NANO LETTERS

2006
Vol. 6, No. 8
1822−1826

Observation of Plasmon Propagation, Redirection, and Fan-Out in Silver Nanowires

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Received December 14, 2005; Revised Manuscript Received June 5, 2006

ABSTRACT

We report the coupling of free-space photons (vacuum wavelength of 830 nm) to surface plasmon modes of a silver nanowire. The launch of propagating plasmons, and the subsequent emission of photons, is selective and occurs only at ends and other discontinuities of the nanowire. In addition, we observe that the nanowires redirect the plasmons through turns of radii as small as 4 μm. We exploit the radiating nature of discontinuities to find a plasmon propagation length >3 ± 1 μm. Finally, we observe that interwire plasmon coupling occurs for overlapping wires, demonstrating plasmon fan-out at subwavelength scales.

Nanoscale waveguides and photonic circuits require subwavelength optical elements.[1,2] Several different strategies coupling light to submicrometer structures have been employed. For example, coupling and redirection has been achieved through the use of semiconductor nanowires,[3,4] passive dielectric fibers,[5,6] photonic crystals,[7] and coupled metallic islands.[8] Structures coupling free-space photons to fluctuations in the surface density of electrons (plasmons) inherently reduce the spatial extent of propagating electromagnetic fields.[9] Metallic nanowires are likely candidates for plasmonic fibers. Recent experiments have demonstrated propagating plasmon modes in silver nanowires;[10,11] however, realization of highly selective excitation, mode bending, and cross coupling has yet to be achieved.

Here we present simple approaches for both coupling to propagating plasmon modes and their observation in metallic nanowires. Specifically, our experiment couples to propagating modes in a radially symmetric nanowire by using one end as a scattering center. This scattering center creates an overlap between the incident radiation (focused laser) and the propagating plasmon mode. Focused laser light excites plasmons that propagate along the length of silver nanowires and couple to free-space photons, radiating at the ends. Plasmons are also observed to couple between overlapping nanowires and fan-out from one wire into multiple nanowires.

The wires used in this study have a mean diameter of ∼100 nm and lengths that vary from 3 to 20 μm. The nanowires were synthesized in a mixture of ethylene glycol (EG) and poly(vinyl pyrrolidone) (PVP) as reported previously.[12,13] The wires were washed once in acetone to remove the EG, four times with ethanol to remove the PVP, and once with water. The final aqueous suspension consisted of silver nanowires, a small fraction of silver nanoparticles, and trace amounts of PVP and ethanol. The structure of the nanowires was characterized by transmission electron microscopy (TEM), as seen in Figure 1. The nanowires are observed to have tapered ends (Figure 1A) and are smooth to within the resolution of the TEM micrographs (∼1 nm). Additionally, a thin layer of PVP surfactant (2−5 nm) can be resolved in many of the micrographs. An electron diffraction pattern shows that the bulk of the wire is highly crystalline (see Figure 1B) and has face centered cubic (FCC) lattice symmetry.

Aqueous nanowire suspensions were deposited on No. 1 $^1/_2$ cover glasses (Corning No. 0211 zinc titania glass) and allowed to dry in open air. Dried nanowires were then mounted on an inverted optical microscope (Nikon Eclipse TE-2000). A 100× oil immersion objective (N.A. = 1.4) lens was used to focus the laser light and to collect a bright-field image. The laser illumination was coupled into the

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10.1021/nl052471v CCC: $33.50
Published on Web 06/28/2006

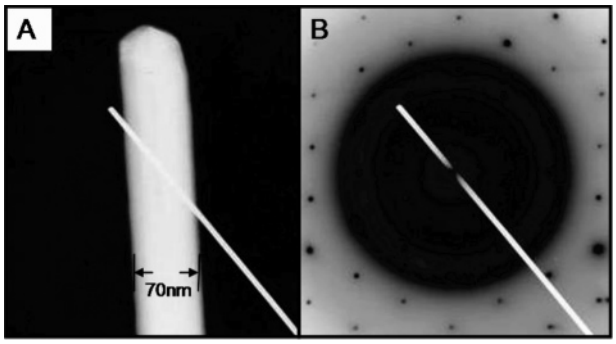

Figure 1. Structure of silver nanowires. (A) Transmission electron micrograph (TEM) of the silver nanowires. (B) Electron diffraction pattern of the same nanowire, showing FCC crystalline structure.

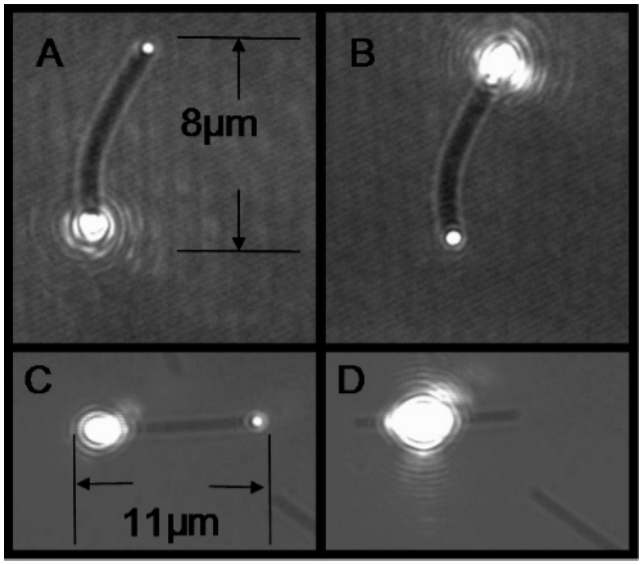

Figure 2. Micrographs showing the spatial sensitivity of launching plasmons. (A) Nanowire with excitation at the bottom end. (B) Same nanowire when excited from the top end. (C) Nanowire excited at left end. (D) Same nanowire with laser positioned at the middle of the nanowire. Notice that the plasmon is not excited in this geometry.

microscope via a dichroic mirror that selectively reflects 96% of light at 830 nm. The microscope objective focuses the collimated laser light to a diffraction-limited spot in its focal plane. Images were collected with either a CCD (Hitachi, 8 bit, 480 × 640) or a high-speed CMOS (Photron FastCam 1024-PCI), which both received roughly 4% of the light from the sample at the laser frequency (see the Supporting Information). To eliminate the possibility of evanescent waves propagating along the glass surface and preferentially scattering from the tips of the silver nanowires, we immersed all samples with index-matching oil (Nikon Type A immersion oil, $n = 1.515$). Even though scattering from the glass surface disappeared, light continued to radiate strongly from the distal end of the nanowire.

We launch plasmons by illuminating an end of a single nanowire with a diffraction-limited laser spot as shown in Figure 2. Plasmons can be launched from either end of the nanowire (Figure 2A and B); thus, plasmon propagation is reversible. In contrast, plasmon modes are not observed to be launched when the laser is focused on the midsection of a smooth wire (see Figure 2C and D). Because the momentum of the incoming photon (k_{photon}) is not matched to that of the propagating plasmon ($k_{plasmon}$), there needs to be a scattering mechanism to provide an additional wavevector ($\Delta k_{scatter}$). At the midsection of the wire, the nanowire is cylindrically symmetric over the extent of the diffraction-limited spot and therefore cannot scatter in the axial direction. However, this symmetry is broken at the tapered end of the nanowire where light is scattered into propagating axial plasmon modes. A similar strategy has been implemented for thin-film surface plasmons utilizing gratings or dots.[8,14] Likewise, propagating plasmon modes incident upon a sharp discontinuity (e.g., the tapered end of the nanowire) can re-emit as photons.

If the symmetry is gently broken over longer length scales, then plasmon propagation is unaffected. This can be seen in Figure 2A and B, where plasmons propagate around the bend of the nanowire with no observed radiative loss. The smallest naturally occurring optically resolvable bend found in these nanowires is shown in Figure 3A. This nanowire, with a radius of curvature of 4 μm, guides plasmons with no observed radiative loss. However, extremely sharp bends in the nanowire will behave like the ends of nanowires, scattering propagating plasmons into photons. This effect is demonstrated in Figure 3B, where a nanowire shows emission at two "kinks" (radius of curvature below the diffraction limit). The kinks are spontaneous defects that form during the growth process and occur in a small fraction of wires. Scanning electron micrographs reveal that typical kinks are discontinuities in the wire direction. Figure 3C is representative of the structure of these kinks, that is, sharp interior angles and flat exterior faces, with a characteristic size of ~100 nm.

Similar phenomena have been reported recently for propagation of photons around sharp bends in semiconductor[15] structures and for bends above the diffraction limit for dielectrics.[6] The main difference between these and the present approach is that photons guided by dielectrics and semiconductors can propagate efficiently over large distances, whereas propagation in plasmon waveguides have been demonstrated for,[10] and can scale to, much smaller sizes. Additionally, most of the electromagnetic energy resides in the core of dielectric fibers, as opposed to the surface for plasmonic waveguides.

A nanowire with multiple kinks can be used to estimate the plasmon propagation length. Each kink is used dually as a plasmon-launching site and photon-radiating site. We sequentially irradiate each kink and measure the radiated intensity from all of the other kinks, as illustrated in Figure 4A. We find that the radiated intensity is strongly correlated to the distance between points along the nanowire, as shown in Figure 4B. These data are described well by an exponential decay, $I(x) = I_0 e^{-x/L}$, with a characteristic length of $L = 3 \pm 1$ μm. If one makes the assumptions that (i) the photon−plasmon coupling strengths are the same at each junction and that (ii) radiative losses (at kinks) are insignificant compared to dissipative losses (along the nanowire length), then L represents the plasmon propagation length. Even when

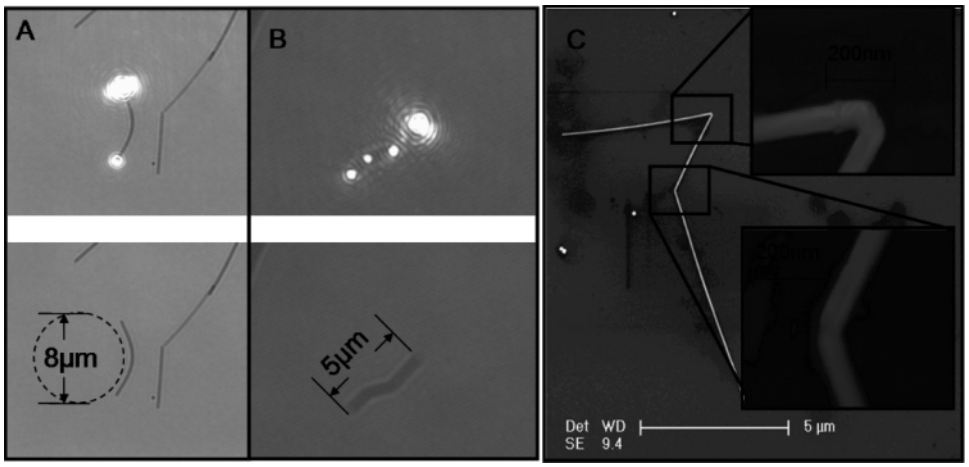

Figure 3. Micrographs of plasmon propagation in silver nanowires and emission (top), control with no laser excitation (bottom). Brightest point in image is scattering from incident beam. (A) A 7 μm wire (excitation top) with a radius of curvature of 4 μm, a wire not radiating is in close proximity. The inset is a circle of radius of 4 μm for comparison. (B) A 5 μm wire (excitation top right) with both the opposite end and two additional points of high curvature that radiate (radius of curvature less than the diffraction limit). (C) An electron micrograph of a typical wire with kinks, with insets of increased magnification.

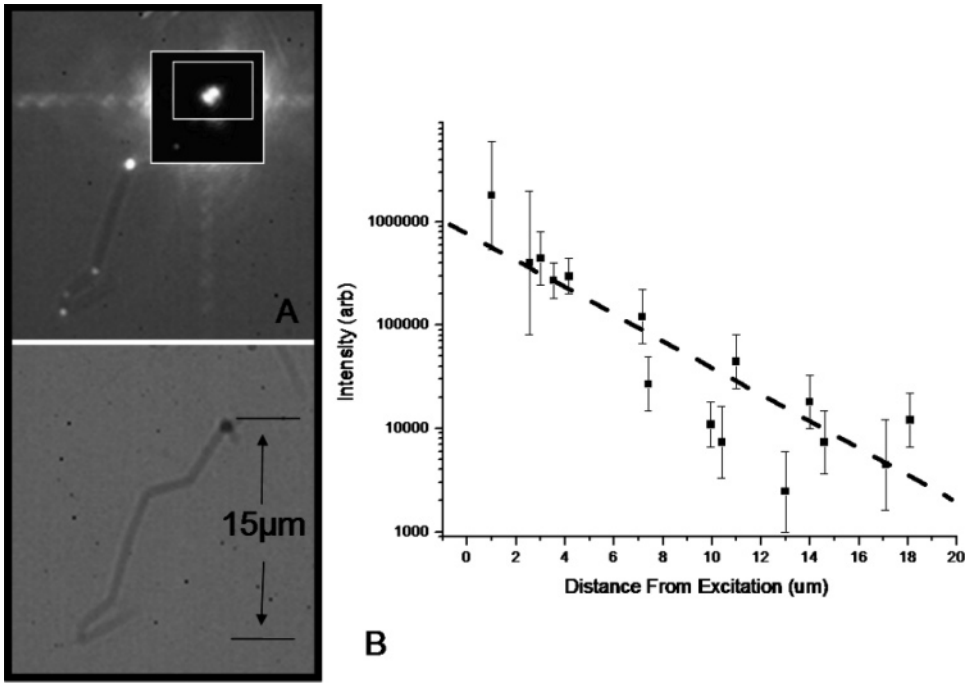

Figure 4. (A) Micrographs of plasmon propagation in a silver nanowire with multiple emission points (top) control with no laser excitation (bottom). Camera shutter speed and laser intensity were varied to increase the total dynamic range. The unsaturated images of the excitation and brightest emission points at shorter exposure times (high shutter speeds) are overlaid for clarity. (B) Semilog plot of intensity versus distance from excitation source. The dashed line is a fit of the data to an exponential. Six distinct points were probed (15 unique combinations). The uncertainty is arrived at by taking the standard deviation of all exposures with unsaturated pixels.

these assumptions are not true, this simple far-field measurement provides a practical lower limit for the propagation length. For comparison, a propagation length of 2.5 μm has been reported for gold nanofabricated structures at 800 nm.[16]

Propagating modes are also seen to couple between overlapping nanowires. In Figure 5, we present an image and an intensity profile from an aggregate of three nanowires, which forms naturally during solvent evaporation. When one of these nanowires is excited, two phenomena are observed. First, radiation is emitted at the intersection of the overlapping nanowires, indicating that the intersection scatters propagating plasmons into photons. Second, visible radiation is emitted at the ends of nanowires that cross the illuminated nanowire, indicating that the intersection couples plasmon modes in the two wires. In order for this to occur, the plasmon modes of the two wires must overlap. In general, the electric field of the propagating surface plasmon modes on a cylinder can be a complicated mixture of electric (TM) and magnetic (TE) waves.[17] For simplicity, we choose the $n = 0$, or lowest order mode, which is azimuthally symmetric. Then, for this mode the field scales as $E \approx e^{-k_\rho \rho}$ where k_ρ is the wavevector in the radial direction and ρ is the distance

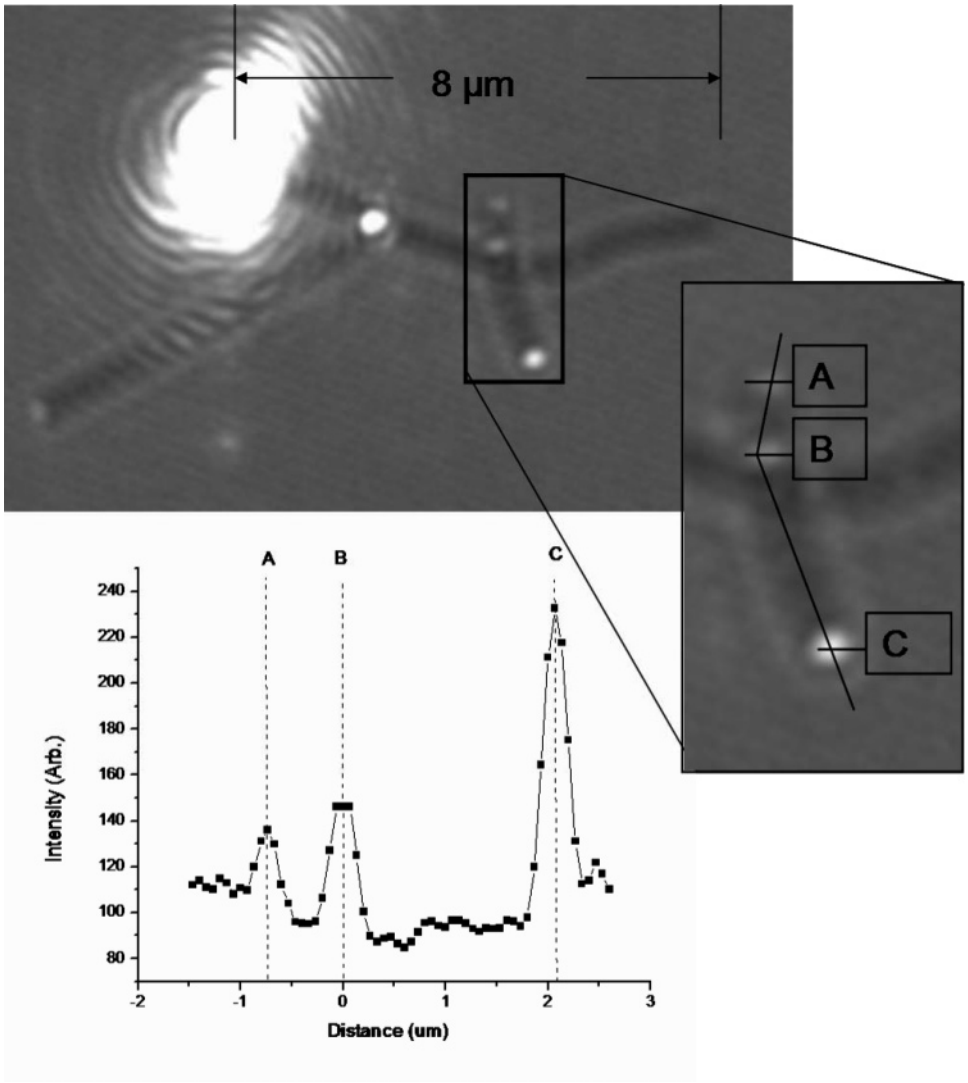

Figure 5. Group of overlaying nanowires that illustrates interwire plasmon coupling. The excitation at the far left nanowire end produces emission at both the nanowire junctions and emission from the coupled nanowires as well. The inset shows an intensity line cut showing the emission intensity profile along wire.

from the surface of the nanowire.[17,18] Neglecting corrections introduced by the curvature of the wire,[17] and taking the dielectric constant of the surfactant to be that of the oil ($\epsilon_{surfactant} = \epsilon_{oil}$), we approximate k_ρ using the dispersion relations of an infinite plane[9,18] $k_\rho^2 + k_z^2 = k^2$ where $k_z^2 = (\omega/c)^2\, \epsilon_m\epsilon_d/(\epsilon_m + \epsilon_d)$ and $k^2 = (\omega/c)^2\epsilon_d$ in the dielectric. Thus, $k_\rho^2 = \omega^2/c^2\ (\epsilon_d{}^2/(\epsilon_m + \epsilon_d))$, where c is the speed of light, ω is the angular frequency, ϵ_d is the relative permittivity of the dielectric, and ϵ_m is the relative permittivity of the metal. Substituting material parameters for the immersion oil ($\epsilon_d = 2.25$) and silver ($\epsilon_m = -36$, extrapolated from ref 19), we find an exponential decay length of about 340 nm. Thus, wires within this distance have overlapping modes and can couple. Interwire coupling has also been seen in subwavelength silica and semiconductor nanowires.[3,6] In our system, we expect capillary stresses to drive nearby wires into contact as solvent evaporates.[20] However, the surfactant coating the wire may frustrate direct contact between the wires, maintaining a dielectric filled gap with a maximum size of twice the surfactant thickness, about 10 nm in our case (see Figure 1A). Therefore, even in the presence of surfactant, the distance between the wires (d) is much less than k_ρ, or $d \ll k_\rho$. The intersections are then, in effect, plasmonic contacts capable of exchanging energy between propagating plasmon modes, with some losses in the form of free-space photons.

In conclusion, we demonstrate the selective launch and propagation of plasmons along silver nanowires using a simple far-field excitation and detection method. We have also observed that these propagating plasmon modes can couple between adjacent nanowires. The phenomena are not specific to nanowire material or excitation wavelength; we have observed similar results in gold and copper nanowires. Technological applications require the positioning of nanowires into a deterministic network, which can be accomplished by a variety of methods, such as flow alignment,[21] biologically derived templates,[22] dielectrophoretic alignment,[23] or holographic optical tweezers.[24,25] The current study represents a new approach in the observation and manipulation of plasmons in nanoscale structures.

Acknowledgment. We thank Dr. Richard Chang and Dr. Vincent Germain for useful discussions. This work was partially supported by ARO (DAAD19-01-1-0592), AFOSR (F49620-01-1-0358), and NASA (NCC 2-1363). After submission of this manuscript, a report showing plasmon propagation in similar Ag nanowires was published.[26]

Supporting Information Available: SEM of silver nanowires deposited from the suspension, block diagram of experimental setup, and SEM of silver nanowires highlighting the crossings. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL052471V