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Direct imaging of nanogap-mode plasmon-resonant fields

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Abstract: We perform direct local-field imaging of a plasmon-resonant gold nanoparticle pair separated by a gap of several nanometers using a scattering-type near-field optical microscope with a sharp silicon tip of atomic force microscope. The sharp tip allows the access for the nanogap and the high spatial resolution. Our results provide experimental evidence that the nanogap structure produces an optical spot with the size of a single nanometer (< 10 nm). This is not only of fundamental importance in the field of nanophotonics, but also provide significant information for the development of plasmonic devices with the nanogap structures.

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Localized surface plasmons (LSPs) of metal nanoparticles and engineered nanostructures have attracted much attention as an approach to overcome the optical diffraction limit [1–4]. They work as effective nanoantennas in the visible and infrared wavelength range due to the optical excitation of LSPs [5–7], which can efficiently convert propagating light into nanoscale-confined and strongly enhanced optical fields. This downscaling from the diffraction limit to the nanometer dimension is a key element in the development of noble optics and photonics, including optical nanolithography [8], nanoscale optical microscopy [9], and nanometric optical tweezers [10].

It has been widely shown that the size, shape, and structure of the nanoantennas determine their optical characteristics, including resonant frequencies, local-field distributions, and field enhancements [12,13]. In particular, many calculations have suggested that plasmon-resonant nanoantennas composed of a pair of metal nanoparticles with a gap below 10 nm (“nanogap”) produce an intense optical spot that is about two orders of magnitude smaller than the wavelength of the light. This effect is understood as the result of the strong coupling of plasmons between the nanoparticles [7,11–13]. Nanogap antennas have led to the wide range of physically interesting and technologically important phenomena, such as single-molecule surface-enhanced Raman scattering [14], nonlinear photochemical reactions induced by an incoherent excitation source [15], and optical trapping of single molecules [16]. For the understanding of these nanogap-induced phenomena and the applications in nanooptics and nanophotonics, it is important to determine the spatial characteristics of the photon localization within the nanogap experimentally with a single nanometer resolution. Unfortunately, such experiment remains as a challenging task.

A few techniques have been used to observe the local-field distribution within the nanogap. In a previous work [15,17], a photopolymerization process was exploited for the near-field imaging of nanogap antennas; in this process, the intensity distributions are
recorded on photoresist films. However, this near-field photochemical imaging technique is not a direct optical-field measurement but rather is mediated by multiple chemical reaction processes; as a result, the recorded photoproducts may not reflect the precise local-field distribution. Another promising technique is near-field scanning optical microscopy (NSOM). In this technique, an aperture-type NSOM is used to illustrate that the electric field is confined at an interstitial site in the gold particle pairs [18]. The spatial resolution, which is restricted by the aperture size of the metal-coated optical-fiber probe, is typically 50-100 nm. However, this resolution is insufficient for the precise observation of a tiny optical spot on the nanogap antenna, for which single nanometer-scale imaging is required. A scattering-type NSOM has been also widely used for the plasmonic local-field imaging [19–29]. This technique demonstrates that a dimer antenna produces the localized field within a gap of several tens of nanometers [26,27]. Furthermore, the local-field distributions of a gold nanocube pair separated by the nanogap were mapped with the high spatial resolution (~20 nm from the full width at half maximum (FWHM) of the intensity maps) and their maps revealed antisymmetric plasmon modes that are different from a simple superposition of two monometric dipole plasmons [28]. However, the visualization of the strong fields within the nanogap was not achieved because of the experimental limitation that the probe tip could not fully access the nanogap area between the nanoparticles. In this paper, we demonstrate the direct observation of nanogap-mode plasmon-resonant fields using a scattering-type NSOM with a very sharp silicon tip of atomic force microscope (AFM). Our results provide experimental evidence that the nanogap antenna generates an optical spot with the size of a single nanometer (< 10 nm).

Fig. 1. Direct near-field imaging of optical nanoantennas with a scattering-type NSOM. The nanoantennas are illuminated under the focused TIR conditions. The confined plasmonic fields are scattered by the sharp AFM tip and transformed to propagating waves during the scanning operation. The near-field and the topography images can be obtained simultaneously. The inset shows SEM image of the AFM tip apex [30]. Bar = 180 nm.

The schematic of the scattering-type NSOM is shown in Fig. 1 [31]. The extremely sharp AFM tip was used to probe the nanoantennas. The samples were illuminated with laser light at the wavelength of 800 nm under a focused total internal reflection (TIR). Therefore, both topographic and scattered near-field images can be obtained simultaneously. A continuous-wave Ti:sapphire laser beam (wavelength = 800 nm, linewidth = 100 kHz) was used for surface plasmon excitation. The linearly polarized beam was introduced into an inverted
optical microscope and was focused by an oil-immersion objective (100 × , numerical aperture = 1.35). A section of the focused beam with the incident angle smaller than the critical angle was masked by a knife edge at the pupil plane of the imaging system; therefore, the sample was illuminated under the focused TIR condition (spot area = 1.2 × 1.7 µm). The TIR illumination technique prevents from being directly heated by the transmitted laser light and greatly reduces the signal background [20,32]. The laser beam was polarized in the parallel direction to the sample surface, i.e., s-polarization along the X-direction in Fig. 1. This polarization could efficiently excite the nanogap-mode plasmon of the dimer nanoantennas. An AFM was placed on the sample stage, and the silicon probe tip was driven at the resonant frequency of the AFM probe. Back-scattered light from the tip was collected by the same objective and detected by a photomultiplier tube (PMT) with a pinhole. This detection configuration allows the efficient measurement of in-plane near-field component (parallel to the sample surface) compared with the vertical component $E_z$ along the Z-direction in Figure. 1. The in-plane component $E_x$ along the X-direction is dominant in the plasmonic fields within the nanogap [25]. The detected signal was demodulated at the second harmonic (~700 kHz) of the resonant frequency of the AFM probe by a lock-in amplifier, which can suppress the scattered light signal from the probe shaft and the sample [32,33]. We note that the output of the lock-in amplifier is proportional to the near-field amplitude rather than its intensity due to the interference between the scattered near-field and the far-field background [34].

The metal-coated AFM probe tips, which are normally used in the conventional scattering-type NSOMs [21–28,35], can greatly improve the scattered near-field signal. However, the metal-coated tips also restrict the spatial resolution to ~20 nm and limit the access into the gap of single nanometer-scale antennas. Therefore, we chose bare silicon AFM probe tips (SSS-NCH Nanosensors from NanoWorld AG (Switzerland)) that feature a very small tip radius of curvature (typically 2 nm) and a high aspect ratio near the apex (full cone angle < 8° at the 50 nm of the pointed end of the tip). Compared to the metal-coated tips, the perturbation in the local-field distribution for the silicon tip was minified because plasmon resonances at visible wavelengths for the silicon tips are not significant.

The AFM topography and the scattered near-field images for a single 50-nm gold nanosphere are shown in Figs. 2A and 2B. The nanosphere produces two optical lobes of ~15 nm around both ends along the incident polarization direction (Figs. 2B and 2C). The characteristic represents dipolar near-field distribution and agrees well with the numerical calculation in Fig. 2D. This result demonstrates that our scattering-type NSOM using the sharp silicon AFM tips allows for reliable observation of antenna near-field modes with improved spatial resolution compared to the conventional near-field microscopy [21–29].
A dimer nanoantenna composed of a pair of diagonally aligned gold nanoblocks with nanogap is shown in the scanning electron microscope (SEM) image of Fig. 3A. The dimer was fabricated on a glass substrate using electron beam lithography and lift-off techniques. The fabrication procedure is described in earlier reports [15,17]. The gap distance of ~7 nm allowed the AFM probe tip to access the bottom of the nanogap. The block dimension of 115 × 115 × 30 nm was chosen so that the far-field resonance is close to the incident wavelength of 800 nm (see the scattering spectrum in Fig. 3B). The calculated near-field distribution of the nanogap model based on the geometry of Fig. 3A is shown in Fig. 3C. The excitation conditions were also chosen as in the experiments; more specifically, an s-polarized plane wave at a wavelength of 800 nm illuminates the antennas on the glass substrate at an incidence angle of 60° under TIR condition, as shown in Fig. 1. The distribution predicts the presence on optical spot in single nanometer size inside the nanogap. Moreover, the theoretical scattering spectrum of the nanogap model (Fig. 3D) is in good agreement with the experimental data in Fig. 3B.
Fig. 3. Dimer nanoantenna with a single nanometer-scale gap. SEM image (A) and experimental scattering spectrum (B) of a single pair of diagonally aligned gold nanoblocks, with an interparticle edge-to-edge separation distance of ~7 nm. The scattering spectrum (B) is normalized by the incident white light intensity. The vertical red line in (B) represents the incident beam wavelength. (C) Calculated near-field distributions of a model gold nanogap antenna; block size = 115 × 115 × 30 nm, curvature radius of each corner = 20 nm, and gap distance = 7 nm. The images show the X-component of the electric field in the X-Y plane at half-height and the X-Z plane along the diagonal line of the antenna. (D) Theoretical scattering spectrum of the same model nanogap antenna as in (C). In the experimental and theoretical scattering spectra, the optical excitation is polarized along the dimer axis.

Figures 4A and 4B show the topography and the corresponding scattered near-field images, respectively, for the nanogap shown in Fig. 3A. An intense scattered near-field signal from the probe tip was observed in the nanogap area, and its magnitude was at a maximum in the narrowest gap. For this measurement, the AFM tip fully accessed the nanogap area between the two blocks, as shown in the topography line-profile in Fig. 4C. From the near-field image and profile in Figs. 4B and 4C, respectively, it can be clearly seen that the nanogap generates a single elliptical nanospot with strength considerably stronger than that of the side spots at the outer ends of the dimer nanoantenna, which corresponds to the theoretical prediction. This nanospot was obtained with high reproducibility for five repeated measurements, and the FWHMs of the nanogap-mode plasmonic field distribution were 9.2 ± 0.5 nm in the dimer axis direction and 12.6 ± 0.8 nm in the perpendicular direction (Figs. 4C and 4D). In this determination of the spot size along the dimer axis, the influence of z-direction motion of the scanning probes was not considered. Our results represent the first experiment in which the nanogap-mode plasmon-resonant fields were directly observed on the single nanometer scale. In addition, we confirmed that the intense fields within the nanogap become negligibly weak when the incident polarization is rotated by 90° (Fig. 4E), i.e., p-polarization, as expected theoretically. These results also support our previous reports on the nanogap-mode plasmon-induced polymerization [15,17].
In conclusion, the direct imaging of nanogap-mode plasmon-resonant fields provides experimental evidence that the nanogap antenna produces a single nanometer-scale optical spot. This result will have a fundamental impact on the field of nanophotonics and promises
potential applications of nanogap antennas, including optical imaging, optical spectroscopy, optical lithography, optical data storage, and optical manipulation.

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