Phys. Status Solidi B 246, No. 11–12, 2771–2773 (2009) / DOI 10.1002/pssb.200982351

physica status solidi b
www.pss-b.com
basic solid state physics

Light scattering of interacting gold nanorods

Baxter McGuirt[1], Jerry Kielbasa[1], Jung-Ho Park[1], Patrick Sisco[2], Junping Zhang[1], Eric Peterson[1], Catherine Murphy[2], Richard D. Adams[2], Richard Williams[1], and David Carroll[*,1]

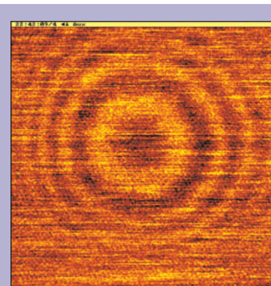
[1] Center for Nanotechnology and Molecular Materials and Department of Physics, Wake Forest University, Winston-Salem, NC 27109, USA
[2] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

Received 31 May 2009, revised 4 August 2009, accepted 21 August 2009
Published online 18 November 2009

PACS 07.79.−v, 78.67.Lt, 81.07.−b

* Corresponding author: e-mail carroldl@wfu.edu, Phone: (336) 727-1806, Fax: (336) 758-6142

The optical field intensity of light scattering from nanorods of gold has been imaged at distances that are intermediate between the near-field and far-field regimes using a near-field scanning optical microscope (NSOM). For scattering from isolated nanorods the Fraunhofer diffractive behaviour is modified slightly by the dipolar nature of metal nanoantannae as would be expected at these imaging distances. However, when the nanorods are brought into close proximity, interactions between the nanorods alter the scattering behaviour substantially creating large field intensities between the structures. By sampling the field with the near-field microscope tip scanned at different heights, detailed maps of the scattering profile can be generated.



The NSOM image of far-field scattered light from an isolated gold nanorod. The nanorod was imaged at a distance of roughly 8 μm above the support substrate using a scanning near-field microscope operated at constant height mode.

1 Introduction Nanorods of metals such as Au have been widely studied for their potential as nanoantenna. Recent near-field microscopic studies suggest that the dipolar nature of the optical near-field can be directly imaged, yielding a deeper understanding of the scattering properties of such nanomaterials as they may be mediated by plasmonic excitations [1–3]. These studies have generally focused on the evanescent field of isolated nanorods and from them we have gained significant insight into the modification of optical absorption profiles of any molecule placed next to such an antenna. Further, the far-field profiles of scattering from isolated nanorods of metal are also well understood [4]. However, when the nanorods are placed close together such that they begin to interact strongly, how the far-field scattering might develop is a bit more difficult to visualize. This is particularly important as assemblies of nanorods are being used to create negative index materials [5, 6], antennae arrays for solar cells [7], and nonlinear optical response such as optical limiting [8].

In this work, we examine the optical field distribution around interacting small clusters of nanorods at several wavelengths of the scattered light away from the particles. Using a near-field scanning optical microscope (NSOM) to image scattered light well outside of the near-field distance from the nanorods, we can fully visualize the scattered field as it approaches its far-field scattered form. We find significant field 'shaping' due to interactions between the nanorods. These results are anticipated to have impact in the use of nanorods in the creation of arrayed interacting mesoscopic systems such as negative index materials.

2 Experimental

2.1 Sample preparation The nanorods had length of 59 ± 3 nm and diameter of 12 ± 0.3 nm corresponding to an aspect ratio of 4.98 ± 0.22. The nanorods were synthesized as described in Ref. [9] at a concentration of gold particles in solution of 3.3×10^{-10} mol/L.

physica status solidi b

The nanorods were deposited on freshly cleaved mica by drop casting. This resulted in a dilute dispersion of nanorods across the surface with a variety of spacings between the particles.

2.2 Imaging The imaging setup is shown in Fig. 1. The NSOM is used in 'transmission mode' where light is introduced from the bottom of the same through the mica substrate and then scattered into the NSOM tip. The scanning head is made by Nanonics Inc. and RHK electronics are used for scanning control. The image is first imaged using the bent-tip of the NSOM as an atomic force microscope. After this, the tip is lifted to a height of roughly 8 μm above the substrate and the field is re-imaged with no feedback.

3 Results Shown in Fig. 2 is the 'intermediate-distance' optical field distribution of a single nanorod's scattering taken 8 μm from the surface of the substrate. Notice the Fraunhofer diffraction rings seen around the nanorod. It is also interesting to note the variation in intensity around the rings. For the isolated particles, the pattern typically has two lobes as shown. This suggests that the diffraction pattern may be modulated by the dipolar nature of the nanorod. The images shown in Figs. 1–3, are all 10×10 μm in size. Further, the images show the total optical field signal from the Hamamatsu Photomultiplier tube (PMT) coupled to the fibre tip. The images were collected with 256×256 pixel resolution and are grey-scaled with 16 bits.

This situation changes when the nanorods are close to each other. Shown in Fig. 3 is the intermediate-field scattering of two particles placed 'near' each other. 'Near' in this example is well outside of the near-field interaction length expected for plasmons, the nanorods are within ~1 μm of each other. Notice that the expected diffraction pattern would be a simple superposition of the two sets of rings as is seen far from the particles. However, near the particles, the lobes of the nanorod's fields yield modulations around the rings that are set off at an angle of ~45° to the bisector between the particles as seen in the drawings in red. The bright intensities are the same for top and bottom particles (i.e. in phase). Further there is a bright spot between the particles.

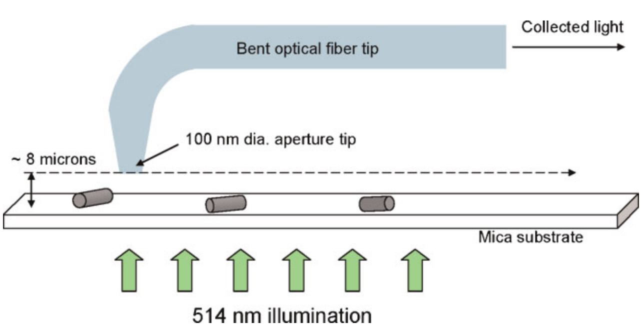


Figure 1 (online colour at: www.pss-b.com) The NSOM setup used to image the nanorods in the intermediate to far-field.

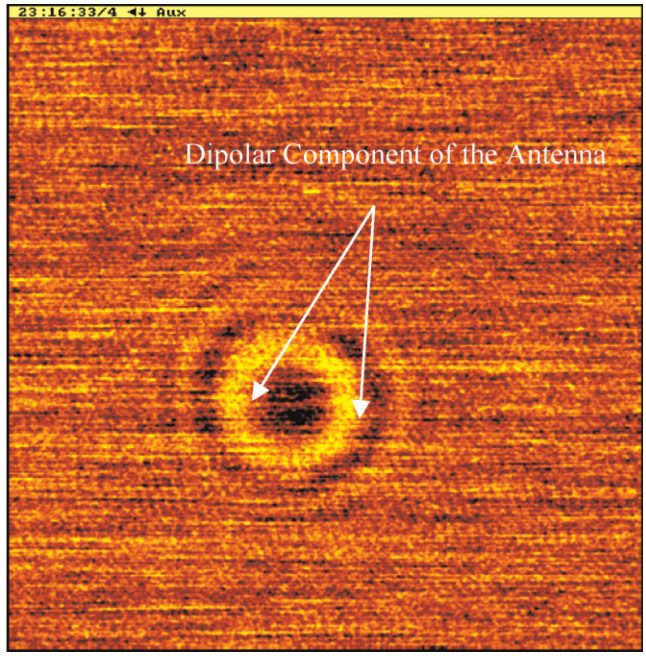


Figure 2 (online colour at: www.pss-b.com) An isolated Au nanorod imaged at 8 μm height.

In Fig. 4 three nanorods have been imaged all within ~1 μm of each other. Now the dipolar symmetry has been broken and notice that the parallel lobes have been lost. However, in this image the field intensity continues to grow between the nanorods. The bright intensity between the rods is seen at every imaging distance between ~2 and 100 μm

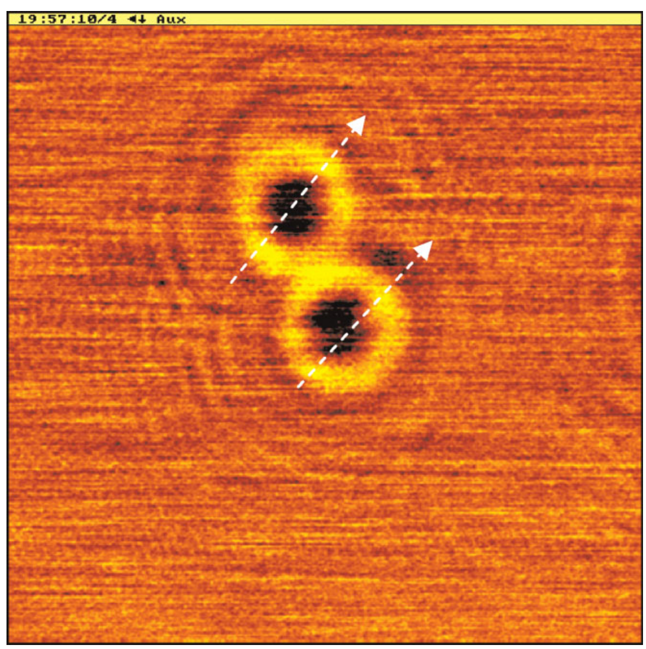


Figure 3 (online colour at: www.pss-b.com) Two interacting nanorods. The bright parts of the diffraction rings are where the dipolar nature of the antennae is being modified.

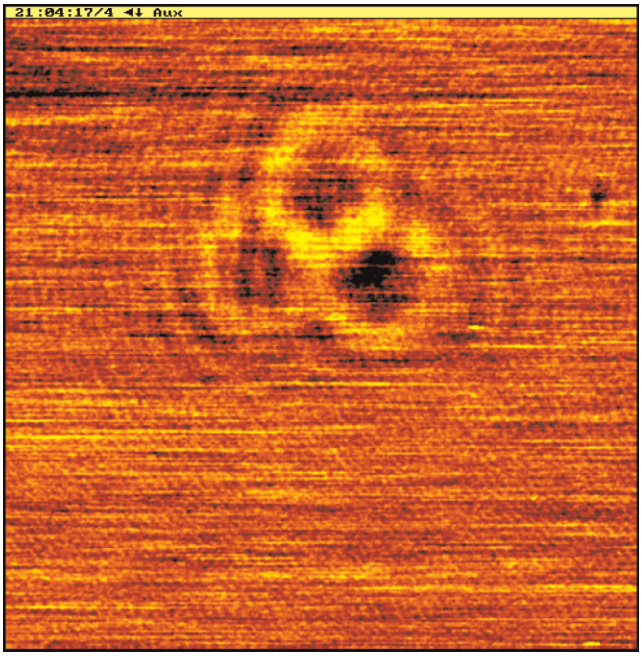


Figure 4 (online colour at: www.pss-b.com) Three interacting particles are shown. The three-particle system breaks the dipole symmetry.

away. This suggests that light transmission between the rods may be supported by the nanorod–nanorod interactions.

4 Conclusions

In this work, we have imaged Au nanorods in the ‘intermediate-field’ regime, which lies outside of the near-field, but before the full development of far-field scattering. Imaging of the optical field shows that for isolated nanorods, the dipolar nature of the plasmonic response modifies the diffractive optical field around the object, even at these large distances. As the nanorods are brought closer and allowed to interact, the development of enhanced field intensity between the nanorods becomes clear. While this result has been suggested by many calculations for interacting particles, it is the first time it has been imaged to our knowledge. These results are surprising for such distances away from the scatterers and suggest that the antenna behaviour of the nanoparticle assembly must be considered in applications that utilize arrays of such particles.

Acknowledgements The authors gratefully acknowledge funding for this work through the AFOSR MURI program grant no. FA9550-06-1-0337 and DOE grant no. DE-FG02-07ER46428.

References

[1] T. Kosako, T. Yamashita, H. F. Hofmann, and Y. Kadoya, Far-Field Analysis of a Metal Nanorod Yagi-Uda Antenna Array, Conference on Lasers and Electro-Optics (CLEO), Pacific Rim, 26–31 August 2007.

[2] M. Schnell, A. Garcia-Etxarri, A. J. Huber, K. Crozier, J. Aizpurua, and R. Hillenbrand, Nature Photonics **3**, 287–291 (2009).

[3] H. Okamoto and K. Imura, Jpn. J. Appl. Phys. **47**, 6055–6062 (2008).

[4] E. Eremina, Y. Eremin, and T. Wriedt, Opt. Commun. **273**(1), 278–285 (2007).

[5] J. E. Kielbasa, J. Liu, K. B. Ucer, D. L. Carroll, and R. T. Williams, J. Mater. Sci., Mater. Electron. **18**(S1), S435–S438 (2007).

[6] J. Zhang, J. E. Kielbasa, and D. L. Carroll, J. Mater. Res. **24**, 1735–1740 (2009).

[7] K. Kim and D. L. Carroll, Appl. Phys. Lett. **87**, 203113 (2005).

[8] S. Chen, S. Webster, R. Czerw, J. Xu, and D. L. Carroll, J. Nanosci. Nanotechnol. **4**(3), 254–259 (2004).

[9] C. J. Orendorff, T. K. Sau, and C. J. Murphy, Small **2**(5), 636–639 (2006).