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Supplementary Information

Strong fluorescence emission localized at a tapered silver-plated sub-wavelength pore

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S1. Preparation of glass tapered holes and determination of the orifice radius

The single glass tapered sub-wavelength pore channels were prepared from glass capillaries according to the previous literature with further modifications. Firstly, the platinum wire was electrochemically etched in 15% $CaCl_2$ to obtain a sharpened tip **Fig S1**. Then, it was sealed into a glass capillary. After that, the glass bottom was polished until Pt was revealed. Finally, the Pt sealed in glass was etched completely to obtain a single tapered glass sub-wavelength pore channel. The diameter of the pore was determined by the polished Pt tip base sealed in the glass capillary, and the diameter can be measured by the steady-state diffusion-limited current of the Pt disk electrode prior to be etched[1]. Electrochemical analyzer CHI 660C was used in the measurement.

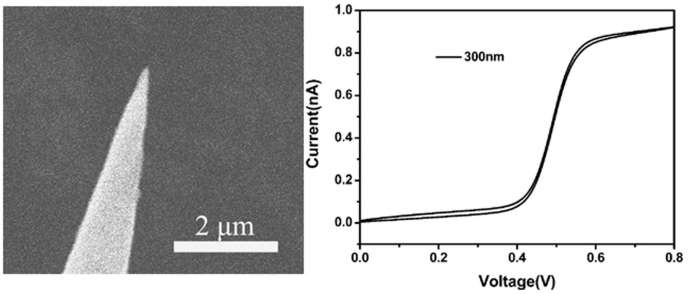
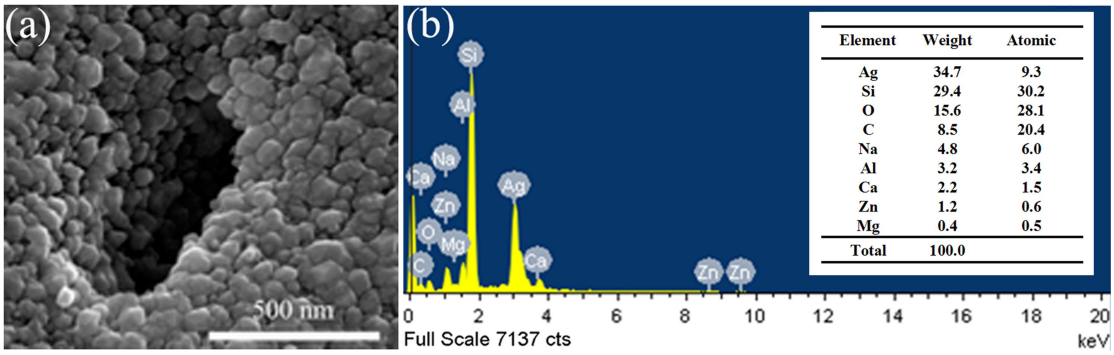


Fig S1 SEM image of the etched Pt tip before sealed into the glass capillary (left). Steady-state voltammetric response of 300nm diameter Pt disk electrode (right).

S2. Deposition of a thin film of silver and characterizations

The pore channel was immersed in piranha acid (80°C, 30 min), followed by washing with de-ionized water and ethanol to obtain clean silica hydroxyl groups on the interior surface. Then 5% 3-aminopropyltriethoxylsilane (APTES) in absolute ethanol was added into the glass tapered pore channel and reacted with the interior pore surface for 30 min. Afterwards, the pore channel was sensitized with $SnCl_2$ and then immersed in ammoniacal $AgNO_3$. The $SnCl_2$ solution was 26 mM $SnCl_2$ and 70 mM TFA (Trifluoroacetic acid), and the pore channel was immersed for 1h under room temperature followed by thoroughly rinsed with de-ionized water. The ammoniacal $AgNO_3$ was a mixture of two components: (a) 20 mM $AgNO_3$ and 67 mM NH_4OH, and (b) 63 mM NaOH and 20 mM NH_4OH, mixed just before the experiment[2]. This mixture was kept at a low temperature 6°C and the pore channel was immersed for 15 min. Finally, *N*-methyl-*D*-glucamine was added as a reducing agent to this solution (6 mM) for the final plating step (6°C, 10 min). The silver coated pore channel was rinsed with de-ionized water and ethanol thoroughly and then dried with nitrogen blow. Note that the remaining air bubbles inside the pore

channels were removed by mild and brief sonication to ensure that the pore channel was fully saturated with such solution. SEM and EDS images were performed with Hitachi-S4800.



Element	Weight	Atomic
Ag	34.7	9.3
Si	29.4	30.2
O	15.6	28.1
C	8.5	20.4
Na	4.8	6.0
Al	3.2	3.4
Ca	2.2	1.5
Zn	1.2	0.6
Mg	0.4	0.5
Total	100.0	

Fig S2 Characterization of the electroless plated tapered sub-wavelength pore channel. (a) SEM image of the tip area of another pore channel at a slightly inclined angle. (c) EDS of the plated material of the tip area.

S3. Confocal laser scanning fluorescence measurement inside the TSSP (pinhole 25μm）

Confocal imaging and confocal Rhodamine B water solution fluorescence intensity measurements on an inverted confocal microscope (Leica TCS SP5, Leica Microsystems). The excitation source was an argon ion laser, wavelength 514nm with emission collecting range 530nm-580nm. Z-stacks taken through x and y-directions scanned across the whole tapered pore channel filled with 10μM water solution of Rhodamine B dye. The pinhole was adjusted at 25μm Fig S3 and at 60 μm Fig S4 respectively.

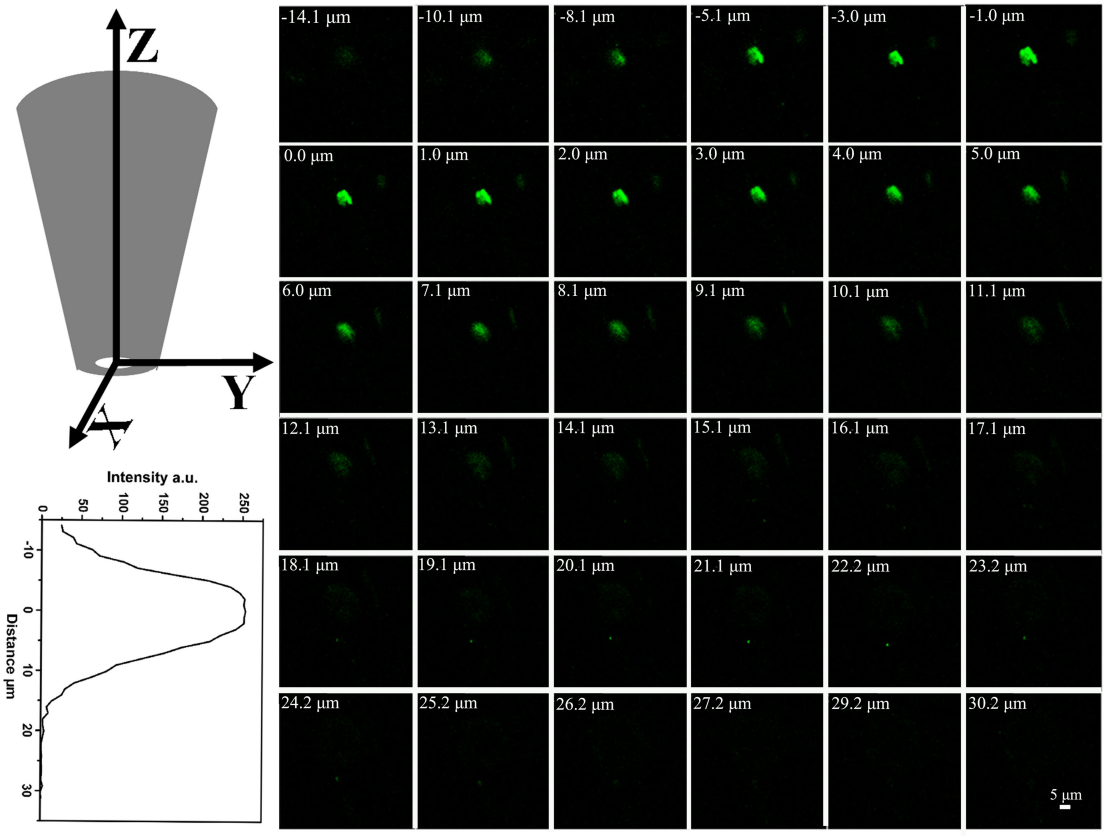


Fig S3 Confocal fluorescence images across the whole pore channel and emission intensity analysis. The measurements were

performed using 20× 0.7 NA objective with a confocal pinhole of 25μm.Z-stacks were taken begin the outside of the pore (-14.1μm) and passed through the pore, then through the dye filled pore channel. The brightest spot was chosen as the position of the pore at 0μm (left). The confocal fluorescence images indicated the emission intensity corresponding to different areas across the pore channel (right)..

S4. Fluorescence intensity in the areas of tip space and outside silver surface of another TSSP (Diameter ~150nm). The outside silver surface has different silver deposition environment from that in the pore channel.

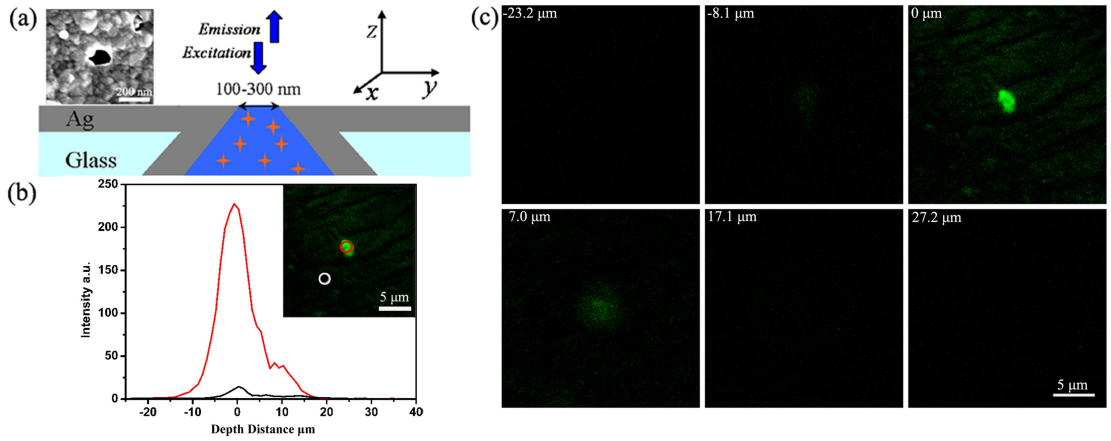


Fig S4 Confocal fluorescence images (1024×1024 pixels)and emission intensity analysis of a D~150nm TSSP filled with 10 μM Rhodamine B. Some dye molecules remained in the outside silver surface. (a) Scheme of the experiment with excitation taken on the small base and the fluorescence collected from the same side. Insert shows the SEM image of the aperture, scale bar 200nm. (b) Two intensity curves of two small areas were calculated as a function of different sections from the (c) scan images localized from outside to inside of the pore channel. The marked circles in the (b) insert represent two chosen small areas: red one around the pore and white one (far away enough from the pore channel) on the outside silver surface. The experiment was performed under an argon laser (514nm 2 mW); pinhole 25 μm; emission collection range 550-620 nm; objective (20×NA 0.7).

S5. Fluorescence intensity analysis inside the TSSP (Diameter ~300nm)

Different small ROIs were chosen to analyze the fluorescence intensity located at different positions within (ROI 1-6) and without (ROI 7) the TSSP. (Selected areas were chosen as small as possible to reduce the error value because the intensity represents a mean value for the selected areas). The peaks of the 1, 2, 3 lines were located around the tip space of the pore channel, while the peaks of the 4, 5, 6 lines represent the emission intensity in the vicinity of the silver surface due to the metal enhanced fluorescence. The bulk solution intensity was taken from the average value of the second part of each line (20-30 μm) where both plasmonic and dimensional effects were not anticipated. Line 7 measured without the channel represented the background signal. Thus the fluorescence enhancement was determined.

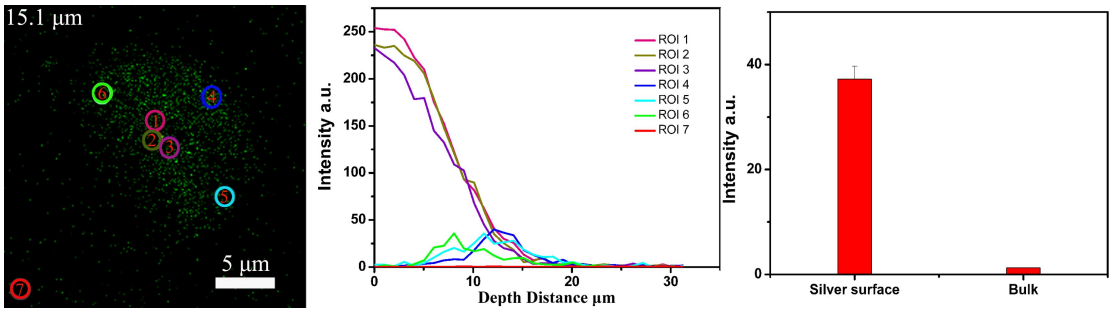


Fig S5 Different ROIs were chosen to analyze the fluorescence intensity. Confocal fluorescence images of the TSSP and 7 ROIs at position 15.1μm (left). The measurements were performed using 20× 0.7 NA objective with a confocal pinhole of 25μm.The fluorescence intensity distribution of different areas with the function of Z axis distance which was from the tip to bulk solution (middle). The emission intensity of the silver surface areas has 30 fold enhancements to the bulk solution (right). The error bars represent the standard deviation (3σ) observed for three chosen circular areas under the same conditions (Scale bar 5 μm).

S6. Fluorescence lifetime measurements

The total lifetime 0.88 ± 0.09 ns in glass tip with diameter ~110nm became shorter than that one 1.53 ± 0.04 ns with diameter ~300nm. For silver tip, the total lifetime change was also declining from 2.39 ± 0.04 ns to 2.19 ± 0.08 ns with decreasing the pore diameter from ~300nm to ~150nm. We suggested that there was existing competition variation between the radiative and nonradiative decay rate under the plasmonic-aperture process when change the pore diameter, which leads to the different total lifetime change ratio between the glass tip and silver tip.

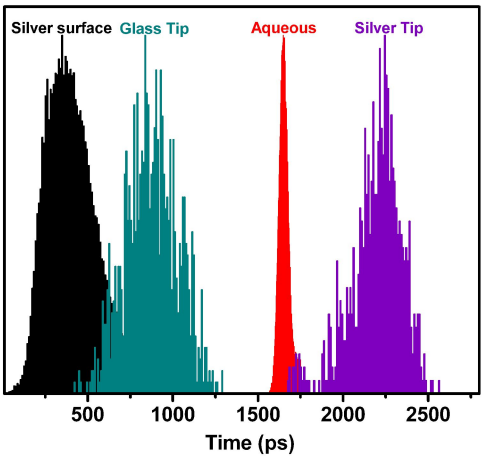


Fig S6 Normalized lifetime statistical histograms for each area from RhB dye molecules FLIM measurements. RhB fluorescence lifetimes in different environments-aqueous solution, silver surface, glass pore tip (D~110nm) and silver pore tip (D~150nm).An area on the outside silver surface was chosen to analyze the lifetime at silver surface. For glass pore tip (D~110nm) and for silver pore tip (D~150nm), the total lifetimes were 0.88 ± 0.09 ns and 2.19 ± 0.08 ns, respectively. The FLIM measurements were carried out using a pulsed 405nm excitation laser. Data analysis was conducted using SPC-830 software.

References

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