Polarization dependence of the light coupling to surface plasmons in an Ag nanoparticle & Ag nanowire system*

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Polarization dependence of the coupling of excitation light to surface plasmon polaritons (SPPs) was investigated in a Ag nanoparticle–nanowire waveguide system (a Ag nanoparticle attached to a Ag nanowire). It was found that under the illumination of excitation light on the nanoparticle–nanowire junction, the coupling efficiency of light to SPPs depends on the polarization of the excitation light. Theoretical simulations revealed that it is the local near-field coupling between the nanoparticle and the nanowire that enhances the incident light to excite the nanowire SPPs. Because the shapes of the Ag nanoparticles differ, the local field intensity, and thus the excitement of the nanowire SPPs, vary with the polarization of the excitation light.

Keywords: Ag nanowire, Ag nanoparticle, surface plasmon, local near field

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1. Introduction

One-dimensional metallic nanostructures, such as crystalline Ag nanowires, are capable of guiding surface plasmon polaritons (SPPs), which are the coupling of electromagnetic wave and collective electron oscillation on their surfaces under visible or near-infrared excitation.[1–8] The propagation of SPPs on these wire surfaces is laterally confined well below the diffraction limit, and extends over distances of 10 μm or longer along the nanowire axes.[9] Since the miniaturization of optical elements is critically important for the further development of photonic devices,[10–15] plasmonic nanowires have become potential candidates as optical components at a subwavelength scale in nanophotonic circuits.[16–20] So far, crystalline Ag nanowires with high quality have mostly been obtained by a wet-chemical synthesis method. They possess good crystalline structures and smooth surfaces, resulting in significantly lower nonradiative losses and hence longer SPP propagation lengths.[21–25] Ag nanowires can be synthesized to be as long as several hundreds of micrometers, which is convenient to integrate various types of components. However, the high-efficiency coupling of far-field light to nanowire SPPs is the first and important step, and has not been accomplished perfectly. In most previous work,[5,8,15–18] the end of a nanowire is the input location for the SPP excitation, where the geometric defects cause the incident light to scatter intensely, providing momentum-pairing between photons and plasmons. The limitation of this method is that the input light location is precisely fixed, so only a small segment (about 10 μm) of the nanowire close to the end can be exploited for device applications due to the short decay length of SPPs, of only 3–10 μm.

It was recently proposed that a metallic nanoparticle in close proximity to the nanowire can act as an optical antenna, making an efficient coupling between far-field light and nanowire SPPs.[26–28] This approach allows for the direct manipulation of a nanoparticle onto the desired position of the nanowire, so the input location of the excitation light can be controlled. In this paper, we report our experimental observations of the influence of the polarization of the excitation light on a Ag nanoparticle–nanowire structure. By coupling the visible light to the SPP, we find that the polarization of the excitation light produces a significantly different coupling effect for the light input at the end of the nanowire versus at the nanoparticle–nanowire junction. When the excitation light is focused on the end of the nanowire, with the polarization parallel (perpendicular) to the nanowire axis, the maximum (minimum) SPP coupling efficiency can be obtained. However, when the excitation light is focused on the nanoparticle–nanowire junction, the coupling characteristic is very complex: some nanowires have a constant coupling efficiency regardless of the polarization direction, some behave the same as if the input light was at the end of the nanowire, and some display a totally inverse rule. Our theoretical simulations reveal that the local near-field coupling between the nanoparti-

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cle and the nanowire plays a major role in the generation of the nanowire SPPs. The polarization dependence is complicated because the local field intensity is sensitive to the geometrical features and the arrangement of the Ag nanoparticle and, furthermore, affects the SPP coupling efficiency in this nanoparticle–nanowire system.

2. Experiments

The silver nanowires were synthesized by an established polyol process.[21] In brief, 0.1 g of polyvinyl pyrrolidone (PVP) was added to 7 ml of ethylene glycol, and then heated to 160 °C for 1 h. Next, 8 mg of AgCl was added for the nucleation of silver seeds. After 5 min, 25 mg of $AgNO_3$ was added, allowing a 60-min reaction for complete reduction. The solution was cooled to room temperature, washed via centrifugation once in acetone to remove ethylene glycol, and then washed twice in ethanol to remove PVP. For our synthesized Ag nanowires, the nanowire diameters are about 100–200 nm; the lengths range from several tens to hundreds of micrometers. The silver nanoparticles were prepared using the citrate reduction process described by Lee and Meisei.[29] The obtained nanoparticles are about 50–200 nm in size. The nanowire solution was first spin-coated on a glass coverslip, and then the nanoparticle solution was drop cast onto the same coverslip, and finally dried with nitrogen gas for measurement.

All of our work was done on a microscope (Olympus BX51). The SPPs were excited by focusing a laser beam with a wavelength of 671 nm through a 100× objective (N.A. = 0.9) to the Ag nanowires. Here, the diffraction-limited laser spot on the nanowires is about 500 nm in size for the 671 nm laser beam. The emission from the nanowire end or the nanowire–nanoparticle junction was collected by the same objective and the optical image was recorded by a TE cooled 1392 × 1040 CCD detector mounted onto the microscope. The intensity of the emission was determined by finding the maximum value in the emission spot from the optical image.

3. Results and discussion

Figure 1(a) shows a Ag nanoparticle attached to a Ag nanowire with a distance of about 6 μm between the nanowire end and the nanoparticle. The arrow oriented to the nanowire axis here indicates the reference polarization of the 671 nm excitation laser light. In Fig. 1(c), the focused light spot (the brightest spot of 1 μm) is fixed on the nanowire end for the excitation of SPPs along the nanowire, and the light emission marked with an arrow can be observed from the location around the nanoparticle–nanowire junction. This indicates that the SPPs are indeed excited at the input location of the nanowire end, propagate along the nanowire, and are converted back to free-space photons at the nanoparticle–nanowire junction due to the scattering effect. That is to say, the end of this nanowire can act as a light scattering source, providing momentum-pairing between photons and plasmons, which mediates the far-field light excitations to transform into plasmons.[2,30,31] As the polarization direction of the incident light varied from 0° to 90° (from parallel to perpendicular to the nanowire axis), figure 1(c) clearly shows that the light emission at the nanoparticle–nanowire junction becomes weaker and weaker, and finally disappears. This result shows that the efficiency of in-coupling between light and SPPs is greatest when the polarization of the light is parallel to the nanowire axis, which is consistent with the previous results.[5,16–18] When the excitation light is focused on the nanoparticle–nanowire junction, the light emission is observed at the nanowire end, marked with an arrow in Fig. 1(d). With the Ag nanoparticle attached onto the Ag nanowire, an antenna-like effect occurs, and can effectively couple light to SPPs along the nanowire. Comparing Fig. 1(c) with Fig. 1(d), the intensity of the light emission is almost constant at the nanowire end with the varied polarization, in contrast to the case of the light emission at the junction. More detailed results are shown in Fig. 1(b), where the light emission intensity at the junction (red line) follows an approximate $\sin^2\theta$ polarization dependence (θ is the angle between the polarization and the reference direction), while the one at the nanowire end (black line) remains almost constant with the varying polarization direction.

Figure 2 plots the light emission intensity versus the polarization direction for two nanoparticle–nanowire systems (the optical micrographs are not shown here). Here, when the light is incident on the nanowire end, the light emission intensity at the junction follows the same polarization dependence for the two samples, also identical to that in Fig. 1, which shows a $\sin^2\theta$ polarization characteristic. However, when the light is incident on the junction, for one sample (Fig. 2(a)) the light emission at the end obeys the rule of $\sin^2\theta$, whereas for the other sample (Fig. 2(b)) the rule is $\sin^2(\theta + 75°)$ within an error of about ±20°. That is to say, when the polarization direction is about perpendicular (parallel) to the nanowire axis, the light emission intensity is maximum (minimum). Note that the other samples we investigated (not shown here) mostly show a different polarization dependence. The two plots have another similar feature in that the light emission intensity at the nanowire end is higher than that at the junction, which is the case for the majority of samples we investigated. This indicates that the antenna-like function of the nanoparticles can significantly increase the efficiency of coupling light to the nanowire's SPPs. These results clearly demonstrate that the conditions of coupling light to nanowire SPPs by means of nanoparticles are very complex because the characteristics of the nanoparticle antenna effect rely on the shape of the nanoparticle, the nature of the gap between the nanoparticle and the nanowire, and so on.

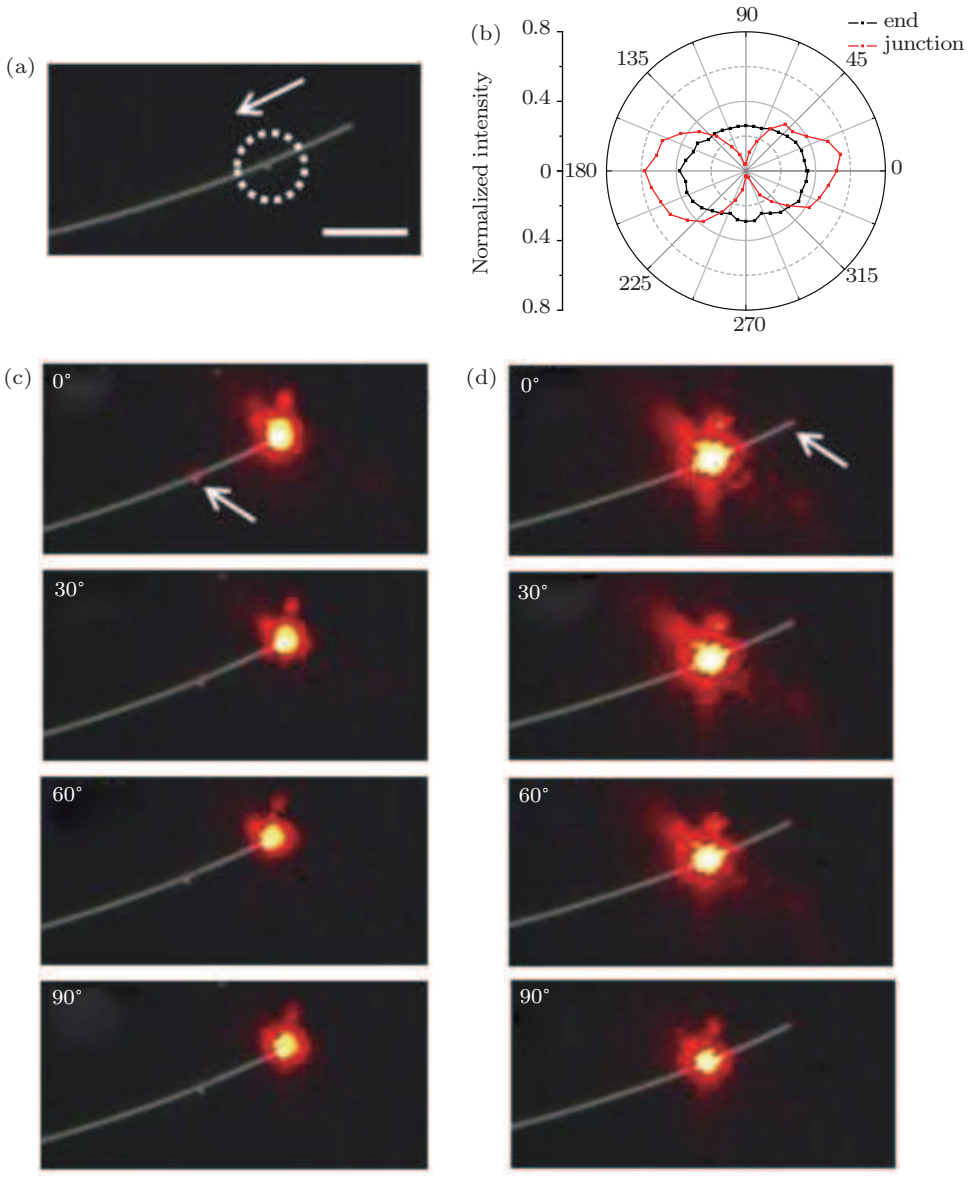


Fig. 1. (color online) (a) Optical micrograph of a Ag nanoparticle (marked by a dotted circle) attached to a Ag nanowire. The arrow is along the nanowire axis, indicating the reference direction of polarization of the excitation light. The scale bar in the frame is 5 μm. (b) The intensity of the output light emission as a function of the polarization direction for different light input regions at the nanoparticle–nanowire junction and the nanowire end. The black line refers to the output light emission at the nanowire end, and the red line for the nanoparticle–nanowire junction. (c) and (d) Two series of optical micrographs of different polarization directions for the input light (c) at the nanowire end and (d) at the nanoparticle–nanowire junction. The white arrows here mark the light emission spots.

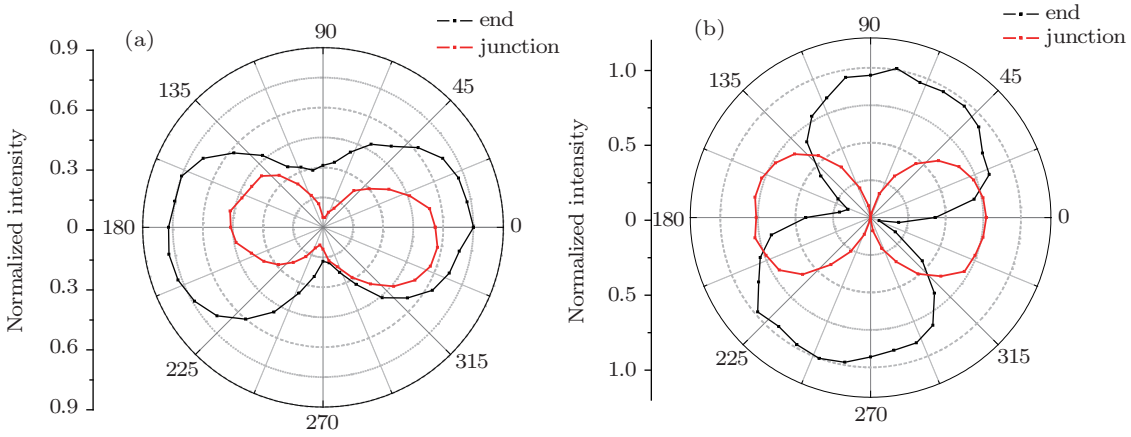


Fig. 2. Polarization dependence of the intensity of the output light emission for two selected Ag nanowires with Ag nanoparticles attached. (a) The light input at the nanowire end gives the same polarization dependence as the input at the nanoparticle–nanowire junction. (b) The light input at the nanowire end gives a polarization dependence opposite to the input at the nanoparticle–nanowire junction.

Figure 3(a) presents a shorter nanowire (13 μm in length) with a nanoparticle attached near its middle. Figure 3(c) shows that when the light is incident on one end of the nanowire, two light emission points are observed, the stronger one at the junction and the weaker one at the other end of the nanowire, both of which follow the same polarization dependence of $\sin^2\theta$ for the light emission intensity. But when the light is incident on the junction, as shown in Figs. 3(b) and 3(d), the light emissions at the two ends of the nanowire are significantly different, the lower end follows $\sin^2\theta$, while the upper one follows $\sin^2(\theta + 25°)$. This effect may be due to the fact that the short nanowire can function as a Fabry–Perot cavity, resulting in geometry specific standing plasmon waves.[1,26,32] With the different cavity lengths (here indicting the distance between the nanoparticle and the two ends), the resonant modes are selected by the light polarization angle.

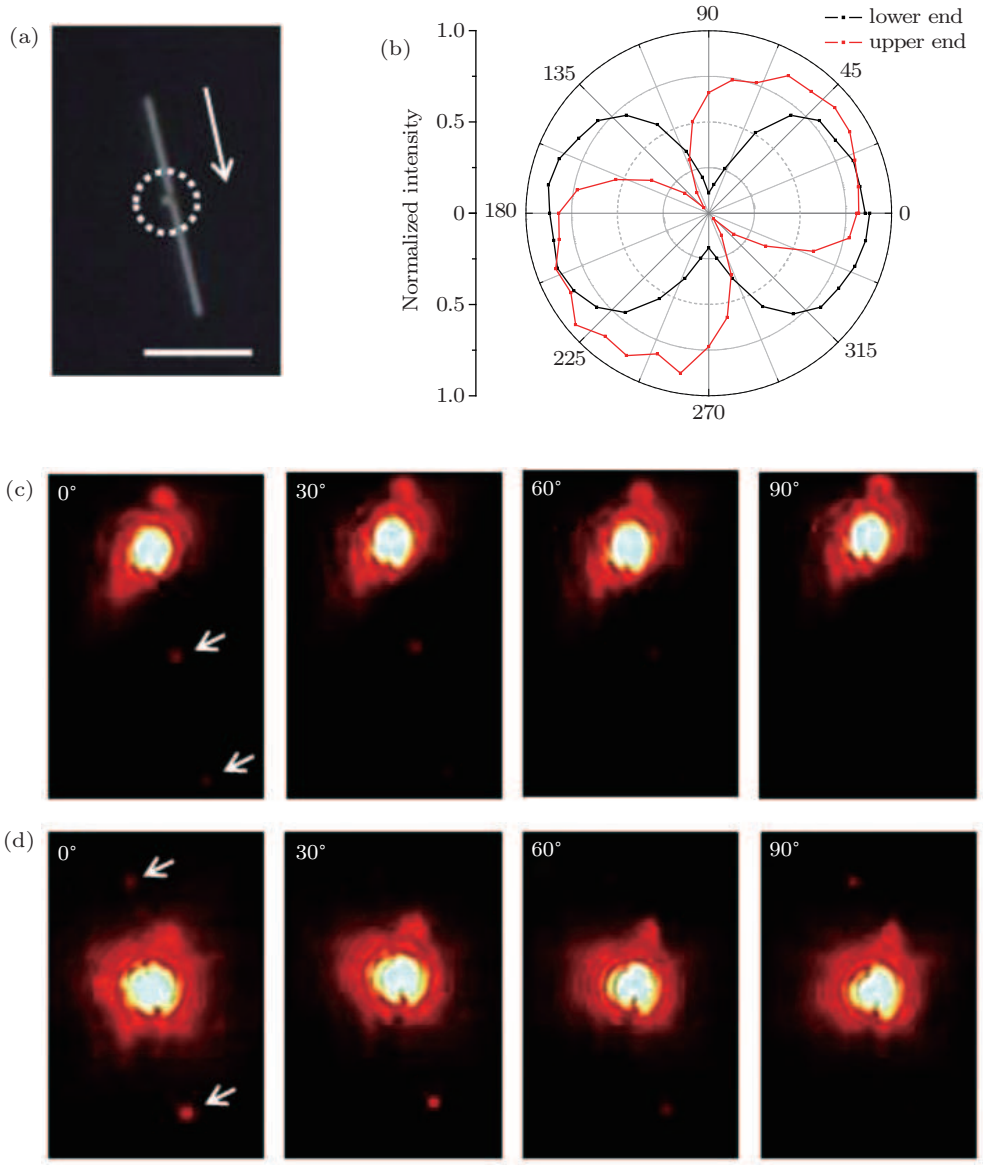


Fig. 3. (color online) (a) Optical micrograph of a shorter Ag nanowire with a Ag nanoparticle attached. The arrow along the nanowire axis indicates the reference direction of polarization of the excitation light. The scale bar in the frame is 5 μm. (b) Polarization dependence of the intensity of the out-coupling light emission at the lower (black line) and the upper (red line) nanowire ends when the light is incident on the junction. Two series of optical micrographs of different polarization directions for input light (c) at the nanowire end and (d) at the nanoparticle–nanowire junction. The white arrows mark the light emission spots.

Numerical simulations using a finite differential time-domain (FDTD) method are performed to gain a physical insight into the mechanism of SPPs generation in the Ag nanoparticle–nanowire system. The simulation models of nanowires and nanoparticles are referenced from the scanning electron microscope (SEM) observations, as shown in Fig. 4, where the SEM images show some representatives of the chemically synthesized Ag nanowires with a Ag nanopar-

ticle attached to each. As expected, the Ag nanowires all display a cylindrical shape with diameters in the range of about 100–200 nm, while the Ag nanoparticles possess a diversity of appearances. For example, figure 4(a) displays a spherical nanoparticle. In Figs. 4(b) and 4(c), the nanoparticles have more cuboidal shapes. In Figs. 4(d)–4(f), the nanoparticles exhibit more complex polyhedral shapes. The sizes of these nanoparticles are in the range of about 70–200 nm. In Fig. 4, it is difficult to view clearly the contacting details between the nanoparticles and the nanowires; however, it is evident that the sides of some polyhedral nanoparticles tilt to form certain angles with respect to the nanowire axis, which obviously implies different contact areas.

Based on the above observations, the simulation model of the Ag nanowire is taken as a cylinder with a diameter of 200 nm and a length of 4 μm, with the nanowire enveloped by a thin layer (2 nm) of PVP introduced in the synthesizing process. For totally reflecting the shapes of the Ag nanoparticles, two models are chosen: one is a sphere with a diameter of 70 nm, the other is a cube with dimensions 140 nm× 140 nm× 140 nm. In addition, they are enveloped by a thin layer (2 nm) of PVP. A polarized Gaussian beam (beam waist 0.5 μm) with a vacuum wavelength of 671 nm is simulated as the excitation source. For a given source polarization, the light emission intensity at the nanowire end is reasonably proportional to the electrical intensity of the corresponding position.

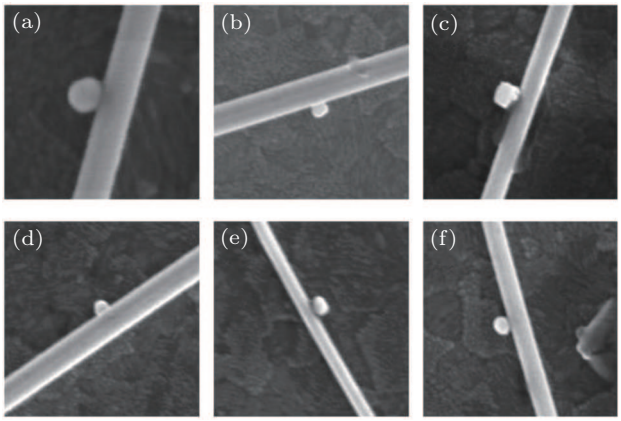


Fig. 4. (color online) SEM images showing (a)–(f) various shapes of Ag nanoparticles attached on Ag nanowires. All frames are 1 μm × 1 μm. The figures here are not the same as those in Figs. 1 and 3.

Figure 5(a) shows, for a Ag nanowire without a Ag nanoparticle attached, the cross-sectional near-field electric field intensity ($|E|^2$) distribution along the nanowire axis when the excitation light with its polarization parallel (0°) to the nanowire axis is focused on one end of the nanowire. Figure 5(b) shows the electric field distribution for a Ag nanowire with a spherical Ag nanoparticle (70 nm in diameter) attached when the excitation light, with its polarization perpendicular (90°) to the nanowire axis, is focused onto the nanowire–nanoparticle junction. The generation of SPP standing waves is obviously distinguished just outside of the nanowire for the two cases, with almost the same $\lambda_{spp}/2 = 285$ nm. By further calculations, as shown in Fig. 5(c), it is found that for the case of the excitation light incident at the nanowire end, the emission intensity (corresponding to the electrical intensity) at the other end reaches the maximum (minimum) when the polarization of the excitation light is parallel (perpendicular) to the nanowire axis; for the case of the excitation light incident at the nanoparticle–nanowire junction, the situation is exactly opposite. The SPPs are a transverse magnetic (TM) wave between the dielectric and the metal interface, whose E component is oriented along the axis of the Ag nanowire. Therefore, the polarization of the excitation light parallel to the nanowire axis should lead to the largest SPP coupling efficiency, considering the electromagnetic boundary conditions, which is in accordance with the case of excitation at the nanowire end. For the nanoparticle–nanowire system, there is a gap (here 4 nm) between the nanoparticle and the nanowire due to the PVP layers, which behaves like an optical nanoantenna under the light illumination. That is, if the polarization of the excitation light is perpendicular to the nanowire axis, the local field in the gap reaches the maximum, and with the polarization perpendicular to the nanowire axis, the local field reaches the minimum. In Fig. 5(c), the emission intensity at the nanowire end obeys the same polarization dependence as the local field, illustrating that this near-field coupling is the reason for the SPP generation along the nanowire axis.

The polarization dependence of the local field intensity between the nanoparticle and the nanowire relies strongly on the details of their geometric arrangement. For example, for the Ag nanoparticles with a cuboidal shape, the highest emission intensity at the nanowire end depends on the relative orientation between a cuboidal side and the nanowire axis. Figure 6 shows the cross-section near-field electric field intensity ($|E|^2$) distributions with different tilting angles between the nanoparticle and the nanowire. The first frame in Fig. 6 illustrates that when one side of the cuboidal nanoparticle is parallel (0°) to the nanowire axis, the local field in the gap is maximized when the polarization of the excitation light is perpendicular to the nanowire axis, and the emission intensity at the nanowire end is also the highest. However, when the side of the cuboidal nanoparticle is tilted to 10°, 20°, and 45°, the local field in the gap is largest as the polarization is changed to 30°, 15°, and 90°, respectively. This change of the local field intensity originates from the variation of the separation between the nanowire and the nanoparticle with the tilting angle. In the above experimental observations, since the practical nanoparticle shape is very complex, the contact situations between the nanoparticle and the nanowire are diverse, which results in very different polarization dependencies of the excitation light.

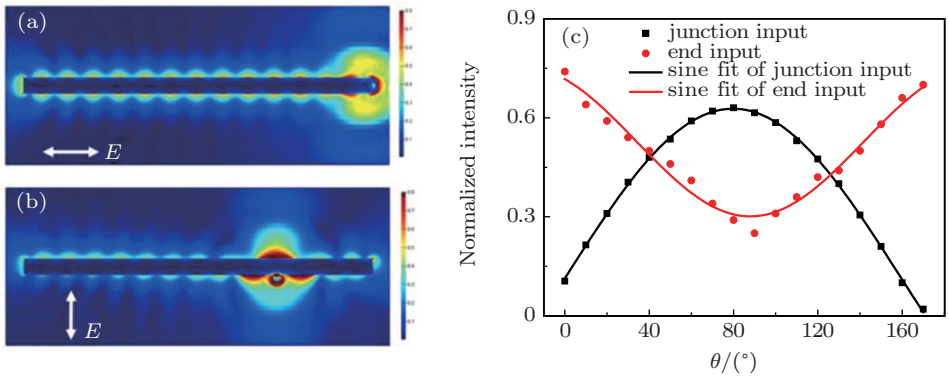


Fig. 5. (color online) (a) FDTD simulations of the near-field amplitude of the electric field for end excitation with polarization along the nanowire axis. The cylinder diameter of the nanowire is 200 nm, the length is 4 μm. (b) Near-field amplitude of the electric field for nanoparticle–nanowire junction excitation with polarization perpendicular to the nanowire axis. The Ag nanoparticle is spherical with diameter 70 nm. The two frames are 4.5 μm × 2 μm. (c) The nanowire end emission intensity as a function of the polarization for end excitation and junction excitation.

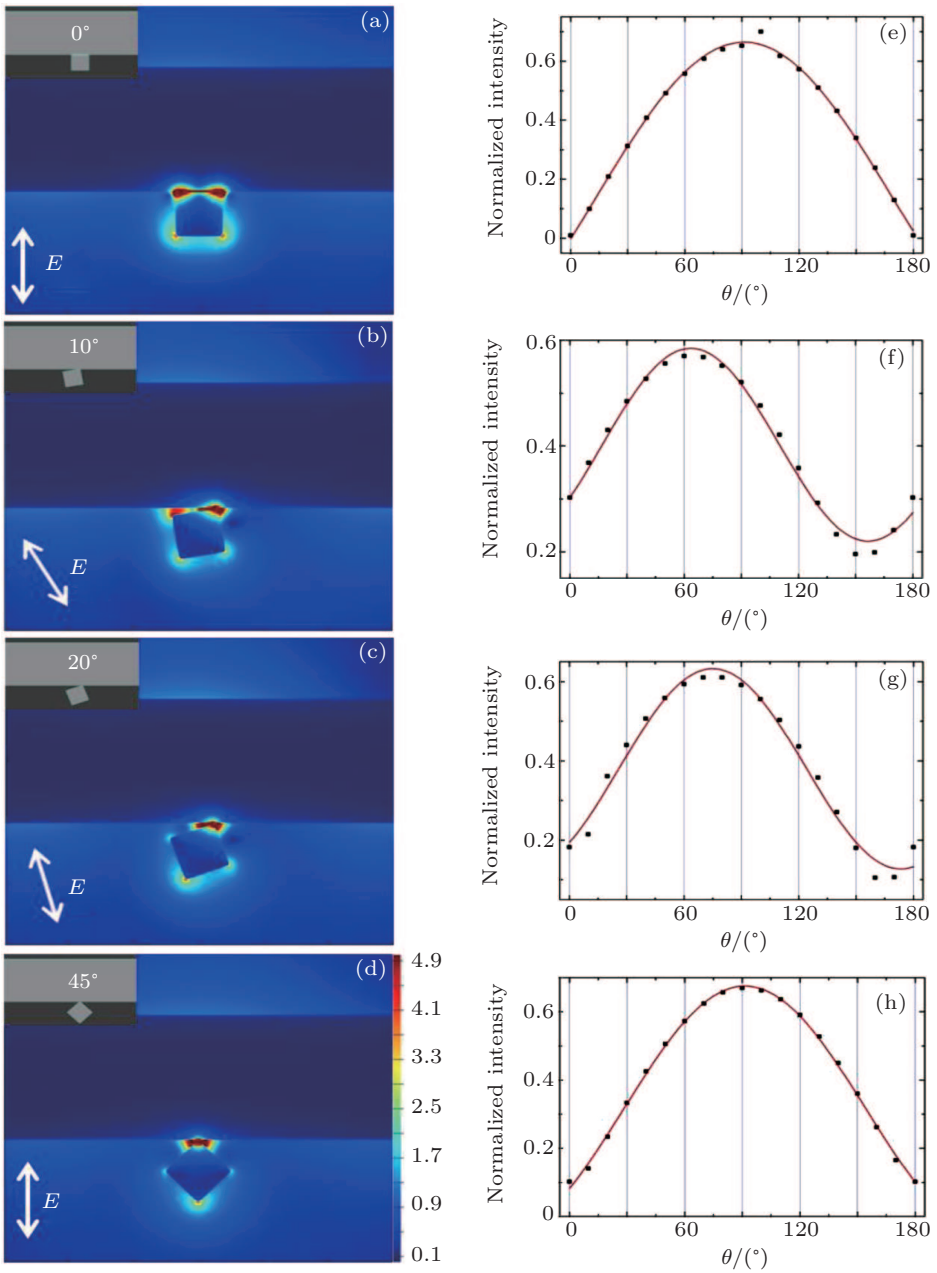


Fig. 6. (color online) FDTD simulations for a cylindrical Ag nanowire with a Ag cuboidal nanoparticle attached. (a)–(d) Near-field amplitude of the electric field respectively corresponding to the angles between the cuboidal side and the nanowire axis being (a) 0°, (b) 10°, (c) 20°, and (d) 45°; (e)–(h) polarization dependence of the intensity of the out-coupling light emission corresponding to panels (a)–(d), respectively. The cylinder diameter of the nanowires is 200 nm; the length is 4 μm. The size of the cuboid is 140 nm × 140 nm× 140 nm. All frames are 500 nm× 600 nm.

4. Conclusion

We have clearly shown that a metallic nanoparticle attached on a Ag nanowire can serve as an antenna for light coupling into nanowire SPPs. In contrast to the case of the coupling region at the nanowire end, where the coupling efficiency is maximum (minimum) as the polarization direction is parallel (perpendicular) to the nanowire axis, the polarization dependence for the coupling region at the nanoparticle–nanowire junction is very complicated, relying on the specific situation of the junction, such as the shape of the nanoparticle and the contact situation in the gap between the nanoparticle and the nanowire. The different situations cause different plasmon enhancement modes that are closely related with the polarization of the excitation light.

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