Published in final edited form as:

Nano Lett. 2009 May ; 9(5): 1956–1961. doi:10.1021/nl9001553.

Optical Properties of the Crescent–Shaped Nanohole Antenna

Liz Y. Wu¹, Benjamin M. Ross¹, and Luke P. Lee^{*}

Applied Science & Technology Graduate Group, Biomolecular Nanotechnology Center, Berkeley Sensor & Actuator Center, and Department of Bioengineering, University of California–Berkeley, Berkeley, CA 94720, USA.

Abstract

We present the first optical study of large–area random arrays of crescent–shaped nanoholes. The crescent–shaped nanohole antennae, fabricated using wafer–scale nanosphere lithography, provide a complement to crescent–shaped nanostructures, called nanocrescents, which have been established as powerful plasmonic biosensors. With both systematic experimental and computational analysis, we characterize the optical properties of crescent–shaped nanohole antennae, and demonstrate tunability of their optical response by varying all key geometric parameters. Crescent–shaped nanoholes have reproducible sub–10 nm tips and are sharper than corresponding nanocrescents, resulting in higher local field enhancement (LFE), which is predicted to be $|\mathbf{E}|/|\mathbf{E}_0| = 1500$. In addition, the crescent–shaped nanohole hole–based geometry offers increased integratability and the potential to nanoconfine analyte in “hot–spot” regions—increasing biomolecular sensitivity and allowing localized nanoscale optical control of biological functions.

Since the discovery of extraordinary transmission of light through subwavelength holes,¹ much attention has been devoted to understanding the role of material properties, film thickness, hole geometry, and relative hole placements in the optical response of hole and hole arrays.^{2,3} Recently, it has been shown that such structures may also act as optical antennae—utilizing local surface plasmon resonances (LSPR) of the nanohole structures to focus electromagnetic fields into extremely small regions.⁴

Such hole–based optical antennae have the potential to become powerful biomolecular sensors. Molecular detection techniques based on LSPR–shift,⁵ surfaced–enhanced Raman spectroscopy (SERS),⁶ surface–enhanced fluorescence (SEF),⁷ and plasmon resonance energy transfer (PRET)⁸ are all highly dependent on the intensity of localized electromagnetic fields, called “hot–spots.” While many nanoparticle–based techniques have been investigated as substrates for plasmonic–based detection via hot–spots,⁹ hole geometries may offer significant advantages, including integratability (i.e. integrated optical devices or optical micro/nanofluidics), robustness, and the potential to nanoconfine analyte in hot–spot regions.^{4,10}

Hole–based plasmonic sensors have suffered from two problems. Firstly, the hole structures have not achieved the sensitivity of nanoparticle–based approaches (e.g.¹¹). This may be largely attributed to limited effort in designing for molecular detection, which is typically focused on creating hot–spots near plasmonic surfaces. The optimal hole structures for hot–spot creation are likely to be different than structures for maximizing transmission, which has been a large focus since the discovery of extraordinary optical transmission. Specifically, sharp–tip and nanogap geometries are required for high molecular sensitivities.

E-mail: lplee@berkeley.edu.

¹Both authors contributed equally to this work.

Secondly, virtually all studies of hole based arrays have been based on slow and expensive “top-down” approaches such as e-beam lithography or focused ion beam (FIB) fabrication. The serial nature of these techniques allows only small regions to be fabricated, and it is both difficult and not cost-effective to integrate such structures into integrated sensing architectures, such as optical microfluidic and nanofluidic devices. In addition, such top-down techniques typically cannot define feature sizes less than 10 nm, which is a critical limitation in creating ultra-sharp features for plasmonic detection. We note that several methods to develop large-area *circular* hole arrays, such as nanosphere lithography,¹² microsphere lenses,¹³ and soft interference lithography¹⁴ have recently been developed.

In this article we present the first demonstration of large-area non-circular random hole arrays. We have used nanosphere lithography to create random arrays of crescent-shaped nanoholes, as shown in Figure 1, and have fabricated such structures on a 4 inch wafer scale, while reproducibly creating sub-10 nm sharp features without using e-beam or FIB. We demonstrate that crescent hole structures serve as counterparts to gold crescent-shaped nanostructures, called nanocrescents, which have been established as powerful plasmonic biosensors in recent years theoretically^{15,16} and experimentally.^{17–23} With both systematic experimental and computational analysis, we characterize the optical properties of crescent-shaped nanohole antennae, and demonstrate their tuning capability by varying all key geometric parameters.

The process flow of crescent-shaped nanohole fabrication is shown in Figure 2. Briefly, a 2 nm thick titanium adhesion layer and a gold layer of defined thickness were deposited onto clean glass slides by e-beam evaporation (Edwards EB3). Random monolayer arrays of polystyrene (PS) spheres (Polysciences) were then deposited on the gold films as follows: PS sphere suspension, 10mM N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide (Sigma-Aldrich) solution in PBS (pH 7.4, Gibco), and DI water (Millipore) were mixed at a ratio of 1:0.9:1. The gold surfaces were immersed in the mixture for 1 hour, during which PS spheres were adsorbed to the substrate. Non-adsorbed spheres were washed away with a copious amount of deionized water and the substrates were dried with N₂ gas. The size of the adsorbed PS spheres can be tailored with oxygen plasmon treatment (Plasma-Therm PK-12 RIE, at 50 sccm, 100 W).

The sphere-coated substrates were then etched using vertical angle ion milling (Veeco Microtech System), after which all of the gold is removed except for a nanodisk masked by each PS sphere. A second gold layer was then deposited on the substrate at a defined angle using e-beam evaporation, at a thickness which matched the initial gold layer. The gold can not enter the area shadowed by the PS sphere, and a crescent-shaped void results. Finally, PS spheres were removed using tape (Scotch, 3M) and sonication in acetone for 1 hour. For comparison, we also fabricated nanocrescents using a similar PS sphere process as shown in Figure 2e–h.²⁰ The resulting crescent-shaped nanohole (as well as nanocrescent) antennae were thus fabricated into large-area random arrays, as shown in Figure 1. We used random arrays to isolate the plasmonic characteristics of individual nanostructures from short- and long-range coupling between structures that can result from periodic arrays.

Dark-field scattering microscopy was used to characterize the optical response of crescent-shaped nanoholes and nanocrescents. While transmission measurements are typical for hole studies, the significant absorption and scattering of sharp crescent-shaped nanohole antennae are more appropriately measured via scattering. In our experimental configuration, broad band white light from a halogen source was passed through a dark-field liquid contact condenser (NA = 1.2–1.4) to illuminate the sample at an angle larger than the collection angle of the objective lens (NA = 0.4). The light scattering from the substrate alone was imaged by a CCD camera and analyzed by a spectrometer.

To complement the experimental scattering results, we developed a three-dimensional numerical model using the commercial finite element software *COMSOL*. We consider a single crescent-shaped nanohole in a large gold sheet with complex permittivity ϵ given by an analytical model²⁴ of the experimental data²⁵ for bulk gold, and with relative permeability $\mu = 1$. The crescent-shaped nanohole shape is approximated by an extruded circle subtracted from an extruded ellipse, where the major and minor axis are determined by the angle of deposition and PS sphere radius, respectively. The surrounding environment is assumed to be vacuum.

Due to the nature of shadow-based nanofabrication, the tips of the crescent-shaped nanohole are extremely sharp—achieving a radius of curvature well under 10 nm without e-beam lithography or FIB. Such dimensions give the crescent-shaped nanohole sharper features than rectangular holes,²⁶ bowtie holes,²⁷ double holes,²⁸ and similar structures which have been fabricated using FIB techniques. Interestingly, the tips are found to be sharper than those of positive nanocrescents fabricated by the same PS sphere template (Fig 2c,g). We expect this is due to the differences in fabrication between the positive and negative crescents: some unavoidable removal of the PS sphere mask during ion milling of the nanocrescent limits tip sharpness (Figure 2g), while the crescent-shaped nanohole is defined by gold evaporation through the shadow of the PS nanosphere (Figure 2c). The increased sharpness causes a higher computed local field enhancement for crescent-shaped nanoholes.

Since it is nearly impossible to completely isolate the positive and negative masking properties of PS spheres during fabrication, a positive nanocrescent typically forms opposite each crescent-shaped nanohole during fabrication, as can be seen in the SEM images of Figure 1b. However it is clear that this “secondary” nanocrescent does not contribute significantly to the optical signal: dark field scattering measurements were nearly identical when taken on both sides of the films (while the nanocrescent appears on only one side), and experimental results agree well with computational results of pure crescent-shaped nanoholes.

For the application of plasmonic based molecular detection, we particularly wish to study plasmon resonances of the sharp tips of the crescent-shaped nanoholes which occur in the optical regime, hence fitting within the “biological window” of visible wavelengths that will not harm biological tissue. For both the crescent-shaped nanohole and its nanocrescent counterpart, in the optical regime the particle plasmon (pp) resonances are dominant, and occur at wavelengths near 600 nm for crescent diameters near 300 nm to 400 nm. Hence, these structures are the focus of this letter.

The geometric asymmetry of the crescent-shaped nanohole antenna causes a significant polarization dependence, as shown in Figure 3. In the case of the crescent-shaped nanohole, the plasmon resonance occurs across the cavity: when the incident electric field polarization is parallel to the long dimension of the crescent-shaped nanohole, denoted pp(c), primarily the tip-cavity modes are excited; when the incident field is perpendicular to the long dimension, denoted pp(u), a resonance across the center of the cavity occurs (Fig 3a–c). These resonances are mirrored in the nanocrescent (Fig 3d–f). While the peak positions of the two modes appear almost identical, the pp(u) resonance exhibits a slight redshift compared to the pp(c) mode, and this trend has also been observed in nanocrescents.²⁰ This supports that the polarization dependence is related to separate resonance modes, while the sharp tips may contribute significantly to the signal in both modes (as is discussed further below).

Since resonances of sharp tips are known to achieve sensitive biomolecular detection, we focus on the pp(c) polarization in the remainder of this letter, and note that the plasmon band tuning is nearly identical for pp(u) polarization.

Nanosphere lithography offers three primary handles for geometric control: namely sphere diameter d , gold deposition angle θ , and thickness of the gold film h . Understanding the effect of each of these handles is crucial for designing useful devices well as in probing the underlying physics.

We fabricated crescent-shaped nanoholes with a wide range of PS sphere sizes, finding that a strong plasmonic response in the optical regime occurred primarily for PS sphere diameters d near 300 nm, as shown in Figure 4. Within the size regime of $d \approx 300$ nm to 400 nm a red-shift in the scattering peak occurs with crescent-shaped nanohole size: for example increasing the sphere diameter from 307 nm to 333 nm results in a 25 nm resonance peak position difference. This behavior has been observed for many different particle and cavity geometries, and is due to radiation damping and retardation.⁹ We note the magnitude of redshift agrees well with that seen for nanocrescents.²⁰ In each case in Figure 4, the computed local field enhancement is redshifted roughly 100 nm compared to the experimental results. This difference can likely be explained from oversimplification of the computational model, and real differences between resonances in the near- and far-field. Specifically, the effect of the substrate has been shown to be significant for circular holes,²⁹ and we suspect the presence of the substrate causes differences between single and double peaks observed in the experimental and computational results. The magnitude of peak change with increasing nanohole size is nearly identical in the experimental and computational results.

Varying the gold deposition angle during crescent-shaped nanohole fabrication allows some control over the nanohole geometry without significantly changing its size, as shown in Figure 5. Surprisingly, though the nanohole shape changes significantly as the deposition angle θ ranges from 10° to 45° , the peak scattering position remains nearly unchanged. To understand this result, we computationally investigated the electric field inside the crescent-shaped nanohole. It is clear from the local electric field presented in Figure 5c that the plasmonic response of the crescent-shaped nanohole is dominated by the sharp tips. Since the tip geometry changes only minimally with deposition angle, little change in plasmon peak wavelength would indeed be expected. Thus, the computational and experimental results are in good agreement.

For a small deposition angle, a thin slit-like crescent-shaped nanohole forms, which results in increased coupling—and a sharper peak. In the near-field, our computation predicts local fields of $|\mathbf{E}|/|\mathbf{E}_0| = 1500$ (Fig 5c) at resonance, where this value is taken at least 2 nm from the gold surface. The reduction of this coupling mode with increasing deposition angle causes a broadening of the plasmon peak, as seen in Figure 5d.

We also considered the effect of varying film thickness as shown in Figure 6. Since the skin depth thickness of gold is roughly 30 nm at optical frequencies, in varying the film thickness from 13 nm to 65 nm we progress from an optically thin film toward an optically thick film. There is an experimental limitation of the aspect ratio of crescent-shaped nanohole size to height of roughly 4 to 1, since the PS sphere template is also deformed during the ion milling process (etching rate of PS : gold $\approx 1 : 2$). This limitation may be overcome in the future by replacing PS nanospheres with a more resilient material such as silica.

The effect of film thickness on the crescent-shaped nanohole resonance position stresses that the resonance is not purely a 2D effect. Simulation results suggest that at resonance the locally enhanced field progresses completely through the cavity. This is consistent with observations in holes, where the electromagnetic field is concentrated into a plasmon mode inside the cavity, and is then re-emitted as light on the other side.³ In the crescent-shaped nanohole structures in this study, we found transmission minima at the resonance wavelength, which is in contrast to transmission enhancement reported in many hole and hole arrays in films much thicker than the skin depth of gold. At the thicknesses below 65 nm used in this study, light that transmits

directly through the gold film may destructively interfere with, or become significant in comparison with, the re-emitted light resulting from the plasmon resonance.³⁰ Similar transmission minima of hole structures have also been reported in hole studies in films of thickness close to the skin depth.^{31–33}

It is clear in Figure 6 that as the film thickness decreases, the scattering peak is redshifted. This follows a general rule seen in many plasmonic structures⁹ including holes,³² namely that as the aspect ratio of structure size to height is increased, a redshift in plasmon peak position occurs. This can occur either by increasing the size (Figure 4) or by decreasing the height (Figure 6) of the nanostructure. We also note that similar shifts are seen in the resonance of positive nanocrescents.²⁰ Again, experimental and computational results are in good agreement. As the film thickness increases, two distinct peaks in the plasmon band begin to emerge. As shown in Figure 6d, this splitting is caused by a secondary coupling mode on the rounded side of the crescent-shaped nanohole. This splitting is also observed for thin crescent-shaped nanoholes with smaller diameter, as shown in Figure 4a, which indicates that a critical aspect ratio is required for the double peak to emerge.

It is clear that strong similarities exist between the optical responses of crescent-shaped nanoholes and nanocrescents. While Babinet's principle does not rigorously apply in the regime studied here of finite conductivity and films of finite thickness,³⁴ the similarities presented here between the complementary structures imply that Babinet's principle is at least qualitatively upheld in this nonideal regime. This has also been recently noted in slit ring resonators (SRR's) and their hole complements.³⁵

Like the positive nanocrescent, we have shown the crescent-shaped nanohole can be readily tuned by varying its geometric parameters. However, the crescent-shaped nanohole geometry may offer significant advantages over its positive nanocrescent counterpart. As we have shown, the crescent-shaped nanoholes can be fabricated in large-area arrays with sub-10 nm tips. The tip sharpness exceeds that of positive nanocrescents obtained with the same nanosphere mask, and is sharper than rectangular holes, bowtie holes, and double holes that have been fabricated. Such sharp features will be critical in improving molecular sensitivity of hole-based devices. In addition, the hole geometry offers significant advantages over particle-based sensors, including integratability, robustness, and the potential to nanoconfine analyte in hot-spot regions. In short, the crescent-shaped nanohole may provide the best-of-both-worlds between hole-based and particle-based biological and chemical plasmonic sensors.

Acknowledgments

This work was supported by the National Institutes of Health Nanomedicine Development Center for the Optical Control of Biological Function (PN2 EY018241) and DARPA for the fundamental study of SERS. LYW acknowledges support from Taiwan Merit Scholarship. BMR acknowledges support from a NSF graduate research fellowship.

References

1. Ebbesen T, Ghaemi HF, Thio T, Wolff PA. *Nature* 1998;391:667.
2. Genet C, Ebbesen TW. *Nature* 2007;445:39. [PubMed: 17203054]
3. Coe JV, Heer JM, Teeters-Kennedy S, Tian H, Rodriguez KR. *Annu. Rev. Phys. Chem* 2008;59:179. [PubMed: 17988200]
4. Gordon R, Sinton D, Kavanagh KL, Brolo AG. *Acc. Chem. Res* 2008;41:1049. [PubMed: 18605739]
5. Willets K, van Duyne RP. *Ann. Rev. Phys. Chem* 2006;58:267. [PubMed: 17067281]
6. Kneipp, K.; Moskovits, M.; Kneipp, H. *Surface-Enhanced Raman Scattering: Physics and Applications*. Germany: Springer; 2006.
7. Fort E, Grésillon S. *J. Phys. D* 2008;41:013001.

8. Liu GL, Long Y-T, Choi Y, Kang T, Lee LP. *Nat. Methods* 2007;4:1015. [PubMed: 18026109]
9. Maier, SA. *Plasmonics: Fundamentals and Applications*. NY: Springer; 2007.
10. Sinton D, Gordon R, Brolo AG. *Microfluid. Nanofluid* 2008;4:107.
11. Pieczonka NPW, Aroca RF. *Chem. Soc. Rev* 2008;37:946. [PubMed: 18443680]
12. Wu W, Dey D, Memis OG, Katsnelson A, Mohseni H. *Nanoscale Res. Lett* 2008;3:351.
13. Wu W, Dey D, Memis OG, Katsnelson A, Mohseni H. *Nanoscale Res. Lett* 2008;3:123.
14. Henzie J, Lee MH, Odom TW. *Nat. Nanotech* 2007;2:549.
15. Kim J, Liu GL, Lu Y, Lee LP. *Opt. Express* 2005;13:8332. [PubMed: 19498862]
16. Ross BM, Lee LP. *Nanotechnology* 2008;19:275201.
17. Liu GL, Lu Y, Kim J, Doll JC, Lee LP. *Adv. Mater* 2005;17:2683.
18. Shumaker-Parry JS, Rochholz H, Kreiter M. *Adv. Mater* 2005;17:2131.
19. Lu Y, Liu GL, Kim J, Mejia YX, Lee LP. *Nano Lett* 2005;5:119. [PubMed: 15792424]
20. Rochholz H, Bocchio N, Kreiter M. *New J. Phys* 2007;9:53.
21. Bukasov R, Shumaker-Parry JS. *Nano Lett* 2007;7:1113. [PubMed: 17432920]
22. Li K, Clime L, Cui B, Veres T. *Nanotechnology* 2008;19:145305.
23. Bocchio NL, Unger A, Álvarez M, Kreiter M. *J. Phys. Chem. C* 2008;112:14355.
24. Etchegoin PG, Ru ECL, Meyer M. *J. Chem. Phys* 2006;125:164705. [PubMed: 17092118]
25. Johnson PB, Christy RW. *Phys. Rev. B* 1972;6:4370.
26. van der Molen KL, Koerkamp KJK, Enoch S, Segerink FB, van Hulst NF, Kuipers L. *Phys. Rev. B* 2005;72:045421.
27. Jin EX, Xu X. *Appl. Phys. B* 2006;84:3.
28. Lesuffleur A, Kumar LKS, Brolo AG, Kavanagh KL, Gordon R. *J. Phys. Chem. C* 2007;111:2347.
29. Shuford KL, Gray SK, Ratner MA, Schatz GC. *Chem. Phys. Lett* 2007;435:123.
30. Kwak E-S, Henzie J, Chang S-H, Gray SK, Schatz GC, Odom TW. *Nano Lett* 2005;5:1963. [PubMed: 16218718]
31. Murray WA, Astilean S, Barnes WL. *Phys. Rev. B* 2004;69:165407.
32. Park T-H, Mirin N, Lassiter JB, Nehl CL, Halas NJ, Nordlander P. *ACS Nano* 2008;2:25. [PubMed: 19206544]
33. Prikulis J, Hanarp P, Olofsson L, Sutherland D, Käll M. *Nano Lett* 2004;4:1003.
34. Jackson, JD. *Classical Electrodynamics*. Vol. 3rd ed. USA: John Wiley & Sons; 1999.
35. Zentgraf T, Meyrath TP, Seidel A, Kaiser S, Giessen H. *Phys. Rev. B* 2007;76:033407.

Figure 1.

Overview of the crescent-shaped nanohole and nanocrescent structures; SEM images (false color) of (a)(d) random arrayed and (b)(e) single structures, and (c)(f) a conceptual illustration of molecular detection for (a)–(c) crescent-shaped nanoholes and (d)–(f) nanocrescents. The crescent-shaped nanohole achieves sharper tips with < 10 nm radius of curvature, and is amenable to integrated flow-through architectures for molecular detection.

Figure 2. Crescent-shaped nanohole and nanocrescent fabrication; nanosphere lithography fabrication process for (a)–(d) crescent-shaped nanoholes and (e)–(h) nanocrescents.

Figure 3.

Crescent-shaped nanohole polarization dependence; polarization induced resonant modes of (a)–(c) crescent-shaped nanoholes and (d)–(f) nanocrescents. The $pp(c)$ polarization excites the sharp tips useful for molecular detection. The scattering curves are shown for $d = 293$ nm, $\theta = 30^\circ$, $h = 25$ nm.

Figure 4.

The dependence of crescent-shaped nanohole optical response on size; (a) experimental scattering response and (b) computed near-field show a redshift with increasing crescent-shaped nanohole size ($\theta = 30^\circ$, $h = 53$ nm, polarization is pp(c))

Figure 5.

The dependence of crescent-shaped nanohole optical response on deposition angle; (a) side view schematic of varying deposition angle, (b) SEM images, (c) computed local electric field enhancement at resonance, and (d) experimental scattering peak for the corresponding crescent-shaped nanohole structures ($d = 333$ nm, $h = 53$ nm, polarization is pp(c)). The sharp tips dominate both the local and far-field response.

Figure 6.

The dependence of crescent-shaped nanohole optical response on crescent-shaped nanohole thickness; (a) schematic of varying thicknesses, (b) experimental scattering response and (c) computed near-field and (d) near-field electric field distribution for (top) the secondary peak and (bottom) primary peak shown in part (c) ($d = 333$ nm, $\theta = 30^\circ$, polarization is pp(c)). A redshift occurs with decreasing crescent-shaped nanohole thickness, while a second peak emerges for optically thick films.