Polarization-dependent surface plasmon-driven catalytic reaction on a single nanowire monitored by SERS†

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The polarizing effect of an excitation laser on a plasmon-driven catalytic reaction on a single nanowire (NW) was investigated experimentally and theoretically. The dimerization of 4-nitrobenzenethiol (4NBT) to p,p′-dimercaptoazobenzene (DMAB) due to localized surface plasmon resonance (LSPR) was realized and monitored via surface enhanced Raman scattering (SERS). The SERS signal degradation has been compensated by using different equivalent points on the NW. It was shown that the SERS signals of both the reactant and product were sensitive to the angles (θ) between the longitude of the NW and the polarization direction of the excitation laser. When the polarization is along the transverse direction of the NW, the SERS signals are drastically enhanced by the LSPR. The efficiency of the plasmon-driven catalytic reaction increased significantly. The mechanism of the polarization-dependent plasmon-driven catalytic reaction was revealed by our dark field experiment and numerical finite-difference time-domain simulation. It was demonstrated that the maximum intensity of the electric field near the surface of the NW would also be a function of the angle θ. The theoretical and experimental results were consistent with each other. This research may pave a way for controlling plasmon-driven catalytic reactions by changing the polarization of an excitation laser incident on single anisotropic nanostructures such as a single NW.

I. Introduction

Plasmon-driven catalytic reactions were discovered in 2010 and have recently attracted much attention owing to their application in the fields of physics, chemistry, materials science, and solar energy. Plasmon-driven catalytic reactions can occur on plasmonic metal (Au, Ag) nanoparticles (NPs) via the collective excitation of the electrons on their surface, known as surface plasmons (SPs). SP decays either radiatively via re-emitted photons or non-radiatively through hot electron generation. These hot electrons play a central role in plasmon-induced chemical reactions by providing the required electrons and kinetic energy needed to overcome the reaction potential barrier. Recently, much progress in plasmon-driven catalytic reactions by hot electrons and hot holes has been reported. The polarization-dependent plasmon nanowire enhanced SERS and surface plasmon-driven catalytic reactions have also been reported.

These catalytic reactions can be monitored in situ using surface-enhanced Raman scattering (SERS) spectroscopy, as noble metal nanostructures act as photocatalysts and SERS signal enhancers. It is well known that SERS, as a significant optical technique for spectral analysis, offers ultrasensitivity, molecular fingerprinting and rapid pre-treatment. SERS substrates with a high enhancement factor, robust stability and acceptable reproducibility are required to obtain high-quality SERS spectra. Much effort has been devoted to fulfilling these requirements in recent years. Particularly, the nanogaps and nanodimers can produce hot spots that significantly enhance SERS. As the SPs of nanoparticles have much greater effects on SERS performance, nanoparticle dimers confine much more light energy than monomers for electromagnetic field redistribution, which is extremely useful in the nanoparticle-assisted SERS. However, this redistribution phenomenon requires the polarization of incident light to be parallel to the dimer axis. The diffraction limit makes it difficult to estimate the direction of the dimer axis or the quantity of nanoparticles (monomer, dimer, trimer) in microscopy. The metal NW structure offers a way to overcome the problem associated with the nanoparticle dimer described above. In microscopy, it is easy to judge the direction of a NW with a length of tens of microns. The angle between the polarization direction of the laser and the NW axis is easily changed,
so that the SP properties are dependent only on the polarizing effect of excitation. Hence, the NW is the optimal choice to obtain further details of the catalytic reaction mechanism on a single nanostructure as well as stable SERS substrates owing to these unique properties.30–32

SPs on a NW can be classified as propagating SPs (PSPs) and localized SPs (LSPs). PSPs are associated with collective excitation of conduction electrons that propagate in a wave-like manner along the NW axis, whereas LSPs are associated with oscillations of charge density that are confined to the metallic nanoparticle surface. Recent reports present remote-excitation surface catalytic reactions as a route to enhancing the rate of chemical reactions and offer a pathway to control surface catalytic reactions via PSPs on NWs.33–35

However, LSPs are more sensitive to the polarizing effect of the incident laser. The polarizing effect of the incident laser on catalytic reactions driven by LSPs needs to be investigated thoroughly. In this field, the following questions require urgent answers. How can the polarizing effect of the excitation of LSP-driven chemical reactions on a NW be revealed? What is the mechanism of LSP-driven chemical reactions on a NW? How does the near field distribute on a NW?

II. Results and discussion

The NW sample is a good candidate for micro- and nanoscale experiments, especially for the polarization-dependent SERS experiment. First, the NW sample can be conveniently viewed under a microscope with the naked eye. Second, it possesses well-defined anisotropy in the transverse and longitudinal directions. These two factors are crucial for experimentally locating and manipulating micro- and nanoparticles. By improving the chemical method for preparing the nanowire,26 a well-defined and uniform high quality NW, which is about 15–25 μm, is prepared as shown in Fig. 1(b).

Fig. 1(a) shows a schematic diagram of a nano-wire obtained by microscopy and SERS measurement. θ is the angle between the longitude of the NW and the polarization direction of the excitation laser, indicated by a red line. The NW deposited on the Si film is well dispersed. A single NW viewed with the naked eye under a Zeiss microscope is shown in Fig. 1(c). The green spot around the center of the NW is the excitation laser spot at 532 nm. UV-vis absorption spectroscopy of the NW solution shows a maximum band at 418 nm and a long SP absorption tail extending to the infrared region. Thus this can be employed as a good SERS substrate both at 532 and 785 nm as shown in Fig. 1(d).

Considering the stable SERS signal of the sample R6G molecule, we checked the SERS of R6G on a single NW. Fig. 2(a) shows the SERS spectra of R6G at one spot on a NW at different polarization angles (θ). Fig. 2(d)-I shows a polar diagram of the SERS intensity of the peak 1361 cm⁻¹ in (a) as a function of the polarization angle. This demonstrates that the SERS signal was significantly influenced by the incident polarization; the best enhancement of SERS was obtained by irradiating with a laser polarized vertically to the NW axis, corresponding to the maximum values at θ = 90° and 270°. Generally, this shows that the SERS intensity is proportional to (sin θ)².32 However, it is clearly shown in Fig. 2(d)-I that while θ and θ + 180° represented the same polarization direction, the Raman intensity of the 1361 cm⁻¹ at θ > θ + 180° weakened. As the experiment was conducted in air, with increasing measurement times, the R6G on the NW experienced multiple laser exposure; hence the SERS signal of R6G can be degraded with time and the laser exposure. Our observations from Fig. 2(a) and (d)-I are as follows: first, it is clearly demonstrated that the SERS signal of the molecule on the NW is strongly dependent on the polarization of the excitation laser. Second, the degrading effect on the molecules affected the repeated SERS measurements at a single spot of the NW.

Considering the SERS measurement of the catalytic reaction on a NW as a function of the polarization angle, we must maintain the same initial reaction conditions for each angle. This would be a problem if we were unable to remove or decrease the effect of degradation. A further problem is associated with a decrease in the reactant and the accumulation of the product at one measurement spot, which would affect the results for catalytic reactions induced at different polarization angles. However, the above two problems can be resolved by changing the observation spots on the single NW for different polarization angles. As the NW is uniform, each spot along its axis has the same physical and chemical properties, such as SERS enhancement and adsorption capacity for the reactants.

For example, if the SERS experiments are conducted at two different polarization angles, two different spots can be sequentially selected along the NW axis, ensuring similar initial conditions for different SERS measurement angles, which is crucial for comparing the amount of the product...
was drastically decreased in contrast to that in Fig. 2(d)-I. These observations clearly show that the NW is uniform and different spots on one NW are equivalent for SERS experiment.

Next, we investigated the polarization-dependent plasmon-driven reduction reaction on a single NW by SERS at room temperature. For the plasmon-driven catalytic reaction, 4-nitrobenzenethiol (4NBT) candidate, which was studied in our previous work.1 The reactant 4NBT molecule could be reduced to the product $p,p'$-dimercaptoazobenzene (DMAB) molecule by the dimerization process driven by surface plasmons. For this kind of plasmon-driven reduction reaction, plasmonic hot electrons generated from plasmon decay play a core role and provide not only electrons for the reduction reaction needed but also a large amount of kinetic energy to overcome the potential energy barrier. This catalytic reaction of 4NBT to DMAB driven by SP has been reported previously.37,38 Fig. 3 shows the SERS and the simulated spectra of the 4NBT reactant and the DMAB product. These results are consistent with each other. Here $\nu_1 = 1081$ cm$^{-1}$, $\nu_2 = 1338$ cm$^{-1}$, and $\nu_3 = 1572$ cm$^{-1}$ are characteristic Raman peaks of 4NBT, and $\nu_4 = 1141$ cm$^{-1}$, $\nu_5 = 1386$ cm$^{-1}$, $\nu_6 = 1432$ cm$^{-1}$ are characteristic peaks of DMAB. The normal vibrational mode of $\nu_2$ is attributed to the NO-stretching of 4NBT and $\nu_6$ is associated with the NN-stretching of DMAB.3

Firstly, we checked the uniform properties by catalytic reaction on different detecting points on one NW and at different polarizing angles. We provided the SERS measurements of the catalytic reaction from 4NBT to DMAB at each detection point on one NW at the same polarization angle as shown in ESI, Fig. 1†. It is clearly demonstrated that each detecting point on the same NW is very uniform and almost similar plasmon-driven catalytic reactions occurred at each polarizing angle. The dimerizing catalytic reaction from 4NBT to DMAB driven by SPs at different polarization angles. This prediction was confirmed by performing the SERS measurement of R6G at different spots (named C, D, E, F, G, H, I, and J) on one NW with a polarization angle of $\theta = 45^\circ$ as shown in Fig. 2(b). The prominent Raman bands at $970$ cm$^{-1}$ attributed to the overtone of $520$ cm$^{-1}$ of Si at C, D, E, F, G, H, I, and J spots were enhanced and possess similar intensities. The SERS intensities of the $1361$ cm$^{-1}$ peak of the R6G molecule are very uniform as shown in Fig. 2(e). This clearly demonstrates that different spots on one NW are equivalent for the SERS experiment. Furthermore, the SERS spectrum of R6G at different spots on one NW with different polarization angles was recorded as shown in Fig. 2(c). One spot corresponded to one polarization angle. A polar plot of the SERS intensity of the $1361$ cm$^{-1}$ band at different spots recorded as a function of the polarization angle $\theta$ is shown in Fig. 2(d)-II. The tendency of the SERS intensity of the $1361$ cm$^{-1}$ band was proportional to $(\sin \theta)^2$. Now the Raman intensities of the $1361$ cm$^{-1}$ band at $\theta > \theta + 180^\circ$ are almost equal. The decreasing degrading effect on the NW

![Fig. 2](image)

**Fig. 2** (a) Polarization-dependent SERS spectra of R6G at one spot of one NW with different polarization angles; (b) The SERS spectrum of R6G at different spots (named C, D, E, F, G, H, I, and J) on one NW with a polarization angle of $\theta = 45^\circ$. (c) The SERS spectrum of R6G at different spots on one NW with different polarization angles. One spot corresponded to one polarization angle. (d) A polar plot of the SERS intensity of the $1361$ cm$^{-1}$ band (highlighted by a black straight line) recorded as a function of the polarization angle $\theta$. I, the $1361$ cm$^{-1}$ band recorded in (a); II, the $1361$ cm$^{-1}$ band recorded in (b); III, the $(\sin \theta)^2$ function as comparison. (e) The SERS intensity of the $1361$ cm$^{-1}$ band recorded at different spots (C, D, E, F, G, H, I, and J) shown in (b).
due to SP is increasing with the increasing polarizing angles even though the results of the product coverage are compared via different NWs.

Secondly, by a similar process, we investigated the effect of polarization on the catalytic reaction on ONE NW at different polarization angles $\theta$. As shown in Fig. 4, it was found that the SERS profiles of 4NBT from $\theta = 0^\circ$ to $\theta = 20^\circ$ were identical to those for the Raman spectra of 4NBT, which are mainly $\nu_1$, $\nu_2$, and $\nu_3$ as shown in Fig. 3(a). The three new SERS peaks, $\nu_4$, $\nu_5$, and $\nu_6$, which are attributed to DMAB appeared gradually as the polarization angle of the excitation laser increased from $\theta = 20^\circ$. This demonstrated that 4NBT was gradually reduced to DMAB by SPs. When $\theta$ was increased from $20^\circ$ to $90^\circ$, the intensity of $\nu_4$, $\nu_5$, and $\nu_6$ increased to a maximum, suggesting that more 4NBT was catalytically transformed to DMAB on the surface of the NW.

To estimate the relative surface coverage of 4NBT and DMAB during the reaction, we analyzed the intensities of the SERS peaks at $\nu_2 = 1338$ cm$^{-1}$ (4NBT) and $\nu_6 = 1435$ cm$^{-1}$ (DMAB). The intensities of $\nu_2$ and $\nu_6$ arose from 4NBT and DMAB, respectively. Here, by assuming similar SERS enhancement factors for $\nu_2$ and $\nu_6$, the surface coverage of the product versus reactant species can be weighted by the SERS intensities ($I_{\nu_2}, I_{\nu_6}$). Such relations can be derived from eqn (1)

\[
\begin{pmatrix}
I_{\nu_2} \\
I_{\nu_6}
\end{pmatrix} = \begin{pmatrix}
\sigma_{4\text{NBT},\nu_2} \\
\sigma_{\text{DMAB},\nu_6}
\end{pmatrix} \begin{pmatrix}
\mu_{4\text{NBT}} \\
\mu_{\text{DMAB}}
\end{pmatrix}
\]

where $\mu_{4\text{NBT}}$ and $\mu_{\text{DMAB}}$ are the surface coverages of 4NBT and DMAB, respectively, and $\sigma_{4\text{NBT},\nu_2}$ and $\sigma_{\text{DMAB},\nu_6}$ are the corresponding Raman scattering cross sections of the solid species (the values are taken from ref. 38).

From eqn (1), we obtained the surface coverage rate as follows:

\[
\frac{\mu_{4\text{NBT}}}{\mu_{\text{DMAB}}} = \frac{I_{\nu_2}}{I_{\nu_6}} \times \frac{\sigma_{\text{DMAB},\nu_6}}{\sigma_{4\text{NBT},\nu_2}}
\]

Fig. 4(b) shows the surface coverage of 4NBT and DMAB with different polarization angles. It is clearly shown that as the polarization angle increases, the coverage of product DMAB increases, and that of reactant 4NBT decreases. This suggests that more DMAB is produced at larger polarization angles. This enhanced catalytic reaction is due to the hot electrons decayed by the LSPR on the NW. When the polarization angle $\theta$ is 0, the LSPR induced excitation of the NW is reduced, hence, the probability of hot electrons being decayed by the LSPR is minimal. As $\theta$ increases, the LSPR is enhanced and the hot electrons increase. When $\theta = 90^\circ$, the laser is polarized vertically to the NW axis, such that the LSPR reaches a maximum, which not only enhances the SERS signal but also creates more hot electrons, driving more 4NBT to dimerize to DMAB.

The above conclusions on the LSPR of NW could also be confirmed by the dark-field (DF) experiments. As shown in Fig. 5, they are scattering spectra with a single NW at different polarization angles. The inset in Fig. 5 shows the corresponding DF images of the single NW. It is clearly demonstrated that the intensities of the peaks of scattering spectra

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Fig. 4 (a) SERS spectrum of 4NBT on the NW at different polarization angles $\theta$ at 532 nm. (b) Coverages of the 4NBT reactant and the DMAB product at each polarization angle $\theta$.

Fig. 5 Experimentally measured DF scattering spectra with single NWs at different polarization angles. The inset shows the corresponding DF images of the single NW (scale bar: 40 $\mu$m).
due to LSPR of NW became more intense with the increasing polarization angles.

To theoretically investigate the SERS enhancement of a single NW, the FDTD method was employed to calculate the local electric field intensity distributions $E^2$ around a single NW at different $\theta$. Fig. 6(a–d) show the near electromagnetic field distribution on the $xy$ plane of the surface of section ($z = 0$) on both sides of the NW axis for $\theta = 0^\circ$, $30^\circ$, $60^\circ$, $90^\circ$, respectively. Fig. 6(e) shows the maximum values of $E^2$ increase with $\theta$ and the positions of the maximum values of $E^2$ on the surface of section ($z = 0$) are also approaching the surface of NW. Fig. 6(f) gives the $E^2$ values of the near electromagnetic field at 2 nm from the surface of the NW as a function of the polarization angle $\theta$. Meanwhile the near electromagnetic field $E^2$ values correspond to a $(\sin \theta)^2$ function. These simulation results confirm that the near EM field reaches its maximum intensity when the polarization direction of the laser is perpendicular to the NW ($\theta = 90^\circ$). In contrast, the near electromagnetic field reaches a minimum when the polarization direction of the laser is parallel to the NW axis ($\theta = 0^\circ$).

It is noted that the effect of the Si-substrate cannot be neglected. Here, we consider the coupling effect between the NW and the Si-substrate by FDTD simulation. As shown in Fig. 7, they are the electromagnetic field distributions of the NW/si-substrate system on the $yz$ plane of the surface of section ($x = 0$) in the middle of NW with different polarization angles (the four rows correspond to $0^\circ$, $30^\circ$, $60^\circ$, and $90^\circ$, respectively). The range of the $y$-axis is $-200$ to $200$ nm, and that of the $z$-axis is $-300$ to $600$ nm. Here the four columns correspond to the three $x$, $y$, and $z$ components ($E_x$, $E_y$, and $E_z$) and their total sum of the electromagnetic field ($E$) with different polarization angles, respectively. The coordinate system on the NW is the same as in Fig. 6.

Fig. 6 (a–d) FDTD simulation of the electromagnetic field distributions on the $xy$ plane of the surface of the section ($z = 0$) in the middle of NW with different polarization angles. The range of the $x$-axis is $-3$ to $3 \mu$m, and that of the $y$-axis is $-0.3$ to $0.3 \mu$m. The coordinate system on the NW is shown in the bottom of the figure. (e) The electromagnetic field $E^2$ is at different distances on both sides of the long axis of the NW on the $z = 0$ surface of the section. (f) The polar diagram of the near electromagnetic field $E^2$ at 2 nm from the surface of the NW on the $z = 0$ surface of the section as a function of the polarization angle $\theta$.

angles (the four rows correspond to $0^\circ$, $30^\circ$, $60^\circ$, and $90^\circ$, respectively). The first column $E_x$ shows that the maximum value of the electric field in the $z$ coordinate decreases with increasing polarizing angles. It is shown that the maximum value of the $E_x$ is far from the surface of the NW which is about 200 nm, and that the adsorbate molecules are very near near the surface of NW (less than 10 nm), then this $E_x$ does not affect the plasmon-driven catalytic reaction with increasing polarizing angles so much. The second column $E_y$ has the same results as shown in Fig. 6. However, the third column $E_z$ shows that the electric field is much more focused at the NW-Si-substrate gap with increasing polarizing angles. So the gap cavity due to the coupling between the NW and silicon substrate would play a very important role in plasmon-driven catalytic reactions.

For further confirmation that the catalytic reaction of 4NBT to form DMAB is enhanced by hot electron decay induced by LSPR of NW, we changed the excitation laser wavelength to an infrared wavelength of 785 nm. Here the power of the 785 nm laser is 90 mW, which is much larger than that of the 532 nm laser. Fig. 8 shows the SERS of 4NBT under excitation at 785 nm.
785 nm, when the polarization angles were changed from \( \theta = 0^\circ \) to \( \theta = 90^\circ \), characteristic \( \nu_1, \nu_2 \), and \( \nu_3 \) Raman peaks of 4NBT were gradually enhanced owing to the LSPR on the surface of the NW. However, the characteristic \( \nu_4, \nu_5, \) and \( \nu_6 \) Raman peaks of DMAB did not appear even at \( \theta = 90^\circ \). This can be explained according to the energy of the hot electrons decayed by LSPR at 785 nm (1.58 eV) which cannot cross the potential barrier of the catalytic reaction from 4NBT to DMAB. Although the power of the 785 nm laser is larger, it only enhances the intensity of LSPR, and the SERS signal of 4NBT. However, the 785 nm laser cannot induce or drive the catalytic reaction.

III. Conclusion

We studied the polarization-dependent SP-driven catalytic reaction on a single NW via SERS spectroscopy. A single NW was demonstrated to be an excellent platform for catalytic activity. The polarization angle of the excitation laser can be controlled to change the electromagnetic strength and further change the efficiency of hot electron generation to control the activity of the catalytic reaction. When the laser polarization at 532 nm is parallel to the NW, not only did the Raman peaks of reactant 4NBT weaken, but the Raman peaks of the product DMAB did not appear. As the polarization angles increased, the Raman peaks \( \nu_1 = 1081 \text{ cm}^{-1}, \nu_2 = 1338 \text{ cm}^{-1}, \) and \( \nu_3 = 1572 \text{ cm}^{-1} \) of 4NBT were enhanced, and three new Raman peaks \( \nu_4 = 1141 \text{ cm}^{-1}, \nu_5 = 1386 \text{ cm}^{-1}, \) and \( \nu_6 = 1432 \text{ cm}^{-1} \), associated with DMAB, also appeared and gradually became more prominent. This intense catalytic reaction was due to more hot electrons being decayed by LSPR of the NW as the polarization angle increased. This conclusion was confirmed by our FDTD simulation of the near EM field distribution on the NW surface. Further experimental proof was obtained using an excitation wavelength of 785 nm. As the low energy of hot electrons decayed by LSPR could not overcome the potential barrier of the catalytic reaction from 4NBT to DMAB, changing the polarization angle only enhanced the Raman signal of 4NBT. The plasmon-driven catalytic reaction on a single NW was realized and manipulated by changing the excitation polarization direction of the laser. Determining the mechanism of hot electron transfer from the NW to the reactant and increasing the efficiency of the catalytic reaction on NWs and nanoparticle/NW hybrid nanostructures are problems that will be addressed in our further investigations.

IV. Experimental section

A. Synthesis of NW

The silver NW was synthesized via a wet-chemistry polyol reduction method;\textsuperscript{36} 10 mL of ethylene glycol was placed in a glass beaker on a magnetic stirrer, and then 700 mg of polyvinylpyrrolidone (PVP) and 1000 mg of AgNO\(_3\) were slowly added and stirred until fully dissolved. Next, the mixed solution was placed in a sealed Teflon reactor, which was heated at 160 °C for 90 min. The reactor was then allowed to cool, and the product was washed with acetone and alcohol, centrifuged (2000 rpm, 10 min) and redispersed in ethyl alcohol (10 mL). Finally, a highly pure solution of silver NWs was obtained. The high-quality silver NW was \( \sim 20 \pm 5 \mu \text{m} \) in length and \( \sim 300 \pm 20 \text{ nm} \) in diameter from scanning electron microscope (SEM) observations.

B. Preparation of experimental samples

A solution of \( 10^{-4} \text{ M rhodamine 6G (R6G) in 10 mL alcohol solution was prepared, and then 1 } \mu \text{L bulk NW solution was added and mixed for 6 h. A solution of } 10^{-6} \text{ M 4NBT in 10 mL alcohol solution was prepared and then mixed with 1 } \mu \text{L silver NW solution in the dark for 12 h.} \)

A drop of mixed solution was cast on a photolithographic Si\(_1\) substrate (1 × 1 cm) and allowed to dry under a nitrogen atmosphere for 5 h in the dark. Finally, the single NW sample adsorbed by the reactant was ready for SERS detection. A drop of NW solution was cast on a glass substrate (1 × 1 cm) and allowed to dry in air for dark field experiment.

C. Characterization

Raman spectra were recorded using a microprobe Raman system RH13325 (R-2000) spectrophotometer. The samples were excited with 532 nm and 785 nm lasers with the corresponding effective powers of 0.15 and 90 mW, respectively. A 50\times objective was used to achieve a 180° backward scattering configuration. The distance between each detection point is set as 3 micrometers by considering the size of the laser spot which has a diameter of about 1 micrometer.

UV-visible (UV-vis) spectroscopy was performed using a Shimadzu UV 2401 PC instrument. A ready-made solution of Ag NW was placed in 5 mL quartz cells, which were then placed on the sample table of a UV-visible spectrophotometer for measurements. SEM measurements: for SEM analysis, one drop of solution was placed on a Si film and left to dry in air.
SEM images of the NW were obtained using a Hitachi S-4800 microscope.

Polarization resolved dark-field scattering spectroscopy optical measurements were performed under an inverted microscope equipped with a dark-field condenser (N.A. = 1.2) illuminated by unpolarized light from a halogen lamp, and a 40 objective (N.A. = 0.6) for the subsequent collection of the scattered light. The spectra were obtained by focusing the scattering of the single NW into the entrance slit of the spectrometer, and acquired using a thermoelectrically cooled CCD.

For the emitting-polarization-resolved spectra, a polarizer (LPVIS50, Thorlabs, the extinction ratio of the emitting polarizer from 550 to 1500 nm is larger than 10 000 : 1) was added in front of the entrance slit to resolve the polarization of light scattered by nanostructures. Here, only the collection light passes through the polarizer, while the illumination is still unpolarized. In order to calibrate the polarization dependence of the spectrometer and the scattering intensity, each scattering spectrum has been corrected by the illumination spectrum measured at the same emitting-polarization angle.

D. Theoretical simulation section

The theoretical simulations in this paper were conducted via the finite-difference time-domain (FDTD) method using the Lumerical FDTD Solutions 8.0 software. The nanowire systems configured here consisted of one silver nanowire long cylinder, placed along the data for silicon were used. The single NW for simulation was a amaximum of 1.0 V m−1. A perfectly matched layer boundary conditions are set as a perfectly matched layer (PML) between the NW and silicon substrate. Finally, the FDTD electric field convergence. The simulation mesh size was 2 nm; the duration of all simulations was fixed at 500 fs to ensure full electric field convergence. The simulation mesh size was 2 nm; fine meshes of 1 nm resolution were used to describe the gap between the NW and silicon substrate. Finally, the FDTD boundary conditions are set as a perfectly matched layer (PML) to absorb all incident light.

Conflicts of interest

There are no conflicts to declare.

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References