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Imaging of Nanoscale Light Confinement in Plasmonic Nanoantennas by Brownian Optical Microscopy

Yeon Ui Lee, G. Bimananda M. Wisna, Su-Wen Hsu, Junxiang Zhao, Ming Lei, Shilong Li, Andrea R. Tao, and Zhaowei Liu*



ABSTRACT: The strongly enhanced and confined subwavelength optical fields near plasmonic nanoantennas have been extensively studied not only for the fundamental understanding of light-matter interactions at the nanoscale but also for their emerging practical application in enhanced second harmonic generation, improved inelastic electron tunneling, harvesting solar energy, and photocatalysis. However, owing to the deep subwavelength nature of plasmonic field confinement, conventional optical imaging techniques are incapable of characterizing the optical performance of these plasmonic nanoantennas. Here, we demonstrate super-resolution imaging of ~20 nm optical field confinement by monitoring randomly moving dye molecules near plasmonic nanoantennas. This Brownian optical microscopy is especially suitable



for plasmonic field characterization because of its capabilities for polarization sensitive wide-field super-resolution imaging. **KEYWORDS:** super-resolution imaging, plasmonic nanoantennas, hot spot imaging, Brownian optical microscopy, fluorescence enhancement, nanophotonics, plasmonics

ngineering of well-defined plasmonic nanoantennas (PNAs) and their optical response is extremely / important in various technological applications that take advantage of strongly enhanced electrical fields resulting from the excitation of localized surface plasmon polaritons (LSPPs), ranging from enhanced second harmonic generation¹ to improved inelastic electron tunneling,² solar energy harvesting,³ nano-optical trapping,⁴ sensing,⁵ and photocatalysis.⁶ The LSPP resonance is sensitive to the shape, size, and orientation of the PNA, as well as the material composition of the PNA itself. However, the self-assembled PNAs often possess assembly defects, imprecise particle placement, variation in crystallite size, and inherent inhomogeneous shape and radius of curvature.⁷⁻⁹ In order to achieve optimal optical and electronic performance as it was predesigned, it is crucial to nondestructively detect imperfections or unexpected defects of the PNAs by imaging these LSPP resonances.

Detection of LSPPs and determination of their optical mode quality have been carried out with spectroscopic imaging methods such as dark-field optical microscopy,¹⁰ surface-enhanced Raman scattering (SERS) spectroscopy,¹¹ and two-photon induced luminescence microscopy.¹² However, the spatial resolution of these techniques is diffraction-limited.

Near-field scanning optical microscopy (NSOM)^{13,14} can achieve a spatial resolution below 10 nm, but the resultant local electric field images are significantly perturbed by the near-field tip;¹⁵ moreover, it is very challenging to probe the nanoscale gaps between the PNAs with a tip when the gap size is smaller than the tip. Other electron-based imaging techniques, for example, scanning transmission electron microscopy (STEM)¹⁶ and electron energy loss spectroscopy (EELS),¹⁷ are useful tools for understanding the optical and electronic properties of plasmonic nanostructures by directly mapping the near-field distributions around the PNAs.¹⁸ The complexity and high cost of these electron imaging systems, however, greatly limit their accessibility. Therefore, a userfriendly nondestructive optical technique offering the measurement of wide-field electromagnetic distributions of LSPP

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Figure 1. Super-resolution imaging of plasmonic hot spots by using Brownian optical microscopy. (a) Hot spots appear in PNAs (~100 × 100 × 100 nm³) with extremely tiny (~3 nm) gap under a total internal reflection (TIR)-type illumination with λ = 532 nm. To map out the subwavelength optical field confinement, the Brownian motion of fluorescent dye molecules (rhodamine 6G) in water was utilized, where the dye molecules in solution were diffusing within a static fluidic chamber (-200 nm < z < 0 nm). The molecular dipole orientations are indicated on the images as white arrows. (b) Three-dimensional spatial distribution of the calculated electric field intensity near the PNAs. (c) By SML image reconstruction, a scatter plot of the single-molecule events was obtained.

modes at room temperature with nanometer resolution and high fidelity remains attractive.

Because of their capabilities to meet the aforementioned requirements, single-molecule localization (SML) based superresolution imaging methods, such as stochastic optical reconstruction microscopy (STORM) and photoactivated localization microscopy (PALM),^{19-21'} have attracted much attention over the last few decades. They achieve a superresolution image by localizing the centroid of the point-spreadfunction of individual fluorescent molecules. More recently, diffusive fluorescent molecules in solution have been introduced in these SML based microcopies to map out a wide field of view of local electromagnetic fields near the rough metallic surface,^{11,22–25} nanoisland,²⁶ and tridisk spaced by 30 nm gaps.²⁷ It is worth noting that the Brownian diffusion of plasmonic nanoparticles in solution has also been utilized to scan the topology of 3D dielectric objects.²⁸ Nevertheless, these Brownian-diffusion-based optical microscopies are still in their infancy, and thus more explorations are needed, for example, investigation of their capabilities in polarization sensitivity and tunability of molecular localization near PNAs.

In this work, we demonstrate Brownian optical microscopy to obtain a super-resolution image of ~ 20 nm optical field confinement near a PNA. This microscopy utilizes the dynamic modification of dye molecules near the PNA in fluid and the localization imaging method, enabling super-resolution imaging of electromagnetic field distributions of LSPP modes, that is, plasmonic hot spots, in the spatial domain. Out of several appealing geometries reported so far, cubic PNAs with extremely tiny (\sim 1.5–3 nm) gaps (Figure 1a) were chosen here as the case study for they provide an enormous enhancement of radiative emission rate of nearby fluorophores and thus have vast device applications.^{29–32}

RESULTS

Au-coated Ag nanocube PNAs were used in our experiment, and the fabrication of those PNAs includes several steps (see Methods and Figure S1). The LSPP resonances of these PNAs cover the spectral region between 460 and 650 nm (depending on the structural configurations of multiple PNAs) in water (see Figure S3). The PNAs were sealed inside a static fluidic chamber containing diluted fluorescent rhodamine 6G (R6G) molecules with a concentration of ~1 nM in water. Spacers (200 nm thick) on the bottom surface of the chamber form a small gap between the window and the sample surface, where the R6G molecules freely diffuse (Figure 1a). R6G has absorption in the wavelength range of 450-600 nm and emission in the range of 500-650 nm, ensuring a significant overlap with the LSPP resonance of the PNAs (see Figure S3).

Figure 1 provides a graphical summary of the demonstrated microscopic technique. We use the following guiding principles for implementing this imaging technique: (1) The Au-coated Ag cube PNAs with an extremely tiny gap support LSPP



Figure 2. Plasmonic hot spot localization and visualization. (a, b) SEM images of dimer PNAs. (c, d) Super-resolution polarizationdependent hot spot image reconstruction. Each red (H-polarization) and blue (V-polarization) dot in the scatter plot represents a single molecule event. The hot spot sizes were obtained from the standard deviation calculation, which shows deep subwavelength sizes with an average width of 42.2 nm. FDTD calculation results of averaged electromagnetic field intensity distribution around PNAs (-200 nm < z < 0nm), excited by (e, f) H-polarized and (g, h) V-polarized plane wave with $\lambda = 532 \text{ nm}$, 60° incidence angle, respectively. Scale bar is 100 nm.



Figure 3. FDTD calculated emission enhancement mapping at 588 nm. (a, b) Normalized radiative power, (c, d) normalized dissipated power, (e, f) quantum efficiency (logarithmic scale), and (g, h) Purcell factor of a dipole emitter at different positions. Emission powers were calculated at z = -105 nm plane. Scale bar is 100 nm.

resonances, which strongly concentrate the optical field near the gap of the PNAs under light excitation (Figure 1b). (2) Fluorescent molecules in the fluid were used, and they will more likely diffuse through the most favorable position where the field enhancement is maximum due to an optical trapping effect^{33,34} as individual fluorophores explore the field profile near the nanoantenna (Figure S2). (3) The emission balance between enhancement and quenching depends on the exact position of the fluorescent molecules with respect to the PNAs by the antenna effect³⁵ (discussed below). (4) The radiative emission enhancement near the PNAs allows us to localize the fluorescent molecules, which are stochastically blinking due to absorption–bleaching events.²² (5) Fluorescence images were taken for super-resolution SML image reconstruction³⁶ (Figure 1c).

To evaluate the measurement conditions described in this work, a 532 nm linearly polarized laser beam with intensity of $6.3 \times 10^2 \text{ W/cm}^2$ was used as the excitation source. The PNAs

were illuminated through a TIR fluorescence microscope (TIRF) using a 100× oil immersion objective with a numerical aperture (NA) of 1.49. The fluorescence signal from the R6G molecules was collected by a sCMOS camera with a dichroic mirror and a 588 \pm 10 nm emission color filter. An exposure time of 10 ms was used to collect 5000 frames of images (Figure 1c). In the TIRF configuration, the evanescent field was efficiently coupled to the LSPP modes. The plasmonic near-fields are concentrated at certain locations of the PNA surfaces, depending on the size and orientations of PNAs to each other in various configurations (*e.g.*, monomer, dimer, trimer, and tetrameter).

The fluorescence signal of the R6G molecules was collected via the oil immersion objective. A series of raw images of the fluorescence signals were acquired, and the molecules were individually localized to provide the hot spot size and shape around the PNAs. The linear polarization of the illumination was switched from H (horizontal) to V (vertical) with a liquid www.acsnano.org



Figure 4. Imaging of plasmonic hot spots. (a, b) FDTD calculation results of fluorescence enhancement for (a) H-polarized and (b) Vpolarized excitation laser beam. (c, d) Super-resolution images of plasmonic hot spots for (c) H-polarized and (d) V-polarized excitation laser beam. The distribution of the data points provides the centroid position of the plasmonic hot spot. The size of the hot spot, 2σ , characterized by the standard deviation of the molecule's locations, is shown in Table 1. Scale bar is 100 nm.

crystal variable retarder (LCVR), for which the localization region was actively changed with the applied voltage.

Two PNA dimers with a gap of ~3 nm are studied, and their SEM images are shown in Figure 2a,b. The lateral localization position of R6G molecules was determined by a twodimensional Gaussian fitting of diffraction-limited images, which shows the centroid position of R6Gs in the scatter plots. Superimposing all the individual R6G positions creates a composite reconstructed image. For the reconstruction, the open-source ThunderSTORM³⁶ plug-in module for ImageJ was used (see Supporting Information S3 for reconstruction details). Figure 2c,d shows the reconstructed images of the plasmonic hot spots in the two PNAs dimers. As expected, the local field enhancement is highly dependent on the polarization state of the illumination, which results in different plasmonic hot spot distributions near the PNAs.

Simulated electric field intensity distributions near the PNAs were obtained by solving Maxwell's equations using the threedimensional finite-difference time-domain (FDTD) method (see Supporting Information SI 2 for details); both H- and Vpolarized plane waves with a 60° incidence angle were applied from the glass substrate side. Here, a total-field scattered-field (TFSF) source was used, and the normalized electric field distributions were calculated at a wavelength of 532 nm. The results are summarized in Figure 2e,f for H-polarization and Figure 2g,h for V-polarization. The PNA dimer with a small gap could permit very high local field enhancement for a proper polarization direction. Thus, the PNAs serve as intense near-field excitation sources for R6G molecules on or near their surface, and strong optical forces (Figure S2) result in increase of the excitation rate of these R6G molecules.

To simulate the emission process, a point dipole source near the PNAs was used to calculate the radiated power enhancement by sweeping 520 different source locations (i.e., the distance between the dipole and PNAs) in the z =-105 nm plane. For a simulation of randomly oriented emitters, the emitting powers generated by a single dipole along the x-, y-, and z-axis were obtained by averaging the results from the three separated simulations. Figure 3 shows the spatial mapping of the normalized radiated power (P_r/P_{r0}) into the far-field (Figure 3a,b), normalized dissipated power $(P_{\text{loss}}/P_{\text{r0}})$ (Figure 3c,d), quantum efficiency (QE = $P_{\text{r}}/(P_{\text{r}} +$ P_{loss}), Figure 3e,f), and Purcell factor $((P_r + P_{\text{loss}})/P_{r0})$, Figure 3g,h) near the PNAs, where P_{r0} is the power radiated into the free space in the absence of PNAs. The QE indicates the detectable emitting power from the dipole emitter resulting from the balance between enhancements and losses at different

positions. In the gap region, the maximum radiative emission enhancement occurs at the center and falls dramatically at the PNA surface because of the increased nonradiative emission.

The fluorescence enhancement (Figure 4a for H-polarization and Figure 4b for V-polarization) is defined as $\Gamma_{exc}P_r/P_{r0}$ where $\Gamma_{exc} = |E_{exc}|^2/|E_{exc0}|^2$ is the enhancement of the excitation field near PNAs at $\lambda_{ex} = 532$ nm (Figure 2), and P_r/P_{r0} indicates the enhancement of radiation of the molecules due to the presence of the PNAs at $\lambda_{det} = 588$ nm (Figure 3). The subscript 0 represents the corresponding quantities in free space. The theoretical fluorescence images derived from FDTD simulations (Figure 4a,b) and experimental superresolution fluorescence images (Figure 4c,d) show good agreement.

Figure 4 presents scatter plots of centroid positions of R6G molecules for H-polarization (Figure 4c) and V-polarization (Figure 4d), respectively. The centroid positions of R6G molecules were derived from the SML reconstruction. The standard deviation σ indicates the relative hot spot size or the localization accuracy of the centroid position of a hot spot (Table 1). The measured centroid positions of hot spots are in

Ta	ble	1.	Widths	of I	lasmonic	Hot	Spots"
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		polarization	
	Н		V
standard deviation of x (nm) standard deviation of y (nm)	$\sigma_{1x} = 21.5$ $\sigma_{1y} = 32.5$	$\sigma_{2x} = 46.9$ $\sigma_{2y} = 40.3$	$\sigma_{3x} = 23.5$ $\sigma_{3y} = 41.4$
relative centroid (<i>x</i> , <i>y</i>) (nm, nm)	(69.1, 50.4)	(38.7, -59.2)	(0, 0)

^aExcitation/emission: 532/588 nm. Excitation intensity: 6.3×10^{6} W/m².

good agreement with FDTD calculation results. It is worth noticing that, in the TIRF configuration, the emission signal can come from several different z-planes within the range of -200 to 0 nm. Therefore, there is a slight discrepancy between the experimental results and FDTD results calculated from averaged intensity distributions at different z planes where the monitors are located. We also evaluated plasmonic hot spot images on different types of PNAs, that is, monomer (Figure 5a), trimer (Figure 5b), and tetrameter (Figure 5c). As can be seen, super-resolution images of various plasmonic hot spots can be obtained with our Brownian optical microscopy.

In this localization imaging method, the location of the molecule's centroid is represented with very high accuracy. The standard deviation (localization precision) depends on the а

b



Figure 5. Plasmonic hot spots generated in different types of PNAs. (a, b, c) Plasmonic hot spots generated from monomer (a), trimer (b), and tetramer (c) under the excitation by H-polarized laser beam with a 60° incidence angle. Scale bar is 100 nm.



Figure 6. Localization accuracy estimation around the plasmonic hot spot. (a, b) Super-resolution images of the plasmonic hot spot for Hpolarized excitation laser beam. By including the intensity as the z-coordinate, the scatter plot provides a 3D super-resolution image of enhanced emission profile near the plasmonic hot spot. Scale bar is 100 nm. (c) FDTD calculated plasmonic hot spot. (d) Single-molecule localization precision as a function of fluorescence intensity. The measured localization precision was scaled to the inverse of the square root of the emission intensity, which is consistent with the theory (blue curve) $(\delta_{x,y}^2 \propto s^2/N)$, where $\delta_{x,y}$ is the localization precision, s is the standard deviation of the point-spread function, and N is the total number of photons). (Inset) Standard deviation of the fit is represented as the error bar. Scale bar: 100 nm.

emission intensity as shown in Figure 6. A localization precision of 2 nm was obtained in the central part of the imaged hot spot, indicating a strong emission enhancement near the gap of the PNAs.

CONCLUSIONS

We introduce a Brownian optical microscopy that utilizes the dynamic modification of dye molecules near the PNAs in fluid and the localization imaging method. With this technique, we have obtained super-resolution images of the hidden shape of electromagnetic field distributions of LSPP modes in the spatial domain. The local field enhancement by PNAs and radiative emission enhancement of fluorophores near PNAs enable the precise localization of these fluorophores, which, in turn, reveals the plasmonic hot spot distribution beyond the diffraction limit. As a user-friendly super-resolution imaging technique offering the measurement of wide-field electromagnetic distributions of LSPP modes at room temperature, the proposed Brownian optical microscopy can be used to detect imperfections or unexpected defects of nano-objects.

METHODS

Sample Fabrication. A prepatterned coverslip substrate was prepared by using photolithography, metal deposition of Ti/Au with thicknesses of 10 and 100 nm, and lift-off to pattern several micrometer-sized alignment marks for purpose of overlaying scanning electron microscope images and reconstructed images. The self-assembly method was used to assemble Au-coated Ag cube PNAs on the prepatterned coverslip substrate. The markers and MATLAB code were also used for drift correction of the microscope stage. The acquired image stack was processed using in-house code run in the MATLAB environment to make the SEM images transparent and align them before correlated overlay with the optical images (Figure S2).

Au-Coated Ag Cube PNA Synthesis. There are five steps to achieve the fabrication of Au-coated Ag cube PNAs: (1) silver nanocubes were synthesized *via* a polyol synthetic method;^{37,38} (2) a 1-2 nm Au ultrathin shell was coated on the outside of the Ag cube

by modification of a previous synthetic method^{37,38} (note that the Au coating protects the Ag cube from oxidization); (3) an orderly array was formed at the water—air interface by Langmuir—Blodgett technique and then transferred onto a polystyrene-glass substrate; (4) Au coated Ag nanocubes were self-assembled to generate PNAs in the polystyrene matrix by thermal treatment; (5) the polystyrene was removed in acetone/chloroform to expose the PNA for optical imaging.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c04019.

Plasmonic nanoantennas, overlay of SEM image of PNAs and diffraction-limited fluorescence images, absorption and emission spectra of R6G molecules, extinction spectra of PNAs, fluorescence time trace, FDTD calculations, and reconstructed image of R6G molecules in water above the glass and near PNA (PDF)

AUTHOR INFORMATION

Corresponding Author

Zhaowei Liu – Department of Electrical and Computer Engineering and Material Science and Engineering Program, University of California, San Diego, La Jolla, California 92093, United States; Email: zhaowei@ucsd.edu

Authors

- Yeon Ui Lee Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California 92093, United States; © orcid.org/0000-0001-8857-1251
- **G. Bimananda M. Wisna** Material Science and Engineering Program, University of California, San Diego, La Jolla, California 92093, United States
- Su-Wen Hsu Department of NanoEngineering, University of California, San Diego, La Jolla, California 92093, United States
- Junxiang Zhao Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California 92093, United States
- **Ming Lei** Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California 92093, United States
- Shilong Li Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California 92093, United States
- Andrea R. Tao Material Science and Engineering Program and Department of NanoEngineering, University of California, San Diego, La Jolla, California 92093, United States;
 orcid.org/0000-0003-1857-8743

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.0c04019

Notes

The authors declare no competing financial interest.

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