide unique advantages for optical sensing and imaging. First, a nanowire is visible under an optical microscope due to its large longitudinal dimension, which makes it possible to manipulate the nanowire with high spatial resolution for ultrasmall volume analysis.[7] Second, a nanowire can handle light as a subwavelength waveguide and be used for remote sensing with reduced background noise.[8] Third, individual nanowire or nanowires assembled into networks can be used to create optical devices.[9] Thus, the research of PEF on 1D plasmonic nanowires is of great interest for both fundamental studies and technological applications.

However, up to now, only a few reports have mentioned the PEF on plasmonic nanowires such as Au nanowires (AuNWs),[10] Ag nanowires[11] and striped Au/Ag nanowires.[12] The fluorescence enhancement factor (EF) on these nanowires was much lower than that on other nanostructures and hotspots with high EF were only observed at the two ends or defects of these nanowires, which have greatly limited the application of 1D plasmonic nanowires on fluorescence sensing and imaging. As a result, it is needed to develop new materials and design strategy for archiving high fluorescence EF on entire plasmonic nanowires.

In this report, we demonstrate that single nanoporous gold nanowire could act as a high-efficient 1D platform for PEF (Scheme 1). It is known that to maximize the EF, one important requirement is the matching between localized surface plasmon resonances (LSPR) wavelengths of the plasmonic nanowires and the excitation/emission maximum of the fluorescent dyes. Another requirement is a dense distribution of hotspots on the surface of nanowires. By introducing nanoporous structures to gold nanowires, the LSPR wavelength of the nanowires could be tailored simply to obtain a proper spectrum matching with a Cy5 dye. Also, attributing to the dense and uniform nanoporous structures on the nanowire, strong PEF was observed across the entire nanowire. We measured the dependence of the fluorescence enhancement on pores/ligaments sizes and a maximum of ~62-fold fluorescence enhancement was obtained, which was ~8.3-fold higher than smooth AuNWs. To the best of our knowledge, this is the highest demonstrated EF value on single nanowire and also the first report of PEF on single nanoporous nanowires.[13]

In a typical synthesis procedure of nanoporous AuNWs, $Au_{0.36}Ag_{0.64}$ alloy nanowires with ~10 µm length and ~250 nm diameter were firstly prepared by template-assisted electrodeposition (Figure 1a, 1b, S8). Chloroauric acid and silver bromide were chosen as the metal source for electrodeposition instead of the commonly used toxic cyanide.[13, 14] The length and composition of the nanowires can be tailored by controlling the electrodeposition process. Then

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[a] Institute of Nuclear and New Energy Technology, Collaborative Innovation Center of Advanced Nuclear Energy Technology, Beijing Key Lab of Radioactive Waste Treatment, Tsinghua University, Beijing 100084, P. R. China. *E-mail: luyuexiang@mail.tsinghua.edu.cn, jingxia@mail.tsinghua.edu.cn

[b] Department of Chemistry, Beijing Key Laboratory for Microanalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, P. R. China.

† Footnotes relating to the title and/or authors should appear here.

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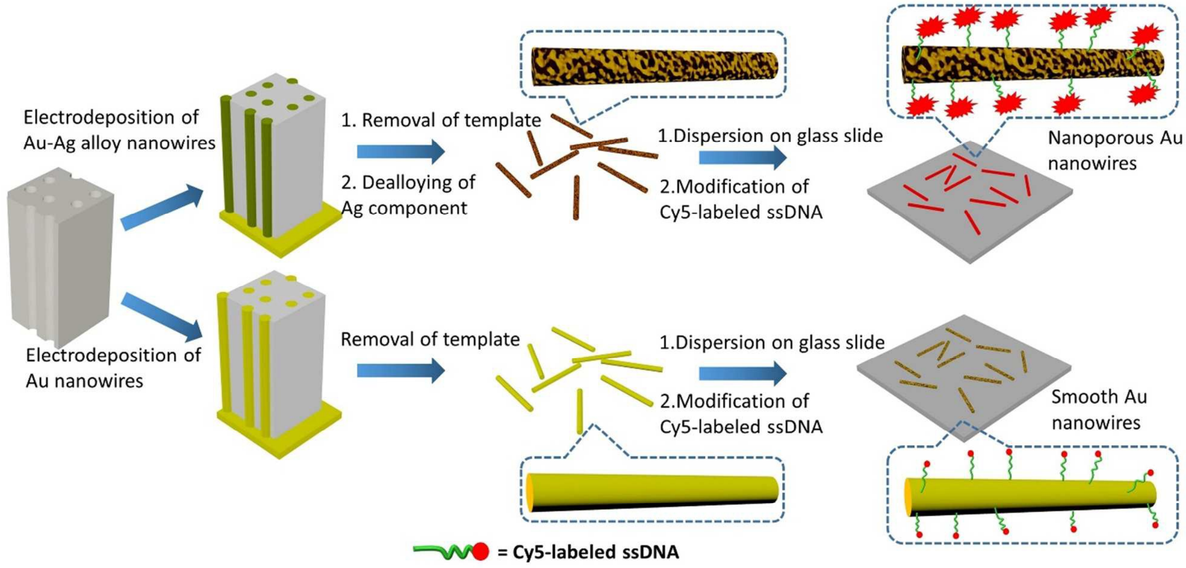
Scheme 1. Schematic illustration of the fabrication procedure of nanoporous/smooth AuNWs and the PEF of the AuNWs.



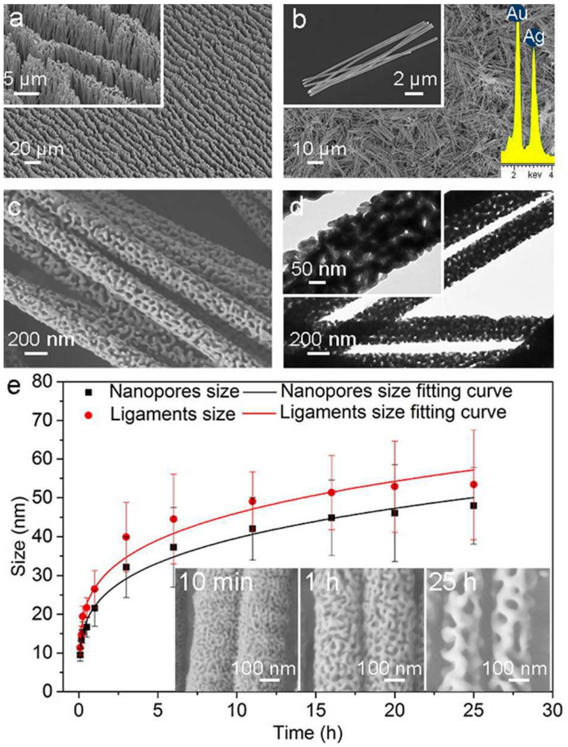


Figure 1. Scanning electron microscopy (SEM) image of (a) the vertical alloy nanowires on substrate and (b) the dispersive alloy nanowires. (c) SEM image and (d) transmission electron microscope (TEM) image of representative nanoporous AuNWs. The inserts are high magnification images and energy dispersive X-ray (EDX) spectrum of the nanowires. (e) The correlation between the pores/ligaments sizes and the dealloying time. The inserts are SEM images of nanoporous AuNWs of different dealloying time.

the alloy nanowires were dispersed in nitric acid for dealloying (see the Supporting Information (SI)). As the silver in the alloy nanowires was dissolved, the remaining gold atoms aggregated to clusters and the bicontinuous nanoporous structures formed (Figure 1c, 1d).[15] The pores/ligaments sizes could be easily tailored from ~9/11 nm to ~48/53 nm as the dealloying time increasing from 5 min to 25 h (Figure 1e). The relationships between the sizes [averaged pores width (d_P/nm) and averaged ligaments width (d_L/nm)] of nanoporous AuNWs and dealloying time (t/h) were well fitted with exponential functions:[16] $d_P(t) = 22.0463t^{0.2546}$ ($R^2 = 0.9838$) and $d_L(t) = 26.7592t^{0.2358}$ ($R^2 = 0.9660$). The smooth AuNWs of the similar sizes were also fabricated without Ag doping and etching.

We first compared the fluorescence intensity on nanoporous (6 h dealloying time) and smooth AuNWs. Both kinds of AuNWs were firstly casted and immobilized on glass slides. Then Cy5, a fluorescent dye widely used in biosensing and imaging, was introduced to the nanowires surface by choosing single-strand DNA (ssDNA) with 22 bases (~7 nm length) as linker and spacer. As shown in Figure 2a, 2d, both kinds of nanowires were visible in a transmission mode, indicating that they could be manipulated under optical microscopy. The fluorescence images of the nanowires excited by 635 nm laser were recorded (emission window: 650 nm-750 nm) (Figure 2b, 2e). By preliminary comparison, the fluorescence intensity of Cy5 on the nanoporous AuNWs was obviously higher than smooth AuNWs. The emission spectra of Cy5 on these nanowires were similar with that in solution (Figure 2g) and the intensity of fluorescence peak at 662 nm could be used for calculating the fluorescence EFs. The apparent EF of the nanoporous AuNWs was ~20-fold relative to the smooth AuNWs. Besides, the uniform distribution of nanoporous structures induced a relatively uniform fluorescence intensity along the longitudinal direction (Figure 2h).

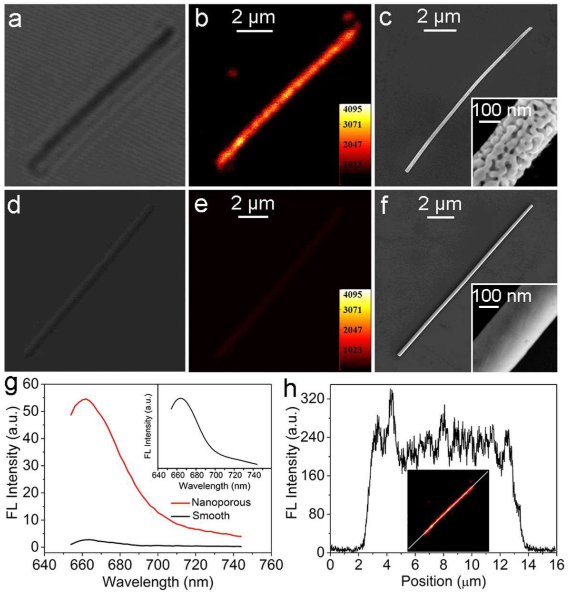


Figure 2. (a, d) Optical microscope images, (b, e) fluorescence images and (c, f) SEM images of (a, b, c) a nanoporous AuNW of 6 h dealloying time and (d, e, f) a smooth AuNW. The inserts of (c, f) are high magnification SEM images. (g) The pixel averaged Cy5 fluorescence spectra of (b) and (e). The insert of (g) is the fluorescence spectrum of Cy5 in solution. (h) The fluorescence intensity along the longitudinal direction (the line of the insert) of nanowire of (b).

It was possible that more Cy5 molecules were absorbed on the nanoporous AuNWs than on smooth AuNWs. To verify that the fluorescence enhancement was mainly caused by PEF but not more absorbed molecules, the fluorescence intensity was corrected by the molecule number and the fluorescence EFs were calculated by using Cy5 on flat glass slide as standard (see the SI). The smooth AuNWs showed a low EF (~7.5). While, for nanoporous AuNWs, the EFs were higher and increased with dealloying time. With 5 min dealloying time, the EF achieved to ~10. A maximum of ~62-fold fluorescence enhancement was obtained on nanoporous AuNWs with 6 h and 11 h dealloying time, which was ~8-fold higher than smooth AuNWs (Figure 3a). We further measured the fluorescence lifetimes of Cy5 on nanoporous AuNWs, smooth AuNWs and flat glass slide, which were 0.19 ns, 0.43 ns and 1.44 ns, respectively (see the SI). The results confirmed that both smooth and nanoporous AuNWs could increase the radiative rate and quantum yield of Cy5 dye, which also contributed to the fluorescence enhancement.[5a,17] Meanwhile, the nanoporous AuNWs performed more remarkably than smooth ones. The shorter lifetime resulted from the near-field coupling between the dye and the nanowires. It is obvious that the Cy5 dye could couple with nanoporous AuNWs more effectively, which might originate from the match between the emission wavelength of the dye and the LSPR wavelength of nanoporous AuNWs.

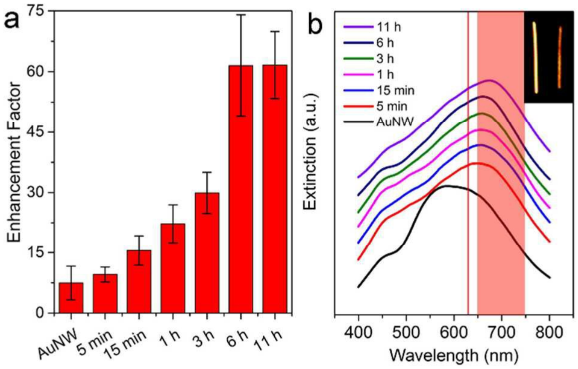


Figure 3. (a) The fluorescence EFs histograms and (b) extinction spectra of smooth and nanoporous AuNWs of different dealloying time overlaid with the excitation (line) and primary emission (shaded area) region of Cy5. The inserts are the dark-field images of smooth (left) and nanoporous (right) AuNWs.

To confirm the suppose above, we measured the LSPR spectra of single AuNWs under dark-field microscope (Figure 3b).[18] The smooth AuNWs appeared a yellow green color while the nanoporous AuNWs were salmon pink (inserts of Figure 3b). The smooth AuNWs showed a LSPR peak at 588 nm, while the LSPR peak of the nanoporous AuNWs appeared an obvious red shift, which is consistent with another report.[13c] Nanowires with longer dealloying time showed a peak at longer wavelength from 646 nm to 675 nm, which matched better with the excitation and emission wavelengths of Cy5. The tunable LSPR wavelength originated from the abundant ligaments and nanopores on the nanowires, the large curvatures of which produced strong electromagnetic fields in the vicinity of them. The pores/ligaments sizes also played an important role. According to literature,[19] the fluorescence intensity detected is the combined action of fluorescence enhancement and quenching. The scattering of large nanoparticles is dominant over absorption, the former enhances fluorescence and the latter quenches fluorescence, while this trend is opposite for small nanoparticles. Larger gold nanoparticles could enhance the fluorescence of dyes with long emission wavelength better.[6a] As a result, the detected fluorescence intensity is higher for nanoporous AuNWs with larger pores/ligaments sizes. These results suggested that the fluorescence enhancement factor of nanoporous AuNWs could be tailored to obtain high fluorescence EFs without changing the size of the nanowires, which is a key factor of 1D nano materials.

To achieve high signal-to-noise ratio and sensitivity, it is very important to reduce the backgound emission, especially when the dyes only have small stokes shift. As a result, we further investigated the background emission of the nanowires, which was manily from the intrinsic photoluminescent of gold.[20] Both AuNWs without Cy5 modification were excited by 635 nm laser and the emission of 650-750 nm was collected. We found that the porous AuNWs showed much lower background emission than the smooth AuNWs. The background emission of smooth AuNWs was ~4-fold stronger than the nanoporous AuNWs (Figure S16). The former obviously distorted the fluorescence spectrum, while the latter didn't (Figure S17).

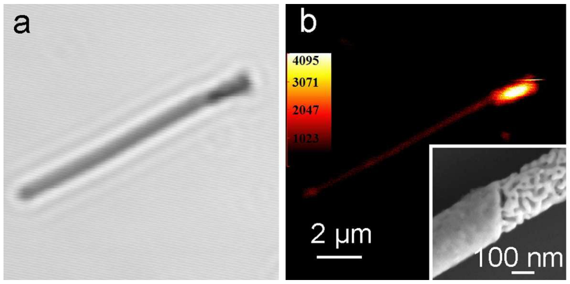


Figure 4. (a) Optical microscope image, (b) fluorescence image of the nanoporous/nonporous segmented AuNW. The insert of (b) is the SEM image of the heterojunction.

We could also grow a section nanoporous Au on the tip of smooth AuNWs. Afterwards, the segmented AuNWs were modified with Cy5. The fluorescence micrograph is shown in Figure 4b. The luminous tip of the segmented nanowire intuitively showed the remarkable fluorescence enhancement of the nanoporous structures. This segmented structure may have application in multiplex sensing and optical biocomputing.

In summary, we have investigated the fluorescence enhancement of Cy5 on nanoporous AuNWs and observed strong PEF across the entire nanowire. By tuning the pores/ligaments sizes and LSPR of the nanowires, a maximum of ~62-fold fluorescence enhancement was obtained, which was much higher than that on nonporous AuNWs. The nanoporous structures of AuNWs can also reduce the background emission, which is necessary for ultrasensitive fluorescence detection and imaging. In addition, segmented nanowires consisting of both nanoporous end and nonporous body could also be obtained. As the micrometers long nanowire could be manipulated accurately under optical microscopy and the ssDNA linker could respond to different kinds of targets by proper design, the nanoporous AuNWs with remarkable luorescence enhancement have potential application in fluorescence detection and imaging in tiny zones such as single-cell endoscopy, optical waveguide, encoded materials, biocomputing, etc.

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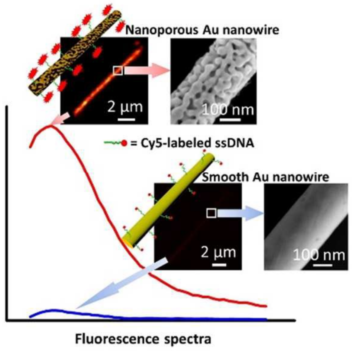

Up to ~62-fold enhancement of fluorescence can be obtained on individual nanoporous Au nanowires, ~8-fold higher than smooth Au nanowires.