Unraveling the Near- and Far-Field Relationship of 2D Surface-Enhanced Raman Spectroscopy Substrates Using Wavelength-Scan Surface-Enhanced Raman Excitation Spectroscopy

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ABSTRACT: Lithographic and nonlithographic two-dimensional (2D) substrates for surface-enhanced Raman spectroscopy (SERS) have gained enormous popularity as analytical platforms for detection and identification of various analytes. However, their near- and far-field properties in most cases remain poorly understood. We have previously developed a metal nanopillar film over nanospheres (FON) platform exhibiting Raman enhancement factors of $\sim 10^3$. These substrates have a reproducible and predictable localized surface plasmon resonance throughout the entire visible region and much of the near-IR region of the electromagnetic spectrum. Extending upon these results, we have utilized wavelength-scan surface-enhanced Raman excitation spectroscopy to unravel the relationship between near- and far-field properties of FON surface-enhanced Raman spectroscopy substrates. We examined by scanning electron microscopy FONs fabricated by either stationary (ST-FONs) or spun (SP-FONs) metal deposition to examine the interrelationships of nanoscale structure and near- and far-field properties. We demonstrate that the line width and spectral position of the far-field and near-field resonances of ST- and SP-FONs directly depend on the nanofeature distribution at the metallic surface. In particular, we show that the actual nanofeature morphology and distribution directly impact the spectral alignment of the far-field and near-field resonances.

INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is a powerful analytical technique that is capable of detecting molecular analytes down to the single-molecule level. Electromagnetic enhancement is demonstrated to be the dominant mechanism contributing to the SERS enhancement. It involves the localization and amplification of the incident optical excitation by surface plasmon resonances (localized and propagating) of noble-metal nanoparticles. Localized surface plasmon resonances (LSPRs) are coherent, incompressible, collective oscillations of the conduction electron gas sustained by noble-metal nanoparticles and nanostructured surfaces. They are responsible for drastic enhancement of the local electric field ($E$) in the vicinity of the metallic nanostructures, which can reach $10^2$--$10^3$ times the incident electric field ($E_0$). The LSPR strongly depends on the plasmonic nanofeature size, shape, material, and local dielectric environment. Therefore, in principle, the knowledge of the LSPR spectral properties, which can be obtained from the far-field scattering spectrum, should be sufficient to determine the excitation wavelength that would give the highest enhancement factor ($EF \propto |E/E_0|^7$) for a given SERS substrate.

Chemically synthesized gold and silver nanoparticles have been routinely used for single-molecule SERS experiments, where their aggregation into nanoparticle clusters provides the sites for electromagnetic field enhancement, also known as hot spots. Nanoparticle synthesis is versatile, allowing for tailoring the sizes and geometries of the nanoparticles to fulfill particular experimental needs. Recently, numerous different kinds of nanoparticles with built-in hot spots, i.e., eliminating the need for nanoparticle aggregation, have been reported. They include porous nanoparticles, octopods/nanostars, octahedra, concave, truncated, and etched nanocubes, and nanocuboids. However, nanoparticle synthesis scale-up can be difficult to implement and often results in an increase of the size polydispersity. Furthermore, precursors of their synthesis, such as cetyltrimethylammonium bromide (CTAB) and citric acid, commonly overcomplicate their practical applications in surface-enhanced spectroscopies and sensing.

Removal of these surfactants commonly leads to random aggregation and precipitation of the metallic nanoparticles, which prevents reproducibility of the resulting SERS enhancement.

Two-dimensional (2D) SERS substrates are ideally suited platforms for the detection of analytes as they provide adequate nanofeatures without the need for stabilizing adsorbants that

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could in fine limit the SERS efficiency by blocking the analyte's access to the metal surface. The bare metallic nanostructured film can then potentially be later functionalized with specific capture ligands. Over the last couple decades, several SERS substrates have been proposed, including films over nanospheres (FONs), colloidal crystal films, nanoparticle arrays, particles grafted on silanized glasses, paper-based three-dimensional (3D) SERS substrates, and plasmonic nanoholes. On the basis of the fabrication techniques used, there are several types of SERS platforms. The fabrication of nonlithographic substrates is commonly carried out through a thermal evaporation of plasmonic metals on a glass or silicon substrate. This results in generation of nanometer-scale plasmonic features. Although the fabrication of nonlithographic substrates such as metal islands or porous films is relatively facile and provides reasonable SERS enhancement ($10^4$–$10^6$), the lack of control in the density of hot spots on the substrate makes it difficult to use as a reliable substrate. Lithographic substrates are characterized by well-defined nanostructures at specific locations on the substrate and hence achieve high SERS enhancement factors (typically $10^6$–$10^9$).

Electron-beam lithography (EBL) is one of the commonly used methods to fabricate nanoparticle arrays with tunable interparticle distances and shapes. However, high labor intensity and time consumption of EBL-based substrates and high fabrication costs limit their broad and large-scale utilization. A well-developed type of lithographic substrate is the FON, which is fabricated by metal evaporation on a mask of close-packed silica or polystyrene spheres. It was previously demonstrated that LSPR of FONs could be tuned between 330 and 1840 nm by varying the diameter of the silica or polystyrene spheres. Moreover, FONs exhibit one of the highest reported EFs of $10^8$ with only 10% variability over substrates of 10 cm diameter. It was also noted that, as a result of metal deposition over the close-packed silica or polystyrene spheres, two major types of nanostructures are grown: elongated nanopillars and nanoscale blobs. Greenelch et al. showed that substrate spinning during the metal deposition promotes the formation of nanopillars. These spun FON substrates (SP-FONs) exhibited EFs nearly an order of magnitude higher than those of FONs prepared under stationary conditions (ST-FONs). These spun FON substrates (SP-FONs) exhibited EFs nearly an order of magnitude higher than those of FONs prepared under stationary conditions (ST-FONs). However, high labor intensity and time consumption of EBL-based substrates and high fabrication costs limit their broad and large-scale utilization. A well-developed type of lithographic substrate is the FON, which is fabricated by metal evaporation on a mask of close-packed silica or polystyrene spheres. It was previously demonstrated that LSPR of FONs could be tuned between 330 and 1840 nm by varying the diameter of the silica or polystyrene spheres. Moreover, FONs exhibit one of the highest reported EFs of $10^8$ with only 10% variability over substrates of 10 cm diameter. It was also noted that, as a result of metal deposition over the close-packed silica or polystyrene spheres, two major types of nanostructures are grown: elongated nanopillars and nanoscale blobs. Greenelch et al. showed that substrate spinning during the metal deposition promotes the formation of nanopillars. These spun FON substrates (SP-FONs) exhibited EFs nearly an order of magnitude higher than those of FONs prepared under stationary conditions (ST-FONs). However, it remains unclear how different the distributions of nanostructures are and how their size, shape, and overall morphology affect the relationship between the near- and far-field properties of these FON substrates. The morphological differences in an SERS substrate family can lead to complex near- to far-field relationships. Elucidation of such relationships allows for even more precise tuning and tailoring of the LSPR of the FON substrate, thus leading to a better optimization of its SERS performance.

Wavelength-scan surface-enhanced Raman spectroscopy (WS-SERES) is capable of unraveling the near-field properties of SERS substrates. Using WS-SERES, Doherty et al. previously demonstrated that highly uniform SERS substrates exhibit a ~50 nm red shift of their near-field maximum compared to the maximum of their optical scattering profile. McFarland et al. observed that near- and far-field profiles of periodic particle arrays (PPAs) would overlap if the substrate was annealed at 300 °C for 1 h. Finally, WS-SERES was recently used to investigate the near-field properties of paper- and fabric-based 3D SERS substrates, which demonstrated extremely weak optical scattering. It was found that nanoparticle dimers and trimers and higher order nanoparticle clusters primarily determine the near-field properties of these substrates. It should be noted that SERS signals are mainly generated at hot spots at plasmonic substrates; thus, SERS excitation spectral shapes are considerably affected by the near-field optical profiles of hot spots that are different from the far-field optical profiles of the overall plasmonic substrates. At the same time, the far-field response of 3D SERS substrates either was shown to primarily originate from the monomers or could not be clearly defined.

In the present study, we have utilized WS-SERES, scanning electron microscopy (SEM), optical scattering, and finite-difference time-domain (FDTD) calculations to explore the near- and far-field properties of FON substrates. Specifically, we unravel the effect of the FON nanofeature distributions on the correlation between the near- and far-field responses of these SERS substrates. We noticed that spun deposition of Ag resulted in the predominant formation of nanopillars on the surface of the FONs. On the other hand, stationary deposition of Au led to nearly exclusive growth of nanoscale blobs. Here, we used these peculiarities of metal deposition to promote the growth of two different kinds of nanostructures, i.e., nanopillars (SP-FON) and nanoscale blobs (ST-FON), on the surface of FONs. New structural models of both FON structures have been developed, and electrodynamics calculations are used with these models to provide a quantitative description of the observed optical properties.

## METHODS

### Fabrication of SERS Substrates

Both SP- and ST-FON SERS substrates were prepared by packing silicon spheres (600 and 540 nm, respectively) on freshly cleaned silicon wafers, as previously described in ref. A 200 nm layer of Ag was deposited on the spheres while the substrates were spun at ~550 rpm (homemade thermal evaporator) for the SP-FONs. ST-FONs were prepared by evaporation of 150 nm of Au on stationary hold substrates (PVD 7S, Kurt J. Lesker, Efferson Hills, PA). Benzenethiol (Sigma-Aldrich, St. Louis, MO) was vapor-deposited onto the ST- and SP-FON SERS substrates by placing 3–4 drops of concentrated (100%) benzenethiol solution in a Petri dish around the substrate. The substrates were left overnight in the atmosphere of benzenethiol vapors and then immediately measured using WS-SERES.

Cyclohexane (Sigma-Aldrich) was used as an intensity standard (1028.3 cm$^{-1}$ normal Raman scattering band) for a correction of the inherent $i^4$ behavior of Raman scattering. Specifically, the intensity of the 1075 cm$^{-1}$ band of benzenethiol, which was used as a reported SERS signal for all substrates, was divided by the intensity of the 1028.3 cm$^{-1}$ band of cyclohexane to obtain the SERS efficiency at each excitation wavelength. Such normalization also allows us to eliminate variations in the SERS intensity that are not due to enhancement by the substrate, as well as the spectral dependence of the detection system. The relationship between the SERS enhancement and the excitation wavelength was divided by the intensity of the 1028.3 cm$^{-1}$ band of cyclohexane to obtain the SERS efficiency at each excitation wavelength. Such normalization also allows us to eliminate variations in the SERS intensity that are not due to enhancement by the substrate, as well as the spectral dependence of the detection system.
laser was used to generate a 633 nm laser excitation. The laser spot size was approximately 2.7 μm × 1.8 μm. The signal was collected in a backscattering configuration and directed to a confocal Raman spectrometer (Princeton Instruments, SP2500i) equipped with a 1200 groove/mm grating blazed at 500 nm (532 nm excitation) or a 600 groove/mm grating blazed at 750 nm (633 and 725–825 nm excitations) with the slit entrance set to 100 μm. Prior to the signal entering the spectrograph, Rayleigh scattering was filtered with a long-pass filter (Semrock, LP03-532RS-25 (532 nm excitation) or LP03-633RS-25 (633 nm excitation)). To filter the Rayleigh scattering at 725–825 nm excitations, a 900/11 nm VersaChrome tunable band-pass filter was used. The dispersed light was then sent to a liquid nitrogen-cooled charge-coupled device (CCD) (Action300i, Spec-10 400B). A motorized stage (Physik Instrumente, 710 Digital PZT) was used to move the sample relative to the incident laser beam. All data were processed using GRAMS/AI 7.0 (Thermo Galactic, Salem, NH).

**UV−Vis Spectroscopy.** Scattering spectra (400–900 nm) were recorded by illuminating the sample with the microscope lamp and analyzing the transmitted light by a fiber-optically coupled Ocean Optics spectrometer (SD200, Ocean Optics, Dundein, FL). The size of the light spot was approximately 1 mm in diameter. The spot to spot variations in the reflectance were negligible (Figure 1S). T_{aq} = 10 ms, with 103 averages. Silver and gold films with the same metal thickness as was deposited on the investigated substrates were used as a reference to reach 100% transmission.

**Scanning Electron Microscopy.** SEM images were acquired with a LEO Gemini 1525 microscope using an InLens detector, operating at an acceleration voltage of 5.00 kV. The working distance was varied between 3 and 7 mm.

**Electrodynamic Calculations.** FDTD simulations were performed using the commercial package Lumerical FDTD Solutions to calculate the plasmonic properties (reflectance and near-field) of the FON substrates. The FONs were modeled on the basis of the SEM data. The silica spheres were modeled with diameters of 600 and 540 nm for the ST-FON and SP-FON, respectively, and are arranged in a hexagonal lattice on a semi-infinite silica substrate. The ST-FON was modeled with a 200 ± 10 nm metallic layer constituted of approximately 3000 elongated spheroids of sizes ranging from 5 to 20 nm randomly distributed on top of each microsphere. Similarly, the SP-FON was modeled with a 150 ± 10 nm metallic layer constituted of ∼3000 randomly distributed 15–20 nm spherical grains. The two FDTD-modeled geometries are shown in Figure 3. Periodic boundary conditions and symmetries were used in the in-plane directions to mimic infinite arrays, and perfectly matched layers (PMLs) were assumed along the out-of-plane direction. Dielectric permittivities tabulated by Palik and by Johnson and Christy were used for Ag and Au, respectively. The optical excitation was taken as a broad-band plane-wave source (total-field scattered-field, TFSF, source). A nonuniform conformal mesh with a minimum mesh size of 0.25 nm was used to describe the overall nanostructures. An auto-shutoff parameter of 10^{−6} was chosen as the convergence parameter, allowing a propagation time τ ≈ 10 ns of the electromagnetic fields. The reflectance spectra were averaged over 15 different morphologies (i.e., nanofeature distributions) to account for experimental heterogeneities.

### RESULTS AND DISCUSSION

Electron microscopy examination provides a means to evaluate the structural uniformity of a substrate, as well as providing information about the size and shape of the observed nanofeatures. This information is commonly used as an input for theoretical and numerical calculations of the substrate near- and far-field properties. We used SEM to examine the morphology of the nanostructured metal film and characterize the shape and sizes of the nanofeatures present at the surface of both ST- and SP-FONs (Figure 1). The morphological analysis reveals that SP-FONs had average feature sizes of 24 ± 5 and 22 ± 5 nm with a full width at half-maximum (fwhm) of 10 nm in the top and side views, respectively. As for the other substrates, namely, ST-FONs, average nanofeature sizes of 28 ± 11 and 47 ± 16 nm with fwhm’s of 20 and 70 nm were observed in the top and side views, respectively. From these data on the side and top views, nanofeatures on ST-FONs appear very asymmetric (28 and 47 nm, respectively), in contrast to their counterparts on the SP-FONs (24 and 22 nm, respectively).

We further characterized the SP-FONs and ST-FONs by measuring both their near- and far-field responses. The near-field SERS response was measured using WS-SERES from nine different, nonoverlapping spots on three SP-FON and two ST-FON substrates. The excitation wavelength employed in all the measurements was tuned from 725 to 825 nm, in increments of 10 nm (Figure 2). Benzenethiol (BZT; inset in Figure 2A) was used as the probed analyte because it forms a monolayer on the metal surface and is not resonant in the 600–900 nm spectral

![Figure 1](image-url) SEM images of SP-FONs (A, B) and ST-FONs (C, D). Scale bars correspond to 200 nm (A, B) and 300 nm (C, D). (E) Size distributions of nanofeatures on the top (upper panels) and side (lower panels) surfaces of SP- and ST-FONs.
window. Overnight exposition of ST- and SP-FON substrates in the atmosphere of BZT results in the formation of a BZT monolayer on the metal surface. A typical SERS spectrum obtained from such a metallic surface is shown in Figure 2A (black line). It should be noted that the SERS spectra of BZT acquired from ST-FONs and SP-FONs are very similar to each other. A normal Raman spectrum of BZT is also shown for comparison (Figure 2A, red line). Finally, the optical scattering responses of both ST- and SP-FONs were also obtained by a home-built UV–vis apparatus.

Both ST- and SP-FONs exhibit Gaussian near-field profiles with the maxima around 755–775 nm. ST-FONs (Figure 2B) showed nearly similar enhancement in the 750–790 nm range (EF ≈ 8.3 × 10^6). We also found that the EF of ST-FONs decreased by nearly a factor of 2 at 725 and 825 nm relative to the maximum, giving rise to an fwhm of ~75 nm, slightly broader than that of their SP-FON counterparts (fwhm of ~65 nm, Figure 2C). The highest enhancement is found at 755–775 nm, which corresponds to EF ≈ 1 × 10^7. The second largest enhancements were measured at 745, 785, and 795 nm (EF ≈ 8.3 × 10^6). Finally, the lowest EF for SP-FONs was observed at 725 nm (EF ≈ 2 × 10^6). The far-field properties exhibit opposite behaviors as shown by the reflectance spectra (Figure 2B,C, dotted lines). The spectrum of the SP-FON substrates appears to be broader than the scattering profile of ST-FONs (fwhm of 160 nm vs 110 nm). Interestingly, we can also notice that the maxima for the far-field scattering and for the near-field response are spectrally aligned in the case of the SP-FONs (Figure 2C). On the other hand, the maximum of the near-field response of the ST-FON is red-shifted by about 45 nm with respect to the reflectance (far-field) maximum (Figure 2B).

To gain further insight into the structure–property relationships of the FON substrates and further understand the relationship between the near- and far-field properties, we have used the FDTD method to calculate the near- and far-field properties of both ST- and SP-FONs (Figure 3A,B, respectively). Due to the structural complexity of these substrates, FDTD calculations were performed for 15 different morphologies (i.e., different surface roughness distributions) and averaged out. The far-field optical properties are also...
The Journal of Physical Chemistry C

Figure 4. FDTD calculations for the SP- and ST-FONs. (A, B) Modeled geometries used in the FDTD simulations for the Au SP-FON and Ag ST-FON, respectively. (C, D) Reflectance spectra (dotted lines) and fourth power of the near field \(\left|E/E_0\right|^4\) calculated within the gap (white mark in panels E and F) for the Au SP-FON and Ag ST-FON, respectively. (E, F) Spatial distribution of \(\left|E/E_0\right|^4\) around the Au SP-FON (\(\lambda = 700\) nm) and Ag ST-FON (\(\lambda = 725\) nm), respectively.

polarization averaged. The simulation details are provided in the Methods. As the SERS signal is experimentally dominated by strong plasmonic hot spots present at the surface of the metallic nanostructured film, we calculate the near-field response in the gap regions, i.e., where the local electric field intensity is the highest (white mark in Figure 3E,F). Similarly to the experimental results, we have found that the maximum of the near-field response (i.e., \(\max(|E/E_0|^4)\)) of the ST-FON is red-shifted by \(\sim 60\) nm with respect to the reflectance minimum, as shown in Figure 3C. However, the SP-FON does not exhibit such a noticeable spectral shift as can be seen from Figure 3D. Instead, near- and far-field profiles of SP-FON appeared to be spectrally aligned as observed experimentally. Additionally, and very similarly to the experimental observations, the reflectance profile of Ag SP-FONs appears much broader than that of Au ST-FONs. These results are in excellent quantitative agreement with the WS-SERES results presented in Figure 2. Note also that the maximum experimental and calculated enhancements for both ST-FONs and SP-FONs are similar and are on the order of \(10^6\) to \(10^7\). It is important to notice that although the morphology is modeled with random surface roughness, small discrepancies in the spectral line shape can be attributed to the high surface heterogeneity of the actual FONs, thus leading to large inhomogeneous spectral broadening.

Parts E and F of Figure 3 show the near-field spatial distribution \(\left|E/E_0\right|^4\) at the LSPR resonance (i.e., when the local electric field is the most intense). It can be seen that most of the near field is located in the gaps between the microspheres. However, due to the surface roughness, some localized hot spots can be found on top of the FON, in particular for the Ag SP-FON (Figure 3F). This is in agreement with previously published work on the distance dependence of SERS.\(^{56}\) As can be seen from Figure 3C–F, the calculated EF reaches values on the order of \(3 \times 10^6\), very good quantitative agreement with the experimental estimations.

To demonstrate that the observed relationship between near- and far-field responses is not due to the nature of the plasmonic metal used in each of the investigated FONs, we have performed the same theoretical analysis with the complementary configurations. Specifically, we calculated the near- and far-field properties of Au SP-FONs and Ag ST-FONs (Figure 4A,B). As can be clearly noticed from Figure 4D, the maximum of the near-field response \(\left(\max(|E/E_0|^4)\right)\) of the Ag ST-FON, similarly to the Au ST-FON in Figure 3, is red-shifted by about \(50\) nm with respect to the reflectance minimum. At the same time, both Au SP-FONs do not exhibit such a spectral shift (Figure 4C).

Unraveling the relationship between the far- and near-field optical responses of plasmonic materials is important to further understand the role and control the fabrication of nanoscale features underlying the SERS effect, as well as for the rational fabrication of SERS substrates and ultimately the optimization of their performance. However, to date, the inter-relationship between the nanoscale morphology of 2D substrates such as the ones found in the metal film of FONs and their properties is not clearly understood. Due to the intrinsic structural heterogeneity of these substrates at the nanoscale, the prediction of their optical far- and near-field properties using theoretical models is challenging. In the current study, we demonstrated that SEM allows for the visualization of morphological heterogeneity of nanostructures on the surfaces of both ST- and SP-FONs. However, these results alone cannot be used for prediction of the far- and near-field properties of FONs. For instance, according to the SEM images, nanopillars on the surface of the SP-FON are \(25–30\) nm in diameter. However, such nanofeatures would exhibit LSPR at \(\sim 500\) nm, which was not experimentally observed.\(^{57,58}\) Similarly, the size of the ST-FON nanofeatures \(28–47\) nm should give rise to a much broader far-field optical response than the optical response of SP-FONs (nanofeatures of \(25–30\) nm diameter). However, direct measurements of the optical scattering from ST- and SP-FONs showed the opposite (Figure 2), which is also supported by the FDTD calculations (Figures 3 and 4).

From the two sets of FDTD calculations, it clearly appears that the spectral shift observed experimentally with the ST-
FONs (Figure 2B), or the spectral alignment observed with ST-FONs (Figure 2C), is directly connected to the actual morphology of the FON rather than to the material. Spectral red shift between near-field and far-field resonances is commonly observed in plasmonic nanostructures. Using coupled harmonic oscillator models, Zuloaga and Nordlander showed that the amount of red shift varies on the basis of the total damping in the system.59 Besides the intrinsic damping of the plasmonic materials, the total damping is directly governed by the type of morphological features forming the nanostructure (radiative damping). Small particles, or in the case of the ST-FONs small nanofeatures (i.e., nanopillars), have minimal radiative damping and very little intrinsic damping, resulting in a negligible red shift (or the absence of a red shift) of the near-field spectrum. As for SP-FONs, the small blobs tend to merge more easily than the nanopillars and form smoother and more continuous metallic films, thus resulting in overall larger features as can be seen in the FDTD models (Figures 3A and 4B). This effect further results in a significant increase of the radiative damping due to prominent retardation effects, leading to important spectral shifts. Furthermore, the actual size distribution of these nanofeatures also directly impacts the inhomogeneous damping of the system.

**CONCLUSIONS**

In conclusion, we unraveled the interrelationships between the structure and near- and far-field properties of SERS substrates made of nanostructured metal films over nanospheres, known as FONs. Depending on the fabrication method (stationary vs spinning metal deposition, designated as ST-FONs and SP-FONs, respectively), we clearly confirmed by SEM analysis that it is possible to control the fine morphology of the metal film in the 10–90 nm range, with the resulting nanofeatures differing in their shape and size dispersity. Using WS-SERES, we directly measured the near-field SERS enhancement profile of both ST-FONs and SP-FONs and clearly showed that the near- and far-field profiles of SP-FONs were spectrally aligned, whereas a ~45 nm spectral shift was observed in the case of ST-FONs. The extensive numerical analysis revealed that the presence of nanofeatures presenting a small size polydispersity results in the spectral alignment of optical far-field and near-field profiles. The absence of, commonly observed, near-to-far-field spectral shift is attributed to a significant increase in the radiative damping originating from the surface morphology of the FONs.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b04787.

Spot to spot variations in the reflectance spectra of SP-FON (Figure S1) (PDF)

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**Author Contributions**

D.K. and N.C. conceived and designed the experimental measurements. A.-I.H. performed the SEM structural analysis. N.L. performed the electrodynamic calculations and theoretical analysis.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


